Natural Tracer Profiles Across Argillaceous Formations: The CLAYTRAC Project

Disposal of high-level radioactive waste and spent nuclear fuel in engineered facilities, or repositories, located deep underground in suitable geological formations is being developed worldwide as the reference solution to protect humans and the environment both now and in the future. An important aspect of assessing the long-term safety of deep geological disposal is developing a comprehensive understanding of the geological environment in order to define the initial conditions for the disposal system as well as to provide a sound scientific basis for projecting its future evolution. The transport pathways and mechanisms by which contaminants could migrate in the surrounding host rock are key elements in any safety case. Relevant experiments in laboratories or underground test facilities can provide important information, but the challenge remains in being able to extrapolate the results to the spatial and temporal scales required for performance assessment, which are typically tens to hundreds of metres and from thousands to beyond a million years into the future. Profiles of natural tracers dissolved in pore water of argillaceous rock formations can be considered as large-scale and long-term natural experiments which enable the transport properties to be characterised.

The CLAYTRAC Project on Natural Tracer Profiles Across Argillaceous Formations was established by the NEA Clay Club to evaluate the relevance of natural tracer data in understanding past geological evolution and in confirming dominant transport processes. Data were analysed for nine sites to support scientific understanding and development of geological disposal. The outcomes of the project show that, for the sites and clay-rich formations that were studied, there is strong evidence that solute transport is controlled mainly by diffusion. The results can improve site understanding and performance assessment in the context of deep geological disposal and have the potential to be applied to other sites and contexts.
Natural Tracer Profiles
Across Argillaceous Formations:
The CLAYTRAC Project

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FOREWORD

An important aspect of assessing the long-term safety of deep geological disposal of radioactive waste is developing a comprehensive understanding of the geological environment in order to define the initial conditions for the disposal system as well as to provide a sound scientific basis for constraining its future evolution. The NEA Working Group on the Characterisation, the Understanding and the Performance of Argillaceous Rocks as Repository Host Formations (the NEA Clay Club) is devoted to improving the scientific basis for clay host rocks in the context of geological disposal. The understanding of the transport pathways and mechanisms by which contaminants could migrate in the geosphere is a key element in any performance assessment and safety case. Relevant experiments in laboratories or underground test facilities can provide important information, but the challenge remains in being able to extrapolate the results to the spatial and temporal scales required for performance assessment, which are typically tens to hundreds of metres and from thousands to beyond a million years into the future. Profiles of natural tracers dissolved in pore water of argillaceous rock formations can be considered as large-scale and long-term natural experiments which enable the transport properties to be characterised. That is, the tracer profiles can be subjected to quantitative analysis and yield information on the dominant transport processes and pathways, as well as on key transport parameters such as the diffusion coefficient. Such situations can be conceived as natural analogues of solute transport experiments, offering the potential to bridge the gap in spatial and temporal scales between laboratory experiments and the needs for modelling and performance assessment.

The CLAYTRAC project on Natural Tracer Profiles Across Argillaceous Formations was established by the NEA Clay Club with the objective to evaluate the relevance of natural tracer data in constraining an understanding of past geological evolution and in confirming the dominant transport processes. An internally consistent methodology for data processing and evaluation was applied to nine argillaceous sites for which significant data was available regarding the spatial distribution of tracers in pore water. Emphasis was placed on the integrated understanding based on the whole suite of tracers available at any specific site. The results provide powerful evidence of non-sorbing solute transport and water movement in clay-rich rocks. Moreover, the interpretation of natural tracers is, overall, scientifically robust and consistent with established physical concepts. The relative advantages and disadvantages of various tracers have been evaluated in terms of sampling, analysis and interpretation.

The outcomes of the project show that, for the sites and clay-rich formations that were studied, there is strong evidence that solute transport is controlled mainly by diffusion; the results can improve site understanding and performance assessment in the context of deep geological disposal and have the potential to be applied to other sites and contexts.
ACKNOWLEDGEMENTS

The CLAYTRAC project would not have been achieved without important support, in many forms, from many people and organisations. Foremost among these are the members of the NEA Clay Club, whose commitment to the project and dedication to scientific excellence underlie all aspects of this report. The Secretariat takes this opportunity to recognise Philippe Lalieux, under whose tenure as chairperson this project was conceived and executed; this report is a tangible indicator of the level of strategic and scientific direction he provided throughout his service with the Clay Club.

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This report was prepared under contract to Dr. Martin Mazurek (University of Bern), who proved adept not only at synthesising diverse data but also at integrating input from numerous co-authors and international experts. The report bears testament to the collective effort and expertise of all those who contributed.
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PREFACE

How to read this report

In order to meet the objectives of the project, nine case studies were considered within CLAYTRAC. In a first stage, the data evaluation and modelling remained on a site-specific level, whereas generalised insights and conclusions were drawn in a second stage. The substantial number of case studies provided a broad basis for an improved understanding of solute transport in argillaceous rocks, but, on the other hand, the full documentation of all sites inevitably led to a massive document. The authors attempted to structure the report such that it contains both detailed information for readers interested in specific sites or in the full basis for the generalised conclusions, as well as for an executive readership for which only the main features and outcomes in condensed form are of interest. The Table below is intended to help each reader to find the information of relevance to him/her.

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1. INTRODUCTION

1.1 Project history and organisation

The CLAYTRAC project has been launched by the NEA Working Group on the Characterisation, the Understanding and the Performance of Argillaceous Rocks as Repository Host Formations (known as “Clay Club”) at the beginning of 2005. This initiative was motivated by the fact that argillaceous formations are considered as potential hosts of geological repositories for radioactive waste in several countries. A number of sites are currently being investigated, and underground research laboratories are in operation. A growing body of data pertinent to natural tracers in such formations is available, in addition to studies documented in the open scientific literature.

CLAYTRAC was funded by Andra (France), BGR (Germany), IRSN (France), Mecsekerc (Hungary), Nagra (Switzerland), NUMO (Japan), Ondraf/Niras (Belgium) and SCK•CEN (Belgium). Ontario Power Generation (Canada) joined the project at a later stage. The funding organisations and their representatives are summarised in Table 1.1-1.

Table 1.1-1: Funding organisations of CLAYTRAC and their representatives

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<td>Andra, France</td>
<td>Stéphane Buschaert</td>
<td>Callovo-Oxfordian at the Site Meuse/Haute Marne (Bure, France) and Couche Silteuse at Marcoule (Gard), France</td>
</tr>
<tr>
<td>BGR, Germany</td>
<td>Hans-Joachim Alheid</td>
<td>Toarcian-Domerian at Tournemire, France</td>
</tr>
<tr>
<td>IRSN, France</td>
<td>Sébastien Savoye</td>
<td>Toarcian-Domerian at Tournemire, France</td>
</tr>
<tr>
<td>Mecsekerc, Hungary</td>
<td>Mihaly Csovari</td>
<td>Opalinus Clay at Benken, Mont Terri and Mont Russelin, Switzerland</td>
</tr>
<tr>
<td>Nagra, Switzerland</td>
<td>Andreas Gautschi</td>
<td>Opalinus Clay at Benken, Mont Terri and Mont Russelin, Switzerland</td>
</tr>
<tr>
<td>Numo, Japan</td>
<td>Yutaka Sugita</td>
<td>Boom Clay at Mol and at Essen, Belgium</td>
</tr>
<tr>
<td>Ondraf/Niras, Belgium</td>
<td>Laurent Wouters</td>
<td>Boom Clay at Mol and at Essen, Belgium</td>
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<td>Ontario Power Generation, Canada</td>
<td>Mark Jensen</td>
<td>Boom Clay at Mol and at Essen, Belgium</td>
</tr>
<tr>
<td>SCK•CEN, Belgium</td>
<td>Mieke De Craen</td>
<td>Boom Clay at Mol and at Essen, Belgium</td>
</tr>
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<td>OECD/NEA Scientific Secretariat, France</td>
<td>Sylvie Voinis, Elizabeth Forinash</td>
<td>Opalinus Clay at Benken, Mont Terri and Mont Russelin, Switzerland</td>
</tr>
<tr>
<td>OECD/NEA Clay Club</td>
<td>Philippe Lalieux, Patrick Landais</td>
<td>Opalinus Clay at Benken, Mont Terri and Mont Russelin, Switzerland</td>
</tr>
</tbody>
</table>

The technical work was carried out by the Core Group, i.e. the authors of this report from the Rock-Water Interaction Group of the Institute of Geological Sciences, University of Bern, Switzerland, and Adrian Bath from Intellisci, UK, under the co-ordination of Martin Mazurek. Site-specific information on the sites considered in CLAYTRAC was provided by the respective representatives, as indicated in the list above.
The project was subdivided into the following stages:

1. Data compilation: Spatial distribution of tracers, formation properties
2. Data compilation: Initial and boundary conditions
   - Milestone 1: Availability of a reviewed and generally accepted database
3. Choice and adaptation of code
4. Model calculations
5. Interpretation, synthesis, reporting
   - Milestone 2: Availability of draft report for review
6. Revision of draft report
   - Milestone 3: Publication of final report.

1.2 Rationale

The existence of a substantial data set from several sites and the potential of these data to increase the understanding of transport processes in argillaceous rocks has been recognised in the FEPCAT project (Mazurek et al. 2003), a preceding OECD/NEA initiative devoted to the characterisation of argillaceous formations. Hydrogeological and geochemical investigations of clay-rich sedimentary formations in varying states of induration have recently been conducted or are under way. At several sites, data sets on the spatial distribution of natural tracer concentrations and isotopic ratios in pore waters are available (anions, water isotopes, noble gases). Regular, curved profiles were observed for some tracers in some formations but are absent in others. Some tracer distributions have been interpreted as diffusion profiles (e.g. Desaulniers et al. 1981, 1986, Bath et al. 1989, Patriarche et al. 2004a,b, Rübel et al. 2002, Gimmi et al. 2007).

Tracer profiles in argillaceous rock formations can be considered as large-scale and long-term natural experiments by which the transport properties can be constrained. They provide complementary information to that obtained from experiments in laboratories or underground facilities, where typical spatial scales are 1 cm to 1 m and temporal scales only rarely exceed 1 a. Natural tracer profiles can bridge the gap between these scales and those required for performance assessment (where typical scales are tens to hundreds of m and 0.1 – 1 Ma) and provide an independent line of evidence for system understanding as well as for safety considerations in qualitative and quantitative terms. In particular, studies targeted at the interpretation of tracer profiles are useful for the upscaling of laboratory experiments.

The degree to which the evidence based on tracer profiles has been exploited to date is quite heterogeneous among sites and formations. Some of the techniques for measuring tracer contents have only been developed in recent years, and so the quality of the data is mixed. However, data sets obtained in the pioneering years can often be adjusted/corrected to represent current state-of-the-art knowledge.

1.3 Objectives

The project does not include the collection of new data but is focussed on the re-evaluation of already existing measurements and on evidence documented in the literature regarding the palaeo-hydrogeological framework. The added value of the work compared to studies dealing with individual sites in isolation lies in the comparison and integration of data, results and conclusions from a variety
of sites and formations. The application of a consistent methodology of data collection, processing and modelling is expected to meet the following objectives:

- To provide an overview of available data sets.
- To develop and apply a consistent way of data processing and evaluation that is the basis for comparability (e.g. consideration of tracer-specific porosities and diffusion coefficients).
- To evaluate the strengths and weaknesses of different tracers for quantitative understanding of transport processes in argillaceous rocks.
- To comment on commonalities and differences among the sites under consideration.
- To identify gaps in existing data sets and make recommendations for future data acquisition campaigns.

The observed spatial distributions of tracers are compared to model calculations based on a variety of parameter sets and conceptual assumptions. Modelling efforts have the following objectives:

- To test the hypothesis that tracer profiles are consistent with diffusion as the dominant transport process.
- To place upper bounds on advection velocity across the argillaceous formation.
- To constrain the spectrum of initial and boundary conditions (based on the shapes of the tracer profiles).
- To compare and integrate the interpretations based on different tracers at any given site (site-specific consistency check).
- To compare and integrate the interpretations among sites (general consistency check). For example, the same conceptual model that explains the existence of a curved tracer profile at one site should also explain the absence of such a profile at another site.
- To fit model calculations to measured tracer distributions and thereby constrain the large-scale diffusion coefficients and/or diffusion times. If independent evidence exists on the latter, diffusion coefficients can be obtained by fitting model calculations to observed data. These large-scale values can then be compared with laboratory measurements on small samples and thus contribute to the issue of upscaling to scales relevant for performance assessment.
- To judge the relevance of observed geological discontinuities, such as faults, for flow and transport over long periods of time in the past.

Hydraulic and other transport properties of argillaceous formations can be addressed by different lines of evidence, such as hydrogeological investigations (e.g. hydraulic packer tests and long-term monitoring) or geological arguments (e.g. the presence/absence of vein mineralisations and wall-rock alterations that would indicate fluid flow in the past). The quantitative evaluation of tracer distributions may add another independent line of evidence.

1.4 Scope

The CLAYTRAC project considers sites that were investigated in the framework of deep disposal projects and of underground research laboratories. Additional information from the open literature was also considered, even though only few suitable case studies are currently available.
Limitations in scope include:

- The project uses existing tracer data sets, while the collection of new data was not foreseen.
- Modelling is performed using an existing code after necessary adaptations. Code development from scratch was not foreseen.
- Transport processes considered include advection and diffusion, while off-diagonal Onsager processes\(^1\) are not addressed. One of several reasons for this limitation is the lack of site-specific data needed to quantify such processes.
- Modelling considers conservative tracers only (water isotopes, anions, noble gases). Reactive tracers are excluded. I\(^-\) is a halogen and is included where data are available, even though there are indications of weak interaction with the rock.

Figure 1.5-1: Locations of sites considered in the CLAYTRAC project

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\(^1\) For definition, see Horseman et al. (1996), ch. 10.
Further limitations arise from the incomplete availability of input data:

- For some sites, the reconstruction of the palaeo-hydrogeological evolution is limited by the incompleteness of relevant data and observations. In such cases, model calculations (if feasible at all) are based on working hypotheses and design calculations.
- Not all tracer profiles carry the potential of providing clear conclusions. For example, flat or highly complex profiles are of limited use for quantitative evaluation.
- In summary, not all objectives can be addressed at each site. There is a symmetry between the availability of information and the potential of providing a full set of conclusions.

1.5 Sites and formations considered

Table 1.5-1 lists the sites that were considered for the study, and the locations are shown in Figure 1.5-1. For some of these sites, information is available from more than one borehole. Table 1.5-1 also shows an overview of available data sets pertinent to the spatial distribution of tracers in pore waters of argillaceous rocks. The data density is heterogeneous. Data sets relating to Cl\(^-\) and stable water isotopes are the most complete ones.

![Table 1.5-1: Tracer data sets currently available at different sites](image)
1.6 Methodology of data acquisition

1.6.1 Conceptual background and principles of interpreting tracer profiles

From a hydrogeological perspective, the idealised field setting (Figure 1.6-1) consists of a low-permeability sequence (aquitard containing one or more generally clay-rich formations, sometimes also limestones) sandwiched between units with higher permeability (aquifers, typically limestones or sandstones). Mass transport in the aquifers is dominated by advection, and the physico-chemical characteristics of the aquifers define the boundary conditions for mass transport in the aquitard.

For the sake of an illustrative example, consider the following situation: Shallow marine conditions prevailed in a sedimentary basin (part of which is schematically shown in Figure 1.6-1) over a very long period of time. During this period, hydraulic and chemical gradients in the sedimentary sequence were very small, resulting in negligible mass transport. Once the basin was inverted, emerged from the sea and was subjected to some erosion, topographically driven hydraulic gradients initiated ground-water flow in the aquifers. Due to the infiltration of meteoric water, the chemical composition of the ground waters changed drastically since emergence. Thus, large hydraulic and chemical gradients were imposed on the aquitard located between the two aquifers. The rate of mass transport in the vertical dimension in response to these gradients depends on the formation properties of the aquitard and is expected to be much smaller than lateral mass transport within the aquifers. It follows that the adjustment of the chemical composition of the pore water in the aquitard to that in the aquifers is a slow process characterised by a long transient stage. A snapshot of such a transient situation can be recorded by analysing the spatial distribution of natural tracers contained in the pore water of the aquitard. If good constraints are available on the time of emergence when the boundary conditions changed, the tracer profile can be subjected to quantitative analysis and potentially yields information on the dominating transport process and on transport parameters, such as the diffusion coefficient. Such a situation can be conceived as a natural analogue of mass-transport experiments conducted in the laboratory or in underground facilities, but yielding information on much larger spatial and temporal scales.
1.6.2 Data requirements for a quantitative evaluation of tracer profiles

The investigation and quantitative interpretation of tracer profiles requires three basic types of input data (“pillars”):

- **Pillar 1**: Spatial distribution of tracers (profiles across the low-permeability sequence);
- **Pillar 2**: Relevant formation properties;
- **Pillar 3**: Palaeo-hydrogeological understanding to constrain initial and boundary conditions.

**Processes considered**

In this report, advection and diffusion are assumed to be the only relevant transport processes. All off-diagonal Onsager processes (see Horseman *et al.* 1996, p. 186) are not explicitly considered. Processes driven by thermal and electric gradients (such as thermo- and electro-osmosis, thermo-diffusion, electrophoresis) are neglected because these gradients and resulting fluxes are thought to be very small across an aquitard (Soler 2001). On the other hand, chemical gradients may be substantial, and so effects of chemical osmosis cannot be fully excluded. For the Callovo-Oxfordian at Bure (France), overpressures in the shale (equivalent to some tens of metres in head) are currently explained as an osmotic effect (Gueutin *et al.* 2007). However, there are only few measurements of osmotic efficiency. In Opalinus Clay, the value obtained is max. 12 %, indicating that this formation is an imperfect membrane (Nagra 2002), and recent data from the Callovo-Oxfordian at Bure yield similar results (Croisé 2007, Rousseau-Gueutin *et al.* 2007). No measurements of membrane properties are currently available for the other formations considered here. In the absence of formation-specific experimental data indicating high osmotic efficiency, there is no basis for including chemical osmosis in a quantitative study of tracer profiles. Flow velocities and their effects on tracer distributions (as discussed in Chapter 5) are mainly driven by hydraulic gradients but may include a minor osmotic contribution. In this sense, osmotic effects are implicitly included. A more detailed discussion is provided in Section 4.2.3.

**Tracers considered**

In order to limit the number of processes that affect transport and retardation, only tracers were considered that do not sorb on mineral surfaces, do not undergo chemical reactions with the minerals and fractionate into the liquid phase. Such conservative tracers include the following groups:

- halogens (Cl\(^-\), Br\(^-\), I\(^-\); \(\delta^{37}\)Cl);
- water isotopes (\(\delta^{18}\)O, \(\delta^2\)H);
- noble gases (He, \(^3\)He/\(^4\)He, \(^{40}\)Ar/\(^{36}\)Ar, *etc.*).

1.6.3 The Data Tracking Documents

On the basis of the general discussion of data requirements in the preceding section, the relevant information needed for the purposes was organised in table format, including 23 items:

**Pillar 1: Spatial distribution of tracers**

1. Anion contents (Cl\(^-\), \(\delta^{37}\)Cl, Br\(^-\), I\(^-\)) in pore water;
2. Water isotope data (\(\delta^{18}\)O, \(\delta^2\)H) in pore water;
3. Noble gas contents (He, \(^3\)He/\(^4\)He, Ar, \(^{40}\)Ar/\(^{36}\)Ar) in pore water;
4. Anion contents (Cl\(^-\), δ\(^{37}\)Cl, Br\(^-\), I\(^-\)) in the upper and lower aquifers (boundary condition);
5. Water isotope data (δ\(^{18}\)O, δ\(^2\)H) in the upper and lower aquifers (boundary condition);
6. Noble gas contents (He, \(^3\)He/\(^4\)He, Ar, \(^{40}\)Ar/\(^{36}\)Ar) in the upper and lower aquifers (boundary condition).

Pillar 2: Relevant formation properties

7. Definition of the bulk geometry;
8. Definition of lithological sub-units of the low-permeability formation(s) between the aquifers;
9. Structural discontinuities (fracture zones, faults);
10. Pore or effective diffusion coefficient for anions (Cl\(^-\), Br\(^-\), I\(^-\));
11. Pore or effective diffusion coefficient for water (often measured by HTO diffusion experiments);
12. Pore or effective diffusion coefficient for He;
13. Salinity of pore water;
14. Hydraulic conductivity;
15. “Total” porosity (derived e.g. from density or water-content measurements, or from diffusion experiments);
16. Fraction of "total" porosity accessible to anions;
17. U and Th contents of the rocks (needed to quantify in-situ production of He by α decay);
18. In-situ temperature;

Pillar 3: Palaeo-hydrogeological understanding

20. Palaeo-hydrogeologic evolution of the low-permeability formation;
21. Evolution of boundaries over time;
22. Erosion/exhumation history;
23. Tectonic evolution.

For each of these items, the following attributes were considered

- Item number;
- Item definition;
- File name where underlying data are stored;
- References;
- Changes performed to the original data set;
- Comments and conclusions.

One such “Data Tracking Document” per site, or, if appropriate, per borehole at a site, was prepared and sent back for review to the organisation responsible for the characterisation of the site. It was considered final as soon as an agreement on its adequacy was achieved. An example of a completed Data Tracking Document is given in Appendix A1.
1.6.4 Data freeze and data clearance

In addition to being the basis for the evaluation and modelling work within the project, the Data Tracking Documents also served the purpose of data freeze and data clearance. More recent information than that documented in the Data Tracking Documents was not considered in the project, so these documents represent the status of knowledge. Publicly accessible information (open scientific literature, published reports) was not subjected to the data clearance procedure. The agreement of the organisation responsible for the characterisation of a site to the Data Tracking Document was formalised in a data clearance letter signed by the responsible representative, confirming that:

- The Data Tracking Document adequately summarises existing knowledge on the site;
- The Core Group is authorised to use the data and information given in the document as well as that in the referenced electronic files and reports/publications for the purposes of the CLAYTRAC project;
- The Data Tracking Document represents a data freeze.

1.7 Overview of previous work

Some data, models and interpretations relating to natural tracers at the sites considered in this report have been previously published in the open scientific literature. Key references include Falck et al. (1990) on chloride and stable water isotopes in London Clay at Bradwell, Rübel et al. (2002) on stable water isotopes and He in Opalinus Clay at Mont Terri, Patriarche et al. (2004a,b) on chloride and δ²H in the Toarcian-Domerian at Tournemire, and Gimmi et al. (2007) on stable water isotopes in Opalinus Clay at Benken.

Early work on other sites was focused on Quaternary surficial clay deposits (e.g. Desaulniers et al. 1981, Desaulniers & Cherry 1989). Apart from this, only one other aquitard site has been subjected to a quite comprehensive level of investigation using multiple tracers: an archetypal, surficial clay-rich aquitard located in Saskatchewan, Canada, termed the King site (e.g. Boldt-Leppin & Hendry 2003, Cey et al. 2001, Harrington et al. 2007, Hendry et al. 2000, 2005a,b, Hendry & Wassenaar 1999, 2004, 2005, Wassenaar & Hendry 2000, Hendry & Woodbury 2007, Shaw & Hendry 1998, Vengosh & Hendry 2001). A decade of multi-isotope and hydrogeological research on the 160 m thick aquitard system at the King site (Quaternary clay till overlying late Cretaceous marine clay) has resulted in detailed, high-resolution profiles of dissolved ions and of stable and radiogenic isotopes (¹H, δ¹H and δ¹⁸O, ¹⁴CDOC and ¹⁴CDIC, ³⁶Cl, ³⁷Cl and ⁴He). Interpretations of data from these independent isotopic tracers reveal that late Pleistocene age pore water remains preserved in the aquitard between 35 and 55 m below ground. Transport modelling of isotopic profiles indicates that this water was emplaced with the till upon deposition between 10 and 20 ka, and that the late Holocene glacial-interglacial climatic transition occurred in this area between 7 and 12 ka. Interpretation of the isotope profiles further shows transport of solutes in this aquitard is by molecular diffusion. These findings clearly demonstrate that solute transport in homogeneous clay-rich aquitards is highly predictable over 20 ka and greater time scales.

Note that the suite of tracers applied at the King site and other clays in Canada is more comprehensive than that available from the sites considered here. This is because the opportunities for pore-water sampling are better at a shallow site when compared to deep boreholes, and are also facilitated by the high porosity of the weakly consolidated clay deposits. Moreover, the time scales recorded in the pore water of these surficial deposits are much shorter than those in deeply buried shales, and this opens the field for relatively short-lived radioactive tracers, such as ¹H, ¹⁴C and ³⁶Cl.
1.8 Definitions of terms and symbols

Table 1.8-1 provides an overview of symbols frequently used in the report. We use the following definitions for diffusion coefficients, in accordance with Horseman et al. (1996):

\[ D_{ei} = D_{pi} n_i = D_0 i \ G \ n_i \]

where
- \( D_{ei} \) = effective diffusion coefficient of species \( i \)
- \( D_{pi} \) = pore diffusion coefficient of species \( i \)
- \( D_0 i \) = diffusion coefficient of species \( i \) in free water
- \( n_i \) = porosity accessible to species \( i \)
- \( G = \delta / \tau ^2 \) = geometry factor
- \( \delta \) = constrictivity
- \( \tau ^2 \) = tortuosity.

Table 1.8-1: Definitions of symbols

<table>
<thead>
<tr>
<th>Category</th>
<th>Symbol</th>
<th>Meaning</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffusion</td>
<td>D0</td>
<td>Diffusion coefficient in free water</td>
<td>m²/s</td>
</tr>
<tr>
<td></td>
<td>Dp</td>
<td>Pore-diffusion coefficient</td>
<td>m²/s</td>
</tr>
<tr>
<td></td>
<td>De</td>
<td>Effective diffusion coefficient</td>
<td>m²/s</td>
</tr>
<tr>
<td>Porosity</td>
<td>n</td>
<td>Diffusion-accessible porosity, flow porosity(^1)</td>
<td>-</td>
</tr>
<tr>
<td>Hydraulics</td>
<td>K</td>
<td>Hydraulic conductivity</td>
<td>m/s</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>Hydraulic head</td>
<td>m</td>
</tr>
<tr>
<td></td>
<td>q</td>
<td>Darcy velocity</td>
<td>m/s</td>
</tr>
<tr>
<td></td>
<td>v_a</td>
<td>Advection velocity</td>
<td>m/s</td>
</tr>
<tr>
<td></td>
<td>a_L</td>
<td>Dispersion length</td>
<td>m</td>
</tr>
<tr>
<td></td>
<td>Pe</td>
<td>Peclet number</td>
<td>-</td>
</tr>
<tr>
<td>In-situ production of He</td>
<td>p</td>
<td>Production rate of He in rock</td>
<td>cm³ STP (^4)He (g_{\text{rock}} ) a</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>Accumulation rate of He in pore water</td>
<td>cm³ STP (^4)He (g_{\text{pore water}} ) a</td>
</tr>
<tr>
<td></td>
<td>A_{He}</td>
<td>Release efficiency of He from rock to pore water</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^1\)According to the discussion in Section 4.3.5, diffusion-accessible and flow porosities are assumed to have identical values for a specific species.

Since deposition, the clay-rich low-permeability sequences have been typically affected by geochemical conditions that varied over time. The establishment of new boundary conditions in the embedding aquifers (Figure 1.6-1) led to changes of the pore-water composition. The tracer profiles that we measure today reflect only the youngest part of this evolution, typically the last few Ma, whereas older signals have been obliterated. The strategy most often pursued here is to assume a homogeneous initial condition, i.e. a spatially constant tracer concentration or isotope ratio, at time \( t_{\text{init}} \), which corresponds to the most recent major change in the chemical and isotopic compositions of the embedding aquifer. This means that the initial condition includes all effects predating the most recent change, even though these effects cannot be described in more detail. Model calculations presented
here start at the time $t_{\text{init}}$ represented by the initial condition. The term \textit{evolution time} refers to the time elapsed since $t_{\text{init}}$ until a specific tracer distribution in the low-permeability sequence builds up in consequence of interactions with the aquifers. Thus, evolution time is counted forward and does not refer to time units before present. In many cases, $t_{\text{init}}$ corresponds to a hydrogeological event, such as the exposure of an aquifer bed on the surface by erosion, initiating fresh-water circulation. In other cases, no specific hydrogeological event can be identified because the geochemical evolution of the aquifers is gradual or signals from external effects unrelated to hydrogeology, such as climate change with its effects of the stable isotopic composition of recharge water, come into play.

Model runs are called \textbf{base-case calculations} if the simulations explain the measured data reasonably well with input parameters and scenarios that are within the independently derived ranges. All base cases consider diffusion as the only transport process. In contrast, \textbf{scoping} or \textbf{alternative models} refer to cases that purposely deviate from known palaeo-hydrogeological scenarios and ranges of input parameters, or to cases that are not sufficiently well constrained by independent information and therefore remain on a hypothetical level.
2. COMPILATION OF SITE-SPECIFIC DATA

Obtaining tracer data from low-permeability, argillaceous formations is a non-trivial task, and a number of new, dedicated techniques have been developed over the last decade. The experimental techniques and the analytical methods on which the tracer data presented in this Chapter are based are documented in Appendix A2.

2.1 Callovo-Oxfordian at the Site Meuse/Haute Marne (Bure), France

Andra have investigated the Meuse/Haute-Marne site since 1994, drilling 27 deep boreholes until 2006, many of which were cored, and collecting thousands of water and drillcore samples. Excavations of two shafts for an underground research laboratory (URL) started near to the village of Bure in 2001 and the galleries of the underground laboratory at 445 m below surface have been excavated during 2004 and put into use for scientific experiments and technical developments in late 2004. A top-level synthesis of information, including geological, hydrogeological and geochemical findings, has been published in 2005, focussing mainly on the Callovo-Oxfordian shale sequence, which is considered as a potential host formation for the disposal of spent nuclear fuel and high-level waste. “Dossier 2005 Argile” comprises the five “knowledge reference documents” (Andra 2005a,b,c,d,e) used in this study.

Thirteen boreholes have been drilled from the surface footprint of the underground laboratory: EST103 – EST104 and EST201 – EST212. Most of these boreholes are vertical, but EST209/210/211 are deviated. A further fourteen boreholes have been drilled within a 15 – 20 km radius of the underground laboratory site, mostly to the north and the west (Figure 2.1-1).

2.1.1 Structure and hydrogeology

The “Laboratoire de Recherche Souterrain Meuse/Haute Marne” (Bure URL) is located in the eastern part of the Paris Basin some 75 km southwest of Nancy (Figure 1.5-1, Figure 2.1-1). The Paris Basin forms a large bowl-shaped structure with a radius of about 300 km. Towards the northeast and east, the Hercynian basement of the Ardennes and Vosges mountains marks the boundary of the basin. The Paris Basin comprises Mesozoic and Cenozoic sediments reaching a maximum thickness of about 3 000 m. Looking westwards from the site, the age of outcropping sediments decreases, as the flat-lying sedimentary sequence gently dips at about 1 – 2° towards the centre of the basin. Post-Triassic sedimentation occurred in a shallow marine environment as a series of transgression-regression cycles. This resulted in an alternating deposition of more permeable limestone and sandstone layers and less permeable marl and shale layers (Figure 2.1-2).

Around the URL site (“Laboratory Sector”), an area of about 300 km² (“Regional Sector”) with exposed calcareous sediments of Kimmeridgian and Tithonian age has been investigated in various drilling campaigns (see Figure 2.1-1 for the location of drill sites). The Regional Sector is delimited by three sub-vertical fault systems, which appear to have affected the entire sedimentary sequence down to the basement (Bergerat et al. 2007): to the east by the Gondrecourt structure (NNE-SSW strike), to the west by the Joinville and Marne structures (NNE-SSW and NNW-SSE strikes) and to the south by the Vittel fault. To the north, the Savonnières syncline (2 – 3 km south of the Flexure d'Aulnois-en-
Pertois in Figure 2.1-1) delimits the area. Vertical displacements along all faults are smaller than the formation thickness of the Callovo-Oxfordian shale, so there are no hydraulic connections between the upper (Oxfordian) and lower (Dogger) aquifers. There are some minor structures between these fault zones, but none has been mapped near to the URL site. Only small-scale fracturing has been observed in the Laboratory Sector – two orthogonal sub-vertical sets.

Figure 2.1-1: Geological map of the Meuse/Haute Marne area and major tectonic structures

From Andra (2005b)
The Callovo-Oxfordian shale was deposited in a shallow-marine setting at 163 – 158 Ma. Due to the stability of the Jurassic basin, the formations have a great degree of lateral continuity at a scale of 10 – 100 km. Various short-lived transgression-regression cycles of the sea during this time period, however, resulted in variable proportions of clay (average of 40 – 45 %), carbonate (20 – 35 %) and quartz (15 – 30 %) contents (Yven et al. 2007; Figure 2.1-3). Also, a distinct depth zonation of clay mineralogy is established with respect to the ordering ratio of illite/smectite mixed-layers. The preserved differences in the clay composition are attributed to differences in the sedimentation rate and the sediment source rather than to later diagenetic effects during burial (Lavastre 2002, Andra 2005b).

The Oxfordian limestone sequence above the Callovo-Oxfordian shale was deposited under shallow to moderately deep marine conditions in a carbonate-platform environment. Laterally, it displays a large variability in sedimentary facies from near-coast, sandy lagoon deposits to reef deposits and more distal clay-rich sediments. At the URL site, the Oxfordian limestone sequence consists of almost pure limestone with a highly variable porosity distribution in the vertical dimension. The mostly low porosity and its heterogeneous distribution are interpreted to partly result from carbonate cementation of the primary porosity induced by meteoric fluid circulation, as deduced from isotopic and fluid-inclusion studies on calcite cements and vein infills (Buschaert et al. 2004).

At the URL site, the Dogger limestone sequence below the Callovo-Oxfordian shale consists of almost pure limestones of Bathonian and Bajocian age, deposited in a shallow carbonate-platform environment under tropical conditions. It comprises a large variety of sedimentary facies (shell debris, reef structures, calcareous sand layers) resulting in a heterogeneous porosity distribution (Andra 2005h). Lateral variability of sedimentary facies is substantial. As for the Oxfordian limestones, isotopic and fluid-inclusion studies of calcite cement and vein infills reveal that the heterogeneous porosity distribution is partly due to localised porosity reduction induced by meteoric fluid circulation, even though the sedimentary facies also plays an important role (Buschaert et al. 2004).

The low-permeability sequence consists of the Callovo-Oxfordian shale (130 m thick at the URL site) and the underlying thin limestone of the Dalle Nacrée (Figure 2.1-2). In addition, the Oxfordian and Dogger limestones that overlie and underlie the Callovo-Oxfordian shale also contain low-permeability layers, which are separated by more porous and therefore more permeable horizons. At the URL site, the nearest water-conducting horizon (‘HP’ – horizon poreux) in the Oxfordian limestone is 63 m above the contact to the Callovo-Oxfordian, and the nearest permeable zone in the Dogger limestone is 63 m below the contact to the overlying Callovo-Oxfordian. This means that the low-permeability sequence is 256 m thick at the URL site (Table 2.1-1). Less detailed information is available for the borehole sites away from the URL site. Given the fact that the lithologic and hydrogeologic properties of the Oxfordian vary laterally, it is not always possible to extrapolate the findings from the URL site to the wider region. For some boreholes, the position of the lowermost permeable horizon is known and has been considered in defining the system geometry as listed in Table 2.1-1. For other boreholes, this is not the case, which introduces uncertainty.

Hydrochemical characteristics of the ground waters suggest that there is no hydraulic connection between the Oxfordian and Dogger limestones and that the Callovo-Oxfordian shale acts as an efficient barrier (Andra 2005f,g,h, Lavastre et al. 2005a, Giannesini et al. 2004). They further indicate that the Oxfordian and Dogger limestones contain waters that are not well mixed either in the vertical or the horizontal dimensions, which is typical of karstic ground-water environments (Andra 2005g,h).
Figure 2.1-2: Stratigraphic profile at the Bure URL
2.1.2 Tracer distributions in the Callovo-Oxfordian shale

Table 2.1-2 provides a summary of available tracer-data sets from the Callovo-Oxfordian. The majority of all data were obtained from a number of boreholes at the URL site, augmented by data from the main access shaft (PPA) and from short boreholes drilled from niches adjacent to the shaft (PAC, SUG2). The horizontal distance between the surface locations of the boreholes at the URL site is max. 400 m. Taking into consideration the inclination of boreholes EST210 and EST211 (Figure 2.1-4), the maximum horizontal distance between samples becomes 600 m. The data originate from a number of investigation programmes that were performed at different times and for different purposes. A general overview of geochemical data and their interpretation is given in Buschaert et al. (2007).

Anions

A good data set is available for Cl\(^-\), while a more limited and therefore less useful data set exists for Br\(^-\). The Cl\(^-\)/Br\(^-\) ratio is 200 ± 47, which is substantially lower than the current sea-water value of ca. 300.

---

2 The PAC and SUG experiments were performed in short vertical boreholes drilled from horizontal tunnels located 150 to 200 m away from vertical borehole EST212.
The recalculation of anion concentrations per kg rock (i.e., the direct result of aqueous leaching tests) to concentrations per L or kg pore water requires knowledge of the anion-accessible porosity (geochemical porosity, Pearson 1999). In limestones (Oxfordian, Dalle Nacrée, Dogger), water-loss porosity was used for the recalculation. In the shaly lithologies of the Callovo-Oxfordian, where anion exclusion limits the pore space available to anions, anion-accessible porosity was derived by comparing Cl\(^-\) concentrations in pore water determined by squeezing and aqueous leaching tests. Both these methods were applied on adjacent materials for 21 samples from boreholes EST211, EST212, EST104, MSE101 and HTM102. On the average, Cl\(^-\) concentrations in squeezed samples are 2.11 times higher than those derived from aqueous leaching when using water-loss porosity for the recalculation to pore-water concentrations. It is concluded that a fraction of \(1/2.11 = 0.5\) of water-loss porosity is accessible to anions in the Callovo-Oxfordian shale, and this value is used here for all leaching data from Bure. It is in line with independently derived values for other argillaceous formations (see below). Locally, the anion-accessible porosity fraction may vary with rock mineralogy, so considering a constant value over a heterogeneous rock sequence inevitably introduces some uncertainty on the estimated pore-water concentration of Cl\(^-\).

### Table 2.1-1: System geometries for boreholes at Bure for which tracer data are available

<table>
<thead>
<tr>
<th>Unit</th>
<th>Lithology</th>
<th>Hydrogeology</th>
<th>Depth below surface [m] at URL site (boreholes EST104, EST207, EST212, PPA shaft)</th>
<th>Depth below surface [m] in borehole EST312</th>
<th>Depth below surface [m] in borehole EST322</th>
<th>Depth below surface [m] in borehole EST342</th>
<th>Depth below surface [m] in borehole MSE101</th>
<th>Depth below surface [m] in borehole HTM102</th>
</tr>
</thead>
<tbody>
<tr>
<td>Callovian (Dalle Nacrée, C1)</td>
<td>Limestone</td>
<td></td>
<td>422 – 552</td>
<td>349.5 – 520</td>
<td>485.5 – 607</td>
<td>544 – 642.7</td>
<td>505 – 651</td>
<td>341.8 – 472.0</td>
</tr>
<tr>
<td>Bajocian/ Bathonian (D3, D4)</td>
<td>Limestone</td>
<td>Heterogeneous aquifer</td>
<td>552 – 560.9</td>
<td>520 – 532</td>
<td>607 – 610</td>
<td>642.7 – 656</td>
<td>651 – 658</td>
<td>472.0 – 483.0</td>
</tr>
<tr>
<td>Bajocian (D2)</td>
<td>Marl</td>
<td>Aquitard</td>
<td>560.9 – 615</td>
<td>532 – 563</td>
<td>610.0 – 661</td>
<td>656 – 748.07 (bottom hole)</td>
<td>658 – 665</td>
<td>483.0 – 628.3</td>
</tr>
<tr>
<td>Bajocian (D1)</td>
<td>Limestone</td>
<td>Aquitard</td>
<td>615 – 633 (bottom hole)</td>
<td>563 – 612 (bottom hole)</td>
<td>661 – 709.56 (bottom hole)</td>
<td>655.0 – 706.3 (bottom hole)</td>
<td>665 – 819</td>
<td>628.3 – 655.0</td>
</tr>
</tbody>
</table>

1 Includes shaly facies of unit C3a (Andra 2005f, p. 41). Shaded areas indicate aquifers.
Table 2.1-2: Overview of available tracer-data sets from the low-permeability sequence at Bure and extraction methods

<table>
<thead>
<tr>
<th>Borehole</th>
<th>Location</th>
<th>Orientation</th>
<th>Cl⁻</th>
<th>Δ³⁷Cl</th>
<th>Br⁺</th>
<th>Δ¹⁸O, δ²H</th>
<th>He</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>EST104</td>
<td>URL site</td>
<td>vertical</td>
<td>leaching, squeezing</td>
<td>-</td>
<td>squeezing</td>
<td>squeezing</td>
<td>-</td>
<td>Andra (2001, Fig. 2.3-02), Reeder et al. (1997c)</td>
</tr>
<tr>
<td>EST210</td>
<td>URL site</td>
<td>inclined</td>
<td>leaching</td>
<td>-</td>
<td>-</td>
<td>diffusive exchange</td>
<td>out-gassing</td>
<td>Bigler et al. (2005), Waber (2005)</td>
</tr>
<tr>
<td>EST211</td>
<td>URL site</td>
<td>inclined</td>
<td>leaching</td>
<td>-</td>
<td>-</td>
<td>diffusive exchange</td>
<td>out-gassing</td>
<td>Bigler et al. (2005), Waber (2005)</td>
</tr>
<tr>
<td>EST212</td>
<td>URL site</td>
<td>vertical</td>
<td>leaching, squeezing</td>
<td>-</td>
<td>-</td>
<td>diffusive exchange</td>
<td>out-gassing</td>
<td>Bigler et al. (2005), Bouchet (2004d), Fernandez et al. (2005), Waber (2005)</td>
</tr>
<tr>
<td>PAC &amp; SUG</td>
<td>URL site</td>
<td>short boreholes from niches direct sampling</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td>Vinsot et al. (in press), Appelo et al. (in press)</td>
</tr>
<tr>
<td>PPA shaft</td>
<td>URL site</td>
<td>vertical</td>
<td>leaching</td>
<td>-</td>
<td>-</td>
<td>diffusive exchange</td>
<td>out-gassing</td>
<td>Bigler et al. (2005), Waber (2005)</td>
</tr>
<tr>
<td>EST312</td>
<td>13 km NNE of URL site</td>
<td>vertical</td>
<td>leaching</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Bouchet (2004a), Rouset et al. (2003a)</td>
</tr>
<tr>
<td>EST322</td>
<td>9 km WSW of URL site</td>
<td>vertical</td>
<td>leaching</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Bouchet (2004b), Rouset et al. (2003b)</td>
</tr>
<tr>
<td>EST342</td>
<td>23 km WSW of URL site</td>
<td>vertical</td>
<td>leaching</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Bouchet (2004c), Mangeot (2003)</td>
</tr>
<tr>
<td>HTM102</td>
<td>2 km SSE of URL site</td>
<td>vertical</td>
<td>leaching, squeezing</td>
<td>leaching, squeezing</td>
<td>-</td>
<td>-</td>
<td>Andra (2001, Fig. 2.3-02), Blackwell et al. (1995a), Lavastre (2002), Lavastre et al. (2005a)</td>
<td></td>
</tr>
<tr>
<td>MSE101</td>
<td>12 km NNW of URL site</td>
<td>vertical</td>
<td>leaching, squeezing</td>
<td>-</td>
<td>leaching, squeezing</td>
<td>-</td>
<td>-</td>
<td>Andra (2001, Fig. 2.3-02), Blackwell et al. (1995b)</td>
</tr>
</tbody>
</table>

Cl⁻ at the URL site

Available data for Cl⁻, based on aqueous leaching and on squeezing, are shown in Figure 2.1-5. The following observations can be made:

- In the upper part of the low-permeability sequence, there is a trend towards higher Cl⁻ contents with depth, starting at very low values in the Oxfordian. The maxima are reached approximately in the centre of the sequence (typically 1 500 – 2 000 mg/L, except for some outliers).
- In boreholes EST207 and EST211, there is an evolution towards slightly decreasing Cl⁻ contents with depth in the lower part of the profile, trending towards the somewhat lower Cl⁻ content in the Dogger aquifer. In the other boreholes, no clear trend is observed, which is due to the absence of data in the uppermost part of the Dogger limestone and to the scatter of the data.
- Data for borehole EST207 show a substantial scatter, which is due to difficulties with the measurement of water-loss porosity (partial evaporation during sample storage), and so are considered less reliable (Bouchet 2004e). Water contents were not measured on the same samples as the Cl\(^-\) concentrations, which leads to additional uncertainty and probably explains the outliers.

- Data of Waber (2005) for EST211 and EST212 show well-defined depth distributions of Cl\(^-\) with depth. All other data are subject to a substantial scatter, which partially masks possible depth trends.

Figure 2.1-4: Projected cross-section of boreholes EST210, EST211, EST212 and the PPA shaft at Bure showing the approximate sample locations

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3 Waber (2005) used a slightly different value for the porosity fraction that is accessible to anions. Therefore, the Cl\(^-\) concentrations are not identical in this report and in Waber (2005). However, the differences are quantitatively unimportant and do not affect the shapes of the profiles.
The high Cl⁻ content in the Dalle Nacrée of borehole EST211 is the only outlier in Waber's (2005) data set (Figure 2.1-5). We note that this thin limestone unit also has a high Cl⁻ content in borehole HTM102 (Figure 2.1-6), and it is also aberrant in its water isotopic signature (see below and Figure 2.1-7). The possibility exists that fluid inclusions affect at least the Cl⁻ signal in this low-permeability unit, but further petrographic studies would be needed to confirm this hypothesis.

Leaching data of Waber (2005) show higher Cl⁻ concentrations in EST211 when compared to EST212. Because the same methodology was applied for samples from both boreholes, this possibly reflects a real lateral heterogeneity over horizontal distances of a few hundreds of metres (Figure 2.1-4). However, for well substantiated conclusions, a better spatial coverage would be needed. At this stage, the total analytical and conceptual uncertainty may be of a similar magnitude as the observed lateral variability.

Two sets of leaching data are available for borehole EST212. Those of Waber (2005) yield lower Cl⁻ contents than those of Bouchet (2004d), even though the shapes of the two profiles are similar.

Direct sampling of pore water (Fig. 2.1-5, PAC and SUG experiments; Vinsot & Mettler 2007, Vinsot et al., in press, Appelo et al., in press) yields Cl⁻ contents that are similar to those in the closest deep borehole EST212 (lateral distance 150 – 200 m).

In borehole EST210, Cl⁻ data from rock leaching are available from the Dogger limestone underlying the permeable layer (not shown in Figure 2.1-5). There is a sharply increasing trend from 633.9 m (1 730 mg/L) to 699.7 m (2 897 mg/L) and 762.8 m (5 658 mg/L) (data from Waber 2005).

Cl⁻ in boreholes EST311, EST312

The ground water in the Dogger limestone is more saline than in all other boreholes, whereas salinity is low in the Oxfordian limestone. The Cl⁻ profile across the low-permeability sequence fits well between the concentrations at the boundaries and shows a trend of sharply increasing contents with depth⁴ (Figure 2.1-6). It could, in principle, be interpreted as a steady-state diffusion profile. However, tracer data are only available from the central part of the low-permeability sequence, and the positions of the boundaries of the low-permeability sequence are somewhat uncertain.

Cl⁻ in borehole EST322

Cl⁻ concentrations in the Oxfordian and Dogger aquifers are low, and those in the pore water of the low-permeability sequence are comparable or somewhat higher (Figure 2.1-6). The substantial scatter is probably due to uncertainties related to water content, which was not measured on the same samples as Cl⁻ concentration. Due to the poor definition of the Cl⁻ profile, the data from EST322 are not suited for quantitative evaluation.

Cl⁻ in borehole EST342

Cl⁻ concentrations from the Callovo-Oxfordian are lower than or similar to that in the underlying Dogger aquifer (Figure 2.1-6). Due to the absence of data in the central and upper part of the low-permeability sequence, a quantitative evaluation is not feasible. As for EST322, water contents were measured on different samples than Cl⁻ concentrations.

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⁴ Note that water contents were not measured on the same samples as Cl⁻ contents.
Cl\textsuperscript{-} in borehole HTM102

Three data sets are available for Cl\textsuperscript{-}, and one data set for Br\textsuperscript{-}. As shown in Figure 2.1-6, the Cl\textsuperscript{-} data sets are internally consistent. In spite of a substantial scatter, Cl\textsuperscript{-} contents clearly increase with depth. There are no tracer data from the adjacent aquifers.

Cl\textsuperscript{-} in borehole MSE101

Cl\textsuperscript{-} data based on leaching and squeezing indicate a trend of increasing concentration with depth, even though scatter is substantial (Figure 2.1-6). The shallowest ground-water sample in the Dogger shows slightly lower Cl\textsuperscript{-} content than the immediately overlying pore waters. A quantitative evaluation of the data is rendered difficult by the absence of pore- and ground-water data from the Oxfordian.

Conclusions for Cl\textsuperscript{-}

A data set suited for quantitative evaluation is available at the URL site and, with some restrictions, for boreholes EST311/312. Data are too scarce and too scattered for the other boreholes. Although there are many data for Callovo-Oxfordian pore waters in HTM102, there is no ground-water composition for the Dogger in this borehole. Given the observed lateral heterogeneity in both pore waters and ground waters, it is not feasible to fill the data gaps in one borehole with data from other boreholes. With the exception of boreholes EST311/312, Cl\textsuperscript{-} concentrations are mostly below 2 000 mg/L.
Figure 2.1-5: **Cl⁻ profiles through the low-permeability sequence at the Bure URL site**

Shaded areas indicate permeable layers within the limestones. Black circles show leaching data from the Oxfordian in the PPA shaft. Blue bars indicate groundwater data from the PPA shaft (Oxfordian, HP1) and from borehole EST210 (Dogger). References: see Table 2.1-2 (pore waters) and Table 2.1-3 (ground waters)
Figure 2.1-6: Cl⁻ profiles through the low-permeability sequence in regional boreholes at Bure

Shaded areas indicate permeable layers within the limestones. Blue bars and squares indicate ground-water data. References: see Table 2.1-2 (pore waters) and Table 2.1-3 (ground waters)
Water isotopes

Data are only available from the URL site and are summarised in Figure 2.1-7. There is a general trend of increasing δ values with depth, with a conspicuous bulge in the Callovo-Oxfordian shale. Below HP1, the lowermost permeable horizon in the Oxfordian (348 – 359 m), δ values increase and reach maxima within the Callovo-Oxfordian shale at about 430 m. Below this depth, δ values decrease but are more scattered, possibly due to lateral heterogeneity. Below the permeable layer in the Dogger, δ values increase with depth but always remain negative.

Figure 2.1-7: δ¹⁸O and δ²H profiles through the low-permeability sequence at the Bure URL site

Circles: Pore water; squares: ground water. References: see Table 2.1-2 (pore waters) and Table 2.1-3 (ground waters)

Helium

He in pore waters at the URL site was studied by Bigler et al. (2005), and the data are shown in Figure 2.1-8. The well-constrained He profile is characterised by increasing concentrations with depth, with steep gradients in the Oxfordian just below the permeable layer HP1 (348 – 359 m) and below the permeable layer in the Dogger at 615 – 633 m. Data from ground waters are not available.

Cl isotopes

All δ³⁷Cl data are based on the work of Lavastre (2002) and Lavastre et al. (2005a,b). A profile of δ³⁷Cl in pore water is available for borehole HTM102 (Figure 2.1-9). A tendency towards lower δ values is observed in the deeper part of the Callovo-Oxfordian. However, no measurements have been made in the over- and underlying aquifers, so the boundary conditions are not known for this borehole. Ground waters in the Oxfordian were analysed at the URL site and for some regional boreholes and show a substantial variability in both the vertical and horizontal dimensions (Figure 2.1-9), suggesting that these data are difficult to extrapolate to borehole HTM102. Values in the Dogger cover a similar range of -1.55 to -0.2 ‰.
Figure 2.1-8:  He profile through the low-permeability sequence at the Bure URL site

Data from Bigler et al. (2005)

Figure 2.1-9:  δ³⁷Cl profiles through the low-permeability sequence at Bure

Left: Pore waters in borehole HTM102; right: ground waters at the URL site (PPA shaft and borehole EST201) and in boreholes EST311, EST331 and EST351. Data from Lavastre et al. (2005a,b). Some additional ground-water data for the Oxfordian limestone shown graphically in Buschaert et al. (2007) are not considered
2.1.3 Upper and lower boundary

An overview of the current understanding of the hydrogeological system in the region of Bure is given in Buschaert et al. (2007).

Upper boundary

The upper boundary of the low-permeability sequence is provided by the Oxfordian limestone, in which a number of flowing, more porous, zones were identified. These porous horizons (“HP”) are discontinuous and non-correlatable at the kilometre scale. Ground water in the Oxfordian limestone sequence is of the Ca-Mg-HCO₃ chemical type at shallower levels and of a general Ca-Mg-SO₄-HCO₃ type at deeper levels (Andra 2005g). Its mineralisation is low to moderate, and it is in chemical equilibrium with the dominant carbonate minerals. Based on the radiogenic (absence of ³H, ¹⁴C generally below 3 pmC; Michelot & Massault 2004) and stable isotope compositions, ground waters in the Oxfordian limestone sequence are interpreted to have infiltrated during present-day conditions and – at deeper levels – during colder climatic conditions with an average residence time in the order of 10 000 – 100 000 a (Andra 2005g).

The Cl⁻ concentration profile in the Oxfordian limestones at the URL site, considering both ground-water and pore-water data, is shown in Figure 2.1-10. Chemical ground-water data were obtained from deep boreholes drilled from the surface and from short boreholes from the floor of the PPA shaft during shaft sinking, drilled across individual porous horizons. Cl⁻ concentration in ground waters obtained from the porous horizons increases with depth, indicating that the hydraulic connectivity between the porous horizons is limited. Cl⁻ concentrations in pore water of the Oxfordian limestone below the deepest porous horizon (HP1) increase sharply towards the values observed in the underlying Callovo-Oxfordian. Similar trends are also observed for stable water isotopes (Figure 2.1-11). It is concluded that HP1, the lowermost porous horizon in which an enhanced transmissivity was observed, can be considered as the upper boundary of the underlying low-permeability sequence, and the tracer data from this horizon are given in Table 2.1-3.

In the boreholes in the Regional Sector, the water samples taken generally represent the one or two major water productive porous layers that were previously detected by borehole logging. Available data are summarised in Table 2.1-3. Cl⁻ contents in Oxfordian ground waters are invariably below 100 mg/L (but pore waters in the lower part of the Oxfordian limestone have higher Cl⁻ concentrations). δ¹⁸O and δ²H of ground waters vary in the relatively narrow ranges of -9.4 to -8.2 ‰ and -64.2 to -55.9 ‰, respectively.
Figure 5.2-21: Cl⁻ contents in ground and pore waters of the Oxfordian at the Bure URL site

Ground-water data are from the PPA shaft and from borehole EST201. Yellow area indicates the low-permeability sequence. "HP" = ground water sampled in porous and permeable horizons, "leach" refers to pore-water data obtained by aqueous leaching of the rock. References: see Table 2.1-2 (pore waters) and Table 2.1-3 (ground waters)

Figure 5.2-22: δ¹⁸O in the Oxfordian limestone at Bure

Bars: Ground waters; circles: pore waters. References: see Table 2.1-2 (pore waters) and Table 2.1-3 (ground waters)
Table 2.1-3: Tracer contents in ground waters of the Oxfordian and Dogger limestones adjacent to the low-permeability sequence at Bure

<table>
<thead>
<tr>
<th>Borehole/shaft</th>
<th>Formation</th>
<th>Depth [m]</th>
<th>Electric conductivity [µS/cm]</th>
<th>CT [mg/L]</th>
<th>δ³⁷Cl [%o v-smow]</th>
<th>δ¹⁸O [%o v-smow]</th>
<th>δ²H [%o v-smow]</th>
<th>He [cm³ STP/g water]</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPA (URL site)</td>
<td>Oxfordian, porous horizon HP1</td>
<td>350</td>
<td>83</td>
<td>n.d.</td>
<td>-8.3</td>
<td>-55.9</td>
<td>3.13E-7 (1)</td>
<td>Cl: Cauier (2004); water isotopes: Giannesini et al. (2004); He: Bigler et al. (2005)</td>
<td></td>
</tr>
<tr>
<td>EST321</td>
<td>Oxfordian</td>
<td>390 – 410</td>
<td>426</td>
<td>2</td>
<td>-0.07 (2)</td>
<td>-9.4</td>
<td>-64.2</td>
<td>n.d.</td>
<td>Andra (2003, 2004, Annex 4)</td>
</tr>
<tr>
<td>EST331</td>
<td>Oxfordian</td>
<td>60 – 335</td>
<td>545</td>
<td>14</td>
<td>-1.25 (2)</td>
<td>-9.3</td>
<td>-64.2</td>
<td>n.d.</td>
<td>Andra (2004, Annex 4)</td>
</tr>
<tr>
<td>EST312</td>
<td>Dogger</td>
<td>559 – 582</td>
<td>12 880</td>
<td>3 960</td>
<td>-0.97 (2)</td>
<td>-5.3 (4)</td>
<td>-34.5 (4)</td>
<td>n.d.</td>
<td>Andra (2004, Annex 4)</td>
</tr>
<tr>
<td>EST342</td>
<td>Dogger</td>
<td>648 – 710</td>
<td>4 530</td>
<td>890</td>
<td>-1.55 (2)</td>
<td>-6.4</td>
<td>-42.1</td>
<td>n.d.</td>
<td>Andra (2004, Annex 4)</td>
</tr>
<tr>
<td>MSE101</td>
<td>Dogger</td>
<td>665</td>
<td>6 280</td>
<td>1 470</td>
<td>-0.55 (2)</td>
<td>-7.0</td>
<td>-46.4</td>
<td>n.d.</td>
<td>Andra (2004, Annex 4)</td>
</tr>
</tbody>
</table>

Only samples closest to the low-permeability sequence are shown, more data are available from more distant intervals

(1) Data based on dissolved gas analysis of rock sample 357.20, 7.2 m below HP1
(2) Data from Lavastre et al. (2005b)
(3) Data based on dissolved gas analysis of a rock sample
(4) From underlying interval 592 – 597 m

Lower boundary

Ground water in the Dogger limestone sequence is of a general Na-Cl chemical type and is more mineralised than that in the Oxfordian limestones. It shows a large variation in solute concentrations over the investigation area and is generally interpreted as a mixture of Holocene meteoric and old (Eocene) formation water with an average residence time in the order of 1E5 – 1E6 a, based on the absence of measurable ³H and ¹⁴C (Michelot & Massault 2004), the stable-isotope composition of water, and high contents of He and ³⁶Cl (Marty et al. 1993, 2003, Matray et al. 1994, Pinti et al. 1997, Dewonck 2000, Andra 2005h).

In general, the transmissivity of the Dogger has been lowered by diagenetic cementation so that it has poor aquifer characteristics. As in the Oxfordian limestone, the Dogger consists of permeable zones separated by low-permeability rock. Ground water from the Dogger was sampled from the permeable horizon at 615 – 633 m in borehole EST212. Ground-water samples were also obtained from regional boreholes EST312, EST322, EST342 and MSE101. Data of the shallowest samples, i.e. those closest to the low-permeability sequence, are listed in Table 2.1-3.
Cl\textsuperscript{-} concentrations in Dogger ground- and pore waters are shown in Figure 2.1-12. Cl\textsuperscript{-} contents in the Dogger are higher than those in the Oxfordian limestones but vary widely within a borehole as well as among boreholes, indicating a high degree of heterogeneity. At the URL site, the ground-water sample at 615 – 633 m has a Cl\textsuperscript{-} concentration of 1 305 – 1 360 mg/L. Pore-water samples from deeper parts of the Dogger indicate sharply increasing Cl\textsuperscript{-} contents. The high value in the Dalle Nacrée (EST211, 556.55 m) is difficult to explain, given the lower values in both the overlying Callovo-Oxfordian and the underlying ground-water sample.

Only a small number of samples are available for stable water isotopes, and the δ values are generally higher than those in the Oxfordian (Figure 2.1-13). At the URL site, a trend of increasing δ values is observed in pore-water samples below the ground water at 615 – 633 m, similar to that for Cl\textsuperscript{-}.

![Figure 2.1-12: Cl\textsuperscript{-} concentrations in the Dogger limestones at Bure](image)

Bars and squares: ground water; circles: pore water. Data from the URL site shown in red. Also includes data from the Dalle Nacrée (uppermost part of the Dogger limestone). References: see Table 2.1-2 (pore waters) and Table 2.1-3 (ground waters)

### 2.1.4 Transport parameters

#### Diffusion coefficients

A substantial number of experimental determinations of diffusion coefficients for various facies within the Callovo-Oxfordian have been performed and are discussed in Andra (2005b, Vol. 3, p.74 ff). The average values and the variability are shown in Table 2.1-4. The effective diffusion coefficients, De, for Cl\textsuperscript{-} and for I were found to be similar and are ca. 5 times smaller than that for HTO. No systematic variability of diffusion coefficients as a function of lithology was observed, and so the overall average values are used. The anisotropy of diffusion coefficients in the Callovo-Oxfordian is limited, and the values given in Andra (2005b) do not distinguish between different directions.
Less data are available for the Oxfordian limestone. According to Descostes et al. (2004) and Andra (2005b), there is a clear distinction between higher diffusion coefficients in the porous horizons and lower values outside such horizons (Table 2.1-4). Note that in the former, the pore dispersion coefficient is dominated by hydrodynamic dispersion and not diffusion. Average $D_e$ for HTO is ca. 2.5 times smaller in the Oxfordian limestone below porous horizon HP1 than in the Callovo-Oxfordian, whereas $D_e$ for anions is comparable in both units. In the absence of formation-specific data, it is assumed that $D_e$ values in the Dogger limestone are equal to those in the Oxfordian limestone.

Experimental determinations of diffusion coefficients for He are very scarce and available for the Callovo-Oxfordian shale only. Bigler et al. (2005) conducted out-diffusion experiments of spherical rock samples and derived a pore diffusion coefficient, $D_p$, value of 7.5E-10 m$^2$/s, corresponding to $D_e = 1.35E-10$ m$^2$/s (using a He-accessible porosity of 0.18). Rebour et al. (1997) report a much lower experimental value of $D_p = 6E-11$ m$^2$/s at 50 °C, which would correspond to $D_e = 5E-12$ m$^2$/s at 20 °C. This value is smaller than that for HTO in the same rock formation, which is most likely not realistic. In the absence of a representative number of experimental determinations, $D_e$ for He is estimated as being 3 times higher than that for $D_e$ for HTO according to the argument presented in Appendix A3.2.
<table>
<thead>
<tr>
<th>Formation</th>
<th>De (HTO)  @ 20 °C [m²/s]</th>
<th>Porosity (HTO) [-]</th>
<th>De (Cl-, I-)  @ 20 °C [m²/s]</th>
<th>Porosity (Cl-, I-) [-]</th>
<th>De (cations)  @ 20 °C [m²/s]</th>
<th>Porosity (cations) [-]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Callovo-Oxfordian shale</td>
<td>2.6E-11 (±38 %)</td>
<td>0.18 (±16 %)</td>
<td>5.0E-12</td>
<td>0.09 (1)</td>
<td>2.5E-10 for Cs (range 2.6E-11 – 5E-10)</td>
<td>0.18</td>
<td>Andra (2005b, Vol. 3, p.74 ff)</td>
</tr>
<tr>
<td>Oxfordian limestone: Porous horizons</td>
<td>7.7E-11</td>
<td>0.18</td>
<td>6.7E-11</td>
<td>0.18 (2)</td>
<td>n.d.</td>
<td>n.d.</td>
<td>Andra (2005b, Vol. 3, p. 139, Tab. 20-13)</td>
</tr>
<tr>
<td>Oxfordian limestone below the lowermost porous horizon (HP1)</td>
<td>9.5E-12 (3)</td>
<td>0.065</td>
<td>4.6E-12 (3)</td>
<td>0.065 (2)</td>
<td>n.d.</td>
<td>n.d.</td>
<td>Descostes et al. (2004), Andra (2005b, Vol. 3, p. 138 ff)</td>
</tr>
<tr>
<td>Dogger limestone</td>
<td>No data – same values assumed as for Oxfordian limestone</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(1) Based on the argumentation presented in Section 2.1.2, half the water-accessible porosity is thought to be accessible to anions, i.e. 0.09. From diffusion experiments, a lower value of 0.06 (range 0.04 – 0.07) would be obtained but is not considered here.

(2) In this report, it is assumed that in limestones the whole pore space is accessible to anions. Therefore, the same porosity values are used for water isotopes and for Cl-. Based on porosities obtained from diffusion experiments, a consistent average anion-accessible porosity of 0.18 is obtained for the porous horizons, whereas the value of 0.052 obtained for the limestone below HP1 is slightly lower than the average water-accessible porosity in this zone (Andra 2005b, Tab. 20-13).

(3) From Fig. 20-16 in Andra (2005b)

Hydraulic conductivity

A large number of in-situ and laboratory investigations were targeted at obtaining representative values of hydraulic conductivity from the Callovo-Oxfordian shale (Distinguin & Lavanchy 2007, Andra 2005b, Vol. 2, ch. 16, p. 51 ff). The full range is 1E-14 to 1E-12 m/s, with no systematic depth dependence, and the reference values are 5E-14 to 5E-13 m/s. Anisotropy is weak, certainly below a factor of x10, probably less. Fractures, whether mineralised or not, were found to have no hydraulic relevance. The low permeability, the kinematic porosity and the low hydraulic gradient at the URL site indicate that the Darcy velocity is around 3 cm per 100 000 a, which corresponds to an advection velocity of about 30 cm per 100 000 a (Andra 2005b). This is much less than the characteristic length for transport by diffusion for that time period. If the hydraulic gradient contains an osmotic component (see Section 2.1.6), the relevance of advection becomes even smaller.

Hydraulic conductivity measured on rock samples outside permeable horizons in the Dogger limestone is in the range of ca. 2E-9 to 1E-11 m/s (Andra 2005b, vol. 2, p. 78, Fig. 16-13). In the Oxfordian sub-units C3a and C3b (corresponding to the profile section below the porous horizon HP1), conductivity is in the range 3E-12 to 5E-11 m/s (Andra 2005b, vol. 2, ch. 16, p. 92).

Porosity

The general pattern of porosity through the Callovo-Oxfordian shale was established primarily by the depositional mineralogy and secondarily by diagenetic changes that occurred until the time of maximum burial at around 100 Ma (Andra 2005b). Physical porosity has two components: mesoporosity and microporosity within the clay matrix that makes up about 90 % of the total, and the macroporosity that occurs at the interface between clay matrix and quartz particles and bioclasts.
Average values for physical porosity are 0.195 for shaly lithologies and 0.14 for more carbonate-rich sub-units. The reference value for the Callovo-Oxfordian as a whole is 0.18 (Table 2.1-4). As discussed in Section 2.1.2, anion-accessible porosity is considered to be half this value, i.e. 0.09. This is somewhat higher than the value of 0.06 (range 0.04 – 0.07) derived from diffusion experiments (Andra 2005b, vol. 3, p. 74 ff). However, more weight is given to the derivation of anion-accessible porosity from the comparison of leaching, squeezing and in-situ sampling data.

For the Oxfordian limestone, porosity is considered to be identical for all dissolved species (i.e. no anion exclusion is thought to occur), and values are given in Table 2.1-4. With a value of 0.065, the limestone below the lowermost porous horizon HP1 has a substantially lower porosity compared to that in the porous horizons themselves. In the absence of data, this value is also used for the Dogger limestone.

In-situ temperature

Current temperature of the Callovo-Oxfordian shale is 22 °C (Andra 2005b).

2.1.5 U and Th contents in rocks

Average U and Th of the relevant rock formations have been compiled by Bigler et al. (2005) and are shown in Table 2.1-5.

<table>
<thead>
<tr>
<th>Formation</th>
<th>U [ppm]</th>
<th>Th [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxfordian limestone</td>
<td>1.79 ± 0.92</td>
<td>3.03 ± 1.16</td>
</tr>
<tr>
<td>Callovo-Oxfordian shale</td>
<td>1.92 ± 0.12</td>
<td>10.09 ± 1.22</td>
</tr>
<tr>
<td>Dogger limestone</td>
<td>0.76 ± 0.35</td>
<td>4.63 ± 1.87</td>
</tr>
</tbody>
</table>

Data from Bigler et al. (2005)

2.1.6 Hydraulic gradient

In the Callovo-Oxfordian shale, there is an overpressure of max. 40 m in relation to the overlying Oxfordian limestone and max. 60 m in relation to the Dogger limestone in the footwall (Figure 2.1-14; Andra 2005b, Vol. 2, ch. 15). The overpressure is currently attributed to osmotic processes, whereby the activity of water in the clay formation is lowered in the clay matrix relative to water activities in the Oxfordian and Dogger limestones (Gueutin et al. 2007). If this interpretation applies, the head difference between the two embedding aquifers can be taken as an indication of the hydraulic gradient driving water flow across the low-permeability sequence. At the URL site, this gradient is small (ca. 0.05 m/m) and directed downwards.
2.1.7 Geological and hydrogeological evolution

Jurassic strata including the Callovo-Oxfordian and the adjacent limestones were deposited in marine conditions on a shallow stable platform (Andra 2005b). The Callovo-Oxfordian layer would have been covered by 500 – 600 m of sediment at the end of the Jurassic. Sedimentation continued into the Cretaceous period, with up to 300 m of chalk being laid over the Jurassic sequence. Maximum burial of the Callovo-Oxfordian shale was only about 800 m and maximum temperatures did not exceed ca. 50 °C as indicated by organic geochemistry (37 – 48 °C, Landais & Elie 1999), fluid-inclusion measurements on calcite cements (31 – 38 °C, Buschaert et al. 2004) and the absence of the smectite to illite conversion (Ruck-Mosser et al. 1999). Minor diagenetic modifications of the petrography, mineralogy and porosity of the formations occurred during this period of maximum burial in the Cretaceous (Clauer et al. 2007). However, isotopic studies suggest that carbonates remained unaltered, with original isotopic signatures characteristic of mid-Jurassic sea-water composition. The region was exposed to continental conditions during the early Cretaceous, until marine conditions were re-established in the late Cretaceous. The Pyrenean N-S compressional stage (starting in the Paleocene, with a peak in the Eocene) led to the final emergence of the region from the sea, persisting until present. The structural imprint in the region is relatively weak and includes conjugate faults. After an extensional phase during the Oligocene, the current Alpine NW-SE compressional regime has been established in the Miocene.

Since final emergence at ca. 65 Ma, the aquifers have been exposed to meteoric infiltration, and karstification has affected the near-surface parts of the limestones (Figure 2.1-15). The substantial heterogeneity of hydrogeological properties of the Oxfordian and Dogger limestones in both the vertical and horizontal dimensions is due to the variability of depositional environments and
diagenetic overprint. On a larger scale, the permeability of both aquifers is only limited. Nevertheless, the stable-isotope composition of the ground waters on the meteoric water line ($\delta^2$H versus $\delta^{18}$O) indicates that advection from the infiltration areas in the SE to the region of interest is the likely transport process. It is worth noting that in more central parts of the Paris Basin, water isotopes lie on the right side of the meteoric water line, indicating very long subsurface residence times. The provenance of salinity in the aquifers is most likely from the underlying Triassic, from where dissolved constituents were transported upwards by diffusion and/or by episodic advection along faults. Current salinity is not related to connate marine waters, which were flushed during the long continental period since emergence. This conclusion is consistent with the non-marine Cl/Br ratios. Measured ground-water pressures in the Dogger limestone indicate that current flow is from NE towards SW, with a gradient in the order of 0.001 m/m (Andra 2005b, Vol. 2, ch. 15, p. 29ff). In the overlying Oxfordian limestone, water flows SE towards NE with a gradient of 0.004 – 0.005 m/m. The unequal spatial distribution of heads in the two aquifers leads to hydraulic gradients that are directed downwards in the southeastern part of the Regional Sector (including the URL site) and upwards in the northern, northwestern and western part.

Figure 2.1-15: **Schematic cross-section of the hydrogeological system at Bure on a scale of kilometres**

![Schematic cross-section of the hydrogeological system at Bure](image)

Not to scale. Displacement along faults not shown. Adapted from Andra (2005b, Fig. 17-4)
2.2 Couche Silteuse at Marcoule (Gard, France)

The Couche Silteuse at Marcoule/Gard (Rhône Valley, southern France) was investigated in the 1990s on the basis of surface investigations and a number of deep boreholes. A preliminary synthesis of geological, hydrogeological and hydrochemical information is documented in a trilogy of Andra reports (Andra 1998a,b,c). Following a political decision, the site fell out of consideration for waste disposal and investigations were stopped thereafter.

2.2.1 Structure

The Couche Silteuse de Marcoule is a late Albian ("Vraconian") to early Cenomanian (Cretaceous, ca. 100 Ma) marine formation. Due to locally very different subsidence rates during and after deposition of the Couche Silteuse, its thickness and current depth position vary greatly over small horizontal distances from the depocentre in the Rhône valley towards the Massif Central (Andra 1998a). The investigation boreholes MAR203, MAR402 and MAR501 are located on the western edge of the depocentre (Figure 2.2-1). In spite of their proximity (the maximum distance between the boreholes is <5 km, see Figure 2.2-2), the thickness of the Couche Silteuse varies from 404 m (MAR203) to 246 m (MAR402) and 163 m (MAR501), and also the current depth is variable (Table 2.2-1).

Figure 2.2-1: Thickness contours (in m) of the “Vracono-Tavian” sedimentary cycle, including the Couche Silteuse de Marcoule and the overlying sandstone unit (Grès à Orbitolines)

Positions of boreholes and major faults are also shown. Adapted from Andra (1998a)

---

5 Location in a basin where deposition rate and therefore sediment thickness are highest at a specific time.
Figure 2.2-2: Geological block diagram of the Marcoule region

Red and blue line depict seismic profiles. Adapted from Andra (1998a)

Table 2.2-1: Geometry and lithology of the Couche Silteuse de Marcoule in boreholes MAR203, MAR402 and MAR501

<table>
<thead>
<tr>
<th>Unit</th>
<th>Lithology</th>
<th>Average mineralogy from borehole logs [wt%]</th>
<th>Depth in MAR203 [m below surface]</th>
<th>Depth in MAR402 [m below surface]</th>
<th>Depth in MAR501 [m below surface]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top of the Couche Silteuse</td>
<td>MAR203, MAR402: Grey shaly siltstones with beds of silty sandstones</td>
<td></td>
<td>377</td>
<td>1 066</td>
<td>502</td>
</tr>
<tr>
<td></td>
<td>MAR501: Glauconitic shaly sandstones and laminated sandstones</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unité supérieure alternante</td>
<td>MAR203, MAR402: Grey shaly siltstones with beds of silty sandstones</td>
<td>Quartz, feldspars: 50 Clay minerals: 38 Carbonates: 12</td>
<td>377 – 484</td>
<td>1 066 – 1 139</td>
<td>502 – 540</td>
</tr>
<tr>
<td></td>
<td>MAR501: Glauconitic shaly sandstones and laminated sandstones</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unité médiane homogène</td>
<td>Grey-black shaly siltstones</td>
<td>Quartz, feldspars: 43 Clay minerals: 37 Carbonates: 20</td>
<td>484 – 700</td>
<td>1 139 – 1 312</td>
<td>540 – 665</td>
</tr>
<tr>
<td>Unité inférieure laminée</td>
<td>Black shaly siltstones with white silty laminae</td>
<td>Quartz, feldspars: 46 Clay minerals: 29 Carbonates: 35</td>
<td>700 – 781</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Base of the Couche Silteuse</td>
<td></td>
<td></td>
<td>781</td>
<td>1 312</td>
<td>665</td>
</tr>
</tbody>
</table>

Reference: Andra (1998a, Figs. 6.1-1 – 6.1-3 [geometry]; Figs. 6.1.12, 6.1.17, 6.1.22 [mineralogy]). Shaded areas indicate aquifers
From a viewpoint of depositional facies, there is a rapid transition from a proximal environment in the west (MAR501) towards a more open marine environment to the east (MAR203). This transition correlates with a decrease of grain size, i.e. a decrease of sandy lithologies and an increase of silty-shaly lithologies. Three lithological sub-units can be distinguished and are listed in Table 2.2-1. The lowermost unit represents deposition in an anoxic environment, and silty laminae are preserved due to the absence of bioturbation. The middle and upper sub-units were deposited in a more oxic environment and so were strongly affected by bioturbation, resulting in the homogenisation of lithologies on a scale of cm to dm. The base of the Couche Silteuse is a diachronous lithological boundary. The lowermost unit (Unité inférieure laminée, consisting of black, shaly siltstones) that occurs only in the MAR203 (see Table 2.2-1) evolves into sandstones towards the west (MAR402 and MAR501). Both lithologically and hydrogeologically, these sandstones do not belong to the Couche Silteuse.

The Cenomanian aquifer overlying the Couche Silteuse is a sandstone unit (Grès à orbitolines) with a thickness of 40 – 60 m, overlain by a sequence of lignite and sandstone. The Couche Silteuse is underlain by the Lower Vraconian aquifer (Grès de base, sandstone).

The area of interest is affected by open folding (undulation) with E-W axes, originating from the Eocene Pyrenean tectonic event. This undulation results in the variable depth location of the Couche Silteuse as shown in Table 2.2-1. Boreholes MAR203 and MAR501 are located in anticlines, while MAR402 is in a syncline. The area in which the investigation boreholes are located is 10 – 20 km away from regional faults, namely the Nîmes fault and the Cévennes fault system (Figure 2.2-1). The smaller-scale Bagnols fault system affects borehole MAR501. The Couche Silteuse in borehole MAR203 is essentially free of tectonic structures, except for two fractures at 570 and 593 m (Andra 1998a). In the upper part of the formation as observed in MAR402, no structures were observed except for some steeply dipping joints completely sealed by calcite. A conjugate strike-slip fracture system with striations occurs at 1 225.2 – 1 232 m and also contains calcitic infills. In borehole MAR501, the formation is more strongly affected by brittle tectonics (normal and thrust faults). The most highly fractured zones are at 553 – 554 m and 601 – 602 m. This is probably due to the proximity to the Bagnols fault system (Figure 2.2-2; see also Andra 1998a, Fig. 7.2-5).

2.2.2 Tracer distributions

Information on relevant tracers is available for anions (Cl\(^-\), Br\(^-\), \(\delta^{37}\)Cl), while no data exist for water isotopes and noble gases in the Couche Silteuse. Most data were derived from aqueous leaching, augmented by a small number of squeezing tests and one in-situ water sample (Reeder et al. 1997a,b, 1999, Andra 1998a, Eggenkamp & Coleman 1998).

In all existing documents, anion contents per kg rock derived from aqueous leaching were recalculated to anion contents per litre of pore water using porosity values from measurements of water loss upon heating. Given the fact that anion-accessible porosity in argillaceous rocks is smaller than water-accessible porosity, a correction procedure needs to be applied in order to obtain free-water concentrations. In cores from borehole MAR203, squeezing and leaching data are available from adjacent samples. As shown in Table 2.2-2, Cl\(^-\) concentrations derived from core leaching are ca. 0.4 times those based on squeezing. Assuming that Cl\(^-\) contents of squeezed water reflect the in-situ composition of free pore water leads to the conclusion that only 40 % of the water-accessible porosity is anion accessible and thus represents geochemical porosity as defined by Pearson (1999). Therefore, all anion concentrations based on leaching are recalculated using a porosity value of 0.4x water-accessible porosity, which leads to pore-water concentrations 2.5 times higher than those.
reported in the original literature. The fraction of anion-accessible porosity as used here is in line with evidence from other sites and formations, such as Boom Clay at Mol and Opalinus Clay at Mont Terri.

Table 2.2-2: **Comparison of anion contents based on aqueous leaching and squeezing in samples from the Couche Silteuse de Marcoule, borehole MAR203**

<table>
<thead>
<tr>
<th>Depth [m]</th>
<th>Method</th>
<th>Cl - [mg/L]</th>
<th>Cl -: value (leaching) / value (squeezing)</th>
</tr>
</thead>
<tbody>
<tr>
<td>404.20</td>
<td>Aqueous leaching</td>
<td>3 515</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3 411</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Squeezing</td>
<td>8 330</td>
<td>0.42</td>
</tr>
<tr>
<td>415.74</td>
<td>Aqueous leaching</td>
<td>2 912</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2 801</td>
<td>0.42</td>
</tr>
<tr>
<td></td>
<td>Squeezing</td>
<td>6 850</td>
<td></td>
</tr>
<tr>
<td>452.96</td>
<td>Aqueous leaching</td>
<td>3 600</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4 638</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td>Squeezing</td>
<td>11 200</td>
<td></td>
</tr>
</tbody>
</table>

Data from Reeder *et al.* (1997a).

**Anions in borehole MAR203**

A large number of leaching and some squeezing data have been produced by Reeder *et al.* (1997a, 1999) and Eggenkamp & Coleman (1998). Cl - and Br - profiles as shown in Figure 2.2-3 represent well defined symmetric shapes with the highest concentrations in the centre, decreasing to very low values towards the embedding aquifers. The highest Cl - contents (25 875 mg/L) are somewhat higher than that of present-day sea water (19 350 mg/L), while the highest Br - contents (65 mg/L) match that of sea water very closely. The shape of the profile of the Cl -/Br - ratio (shown in Figure 2.2-4) is different from that of the individual anions. The Cl -/Br - ratio is constant over much of the profile, with values in the range 380 – 500. Only in the proximity of the aquifers (50 – 70 m), the values tend to decrease and thus adjust to the low values observed in the embedding aquifers.

At a depth of 770 m, *i.e.* in the lowermost part of the Couche Silteuse, water could be sampled *in situ* from a sandy bed. As shown in Figure 2.2-3, its composition fits the overall trend of the data derived from leaching, indicating that it is not connected to any of the aquifers.

The profile of stable Cl isotopes (data of Eggenkamp & Coleman 1998) is illustrated in Figure 2.2-5 and shows a wide and systematic variability of 637Cl with depth.

**Anions in borehole MAR402**

The number of data points reported in Reeder *et al.* (1997b, 1999) is more limited when compared to MAR203. However, the overall pattern is very similar (Figure 2.2-3). The Cl - profile shows a systematic distribution with highest concentrations in the centre (max. 16 830 mg/L, *i.e.* slightly lower than present sea water) that decrease towards the aquifers. The Br - profile is not equally well defined, most probably because of the low concentrations and therefore higher analytical errors.
Anions in borehole MAR501

Only 3 samples from the Couche Silteuse were analysed by leaching by Reeder et al. (1999). Because sampling took place at a late stage, moisture content (and therefore porosity) could not be measured. The data as shown in Figure 2.2-3 are based on a recalculation where porosity is estimated on the basis of data from the other boreholes. Thus, the calculated anion contents are just rough indications not suited for quantitative analysis. However, it is remarkable that the Cl⁻ contents are in any case much lower (more than one order of magnitude) when compared to those of the other boreholes. Reasons for this difference (thickness of the formation, different lithology and transport parameters, faults) are explored below.

2.2.3 Upper boundary

The Cenomanian aquifer overlying the Couche Silteuse de Marcoule contains several sandy beds with high hydraulic conductivity. Infiltration via surface outcrops occurs ca. 10 km northwest of the studied boreholes in an open anticlinal high (Andra 1998b). Flow direction is probably towards southeast, and the likely exfiltration areas are located only a few km southeast of the MAR boreholes. Exfiltration occurs into Pleistocene deposits or into the lower part of the Pliocene canyon fills.

The composition of water in the aquifer evolves from Ca-HCO₃ near surface to Na-HCO₃ at depth (i.e. in the investigation boreholes), and salinity is low (see Table 2.2-3). Stable water isotopes have δ values slightly below those of local recent recharge and are interpreted as either due to cold-climate infiltration or recharge upstream the river Cèze (Andra 1998c). Tritium contents are close to the detection limit, indicating only a small contribution of recent water, if any.

In both aquifers, δ³⁷Cl values in ground water are substantially higher than those in leachates of rock samples, and there is no unequivocal explanation for this discrepancy. Sampling of ground water postdated drilling by at least a month and the drilling mud was removed from the borehole in several flushing events before sampling. Consequently, contamination cannot be fully excluded (Buschaert, pers. comm.).

2.2.4 Lower boundary

The flow regime in the sandy lower parts of the Vraconian (Grès de base) underlying the Couche Silteuse de Marcoule is not well known. The probable infiltration area outcrops ca. 10 – 15 km northwest of the MAR boreholes. The flow direction is not clear but is probably eastwards in the region of interest. Exfiltration occurs over a wide area into Pleistocene deposits or into the lower part of the Pliocene canyon fills. Note that the Cèze palaeo-canyon, in the immediate vicinity of boreholes MAR501 and MAR203, potentially produced a hydraulic connection between the Cenomanian and the lower Vraconian aquifers via the Pliocene canyon fills (Andra 1998b).

The ground-water composition is similar to that of the Cenomanian in that it is a Na-HCO₃ water (Andra 1998c). The salinity is slightly higher (Table 2.2-3), with distinctly higher contents of Sr²⁺, F⁻, B, Cl⁻ and HCO₃⁻. Stable water isotopes have δ values similar to those of near-surface aquifers, indicating warm-climate infiltration. In addition to ground waters sampled in situ, a limited number of leaching analyses of the rock matrix are available. The anion contents are low but typically slightly higher than in the ground waters (Figure 2.2-3). As in the Cenomanian aquifer, δ³⁷Cl values are very scattered, and the water sample yields a much higher value than that based on rock leaching (Figure 2.2-5).
Figure 2.2-3: Distribution of Cl<sup>-</sup> and Br<sup>-</sup> contents in pore- and ground waters of boreholes MAR203, MAR402 and MAR501 penetrating the Couche Silteuse de Marcoule.
Figure 2.2-4: Distribution of the Cl/Br⁻ ratio in pore waters of borehole MAR203 penetrating the Couche Silteuse de Marcoule

Figure 2.2-5: Distribution of δ³⁷Cl in pore- and ground waters of borehole MAR203 penetrating the Couche Silteuse de Marcoule
Table 2.2-3: Tracer contents in aquifers embedding the Couche Silteuse de Marcoule

<table>
<thead>
<tr>
<th>Borehole</th>
<th>Sampling interval [m]</th>
<th>Unit</th>
<th>Aquifer</th>
<th>TDS [mg/L]</th>
<th>Cl⁻ [mg/L]</th>
<th>Br⁻ [mg/L]</th>
<th>$\delta^{37}Cl$ [%oSMOC]</th>
<th>Temperature [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAR203</td>
<td>56 – 329</td>
<td>Cenomanian</td>
<td>Upper aquifer</td>
<td>702</td>
<td>27.4</td>
<td>0.67</td>
<td>+0.39</td>
<td>20.1</td>
</tr>
<tr>
<td>MAR203</td>
<td>320 – 375</td>
<td></td>
<td></td>
<td>1 041</td>
<td>102.5</td>
<td>0.67</td>
<td>20.0</td>
<td></td>
</tr>
<tr>
<td>MAR402</td>
<td>658 – 1 139</td>
<td></td>
<td></td>
<td>826</td>
<td>30.7</td>
<td>&lt;0.1</td>
<td>24.9</td>
<td></td>
</tr>
<tr>
<td>MAR203</td>
<td>468 – 893</td>
<td>Vraconian (Grès de base)</td>
<td>Lower aquifer</td>
<td>1 428</td>
<td>180</td>
<td>0.98</td>
<td>20.0</td>
<td></td>
</tr>
<tr>
<td>MAR203</td>
<td>775 – 804</td>
<td></td>
<td></td>
<td>1 415</td>
<td>167.5</td>
<td>0.58</td>
<td>+0.30(1)</td>
<td>18.7</td>
</tr>
<tr>
<td>MAR501</td>
<td>525 – 746</td>
<td></td>
<td></td>
<td>1 581</td>
<td>306.2</td>
<td>0.67</td>
<td>29.5</td>
<td></td>
</tr>
</tbody>
</table>

(1) A leach sample at 811.85 m yields a contrasting value of -0.37 %oSMOC. Data from (from Andra 1998c, Annexe)

2.2.5 Transport parameters

Diffusion coefficient for HTO

Available data are based on through-diffusion experiments by Vitart et al. (1999), and arithmetic means are shown in Table 2.2-4. The following points can be made:

- Within each borehole, the diffusion coefficient decreases with depth.
- Effective diffusion coefficients in cores from borehole MAR402, where the Couche Silteuse occurs at a much greater depth than in the other boreholes, are markedly lower than in the other boreholes.

Vitart et al. (1999) do not report the orientation of the samples, but it is likely that the measurements reflect the direction normal to bedding. Water-accessible porosities obtained from the diffusion experiments are too high when compared to those derived from other methods. This is due to an analytical artefact observed also for samples from Mont Terri that were analysed in the same laboratory. Therefore, porosities as well as calculated Dp values are not used here.

Diffusion coefficient for anions

Overall, only 3 measurements of De for I⁻ are available, determined on samples from borehole MAR203 (Vitart et al. 1999). They yield much (16 – 165 times) smaller values when compared to those for HTO. This difference is larger than that observed for other argillaceous formations and therefore surprising. In addition, I⁻-accessible porosity values reported by Vitart et al. (1999) are 4 – 9 times smaller than those accessible for water, which is a surprisingly high ratio that would suggest very substantial anion exclusion. The comparison of the Cl⁻ contents based on squeezing and leaching (Table 2.2-2) only yields a factor of 2.5. The reason for the discrepancy is currently unknown. Given the fact that only a very small number of measurements are available, the experimental conditions (such as composition of the test fluid and I⁻ concentration) are not documented and the resulting values are incompatible with independent evidence, they are not considered for modelling tracer transport.

In the absence of reliable and representative De values for anions, an estimation based on the analogy to other argillaceous formations is applied. As shown in Chapter 3 below, the ratio of De(HTO)/De(anions) generally varies in the range 2 – 6. Diffusion coefficients for anions as listed in Table 2.2-4 were calculated using a value of 4.
Table 2.2-4: Diffusion coefficients in the Couche Silteuse de Marcoule (arithmetic means)

<table>
<thead>
<tr>
<th>Borehole</th>
<th>Sub-unit</th>
<th>$D_e$ (HTO) @ 20 °C [m²/s]</th>
<th>$D_e$ (anions) @ 20 °C [m²/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAR203</td>
<td>Unité sup. alternante</td>
<td>1.4E-11</td>
<td>3.6E-12</td>
</tr>
<tr>
<td>MAR203</td>
<td>Unité médiane homogène</td>
<td>0.8E-11</td>
<td>1.9E-12</td>
</tr>
<tr>
<td>MAR203</td>
<td>Unité inf. laminée</td>
<td>0.5E-11</td>
<td>1.3E-12</td>
</tr>
<tr>
<td>MAR402</td>
<td>Unité sup. alternante</td>
<td>0.8E-11</td>
<td>2.0E-12</td>
</tr>
<tr>
<td>MAR402</td>
<td>Unité médiane homogène</td>
<td>0.7E-11</td>
<td>1.7E-12</td>
</tr>
<tr>
<td>MAR501</td>
<td>Unité sup. alternante</td>
<td>2.5E-11</td>
<td>6.3E-12</td>
</tr>
<tr>
<td>MAR501</td>
<td>Unité médiane homogène</td>
<td>1.1E-11</td>
<td>2.7E-12</td>
</tr>
</tbody>
</table>

Data for HTO based on laboratory experiments by Vitart et al. (1999). Data for anions calculated using $D_e$ (anions) = $D_e$ (HTO)/4 (see text for details)

Hydraulic conductivity

Data based on hydraulic packer tests are available for boreholes MAR203 and MAR402, even though the coverage of the Couche Silteuse is not complete (Andra 1998b). For MAR203, hydraulic conductivity is in the range $K = 1.6E-12 – 1.8E-13$ m/s. A sandstone bed at 756.0 – 756.8 m has a higher value of $2E-8 – 2E-9$ m/s.

For MAR402, $K = 7E-14 – 4E-13$ m/s is obtained. A hydraulic test including the faulted section at 1227 – 1229 m has a very low hydraulic conductivity ($4.9E-14$ m/s), suggesting that this section is hydraulically irrelevant.

No packer-test data are available for MAR501, and only a maximum value of $3E-9$ m/s can be obtained from the detection limit of the flowmeter tool (the real value could be much lower). Anomalies in conductivity/temperature logs were identified at 550, 563 and 630 m, partially corresponding to known faults.

Porosity

Water contents measured by weight loss at 110 °C were determined by Blackwell et al. (1995c) and Reeder et al. (1999) for boreholes MAR203 and MAR402. No data are available for MAR501, except for an otherwise undocumented graphic representation in Andra (1998a, Fig. 6.9-11).

As shown in Figure 2.2-6, porosity decreases markedly with depth, with a sharp increase near the base of the formation in MAR203. Average water-loss porosities are listed in Table 2.2-5. Due to the absence of data from MAR501, values from MAR203 are used. In Andra (1998a, Fig. 6.2-9 to 6.2-11), water contents are shown for all boreholes, and the trends and values for MAR203 and MAR501 are very similar, which is taken as a justification for this extrapolation.

As discussed above and shown in Table 2.2-2, the comparison of Cl- contents based on squeezing and leaching yields a geochemical porosity that corresponds to 40 % of water-accessible porosity. This fraction is used for all boreholes.

6 The water contents are reported relative to dry weight in the original reports.
Table 2.2-5: Water-loss porosity in the Couche Silteuse de Marcoule

<table>
<thead>
<tr>
<th>Unit</th>
<th>Porosity in MAR203 [-]</th>
<th>Porosity in MAR402 [-]</th>
<th>Porosity in MAR501 [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unité supérieure alternante</td>
<td>0.181</td>
<td>0.088</td>
<td>0.181</td>
</tr>
<tr>
<td>Unité médiane homogène</td>
<td>0.106</td>
<td>0.077</td>
<td>0.106</td>
</tr>
<tr>
<td>Unité inférieure laminée</td>
<td>0.093</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Data from Blackwell et al. (1995c) and Reeder et al. (1999). In the absence of direct measurements, values for borehole MAR203 are also used for MAR501 (in italics).

Figure 2.2-6: Water-loss porosity in boreholes MAR203 and MAR402 penetrating the Couche Silteuse de Marcoule

Table 2.2-6: In-situ temperature in the Couche Silteuse de Marcoule

<table>
<thead>
<tr>
<th>Borehole</th>
<th>Depth [m]</th>
<th>Position in the Couche Silteuse</th>
<th>Temperature [°C]</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAR203</td>
<td>377</td>
<td>Top</td>
<td>21.9</td>
<td>Calculated</td>
</tr>
<tr>
<td>MAR203</td>
<td>792</td>
<td>Near base</td>
<td>35.2</td>
<td>Measured</td>
</tr>
<tr>
<td>MAR402</td>
<td>1 066</td>
<td>Top</td>
<td>36.1</td>
<td>Calculated</td>
</tr>
<tr>
<td>MAR402</td>
<td>1 312</td>
<td>Base</td>
<td>42.1</td>
<td>Calculated</td>
</tr>
<tr>
<td>MAR402</td>
<td>1 430</td>
<td>Below</td>
<td>45.0</td>
<td>Measured</td>
</tr>
<tr>
<td>MAR501</td>
<td>502</td>
<td>Top</td>
<td>26.8</td>
<td>Calculated</td>
</tr>
<tr>
<td>MAR501</td>
<td>660</td>
<td>Near base</td>
<td>32.0</td>
<td>Measured</td>
</tr>
</tbody>
</table>

There is only one temperature measurement in each of the boreholes. Temperatures at different depths were calculated by interpolation of the measured value and a surface temperature of 10 °C.
Temperature

Available data on *in-situ* temperature are documented in Mouroux & Brulhet (1999). The current geothermal gradient is around 30 °C/km. Measured and calculated data are summarised in Table 2.2-6.

2.2.6 *U and Th contents in rocks*

No data available.

2.2.7 *Hydraulic gradient*

The overlying Cenomanian aquifer has a head of 45 m a.s.l. all over the Marcoule area. Head values in the underlying Vraconian aquifer are 45 m (MAR203) and 47 m (MAR402 and MAR501), resulting in small hydraulic gradients across the Couche Silteuse (0 – 0.01 m/m).

Within the Couche Silteuse, pressure data could only be obtained from the short-term hydraulic packer tests. Thus, the results are uncertain and could also be affected by artefacts, such as borehole convergence. However, all results indicate that some degree of overpressure exists relative to the embedding aquifers (Andra 1998b).

2.2.8 *Geological and hydrogeological evolution*

*Stratigraphic and structural record*

In the late Cretaceous, the Marcoule region was located in a marginal position between the high of the Massif Central to the west and the sedimentary basin to the east. The depositional environment was predominantly marine, but several stages of emergence and limited erosion are recorded. Syn-sedimentary tectonics, namely in the Albian, led to variable thickness and facies of the sediments (*e.g.* in the Couche Silteuse de Marcoule). A depositional gap is found between the Santonian (*ca.* 85 Ma) and the late Eocene (*ca.* 35 – 40 Ma). Maximum burial depth of the Couche Silteuse in the whole region of interest is estimated at 1 500 – 2 000 m (Mouroux & Brulhet 1999). The Pyrenean deformation (*ca.* 50 Ma) led to a weak undulation resulting in syn- and anticlinal structures with E-W axes. Due to this undulation and the subsequent erosion focussed mainly in anticlines, the current depth location of the Couche Silteuse is closer to maximum burial depth in synclines (MAR402) than in anticlines (MAR203, MAR501). A distensive tectonic regime in the Paleogene leads to thick graben fills (800 – 3 000 m) in the region (Séranne 1999) but not in the area of the investigation boreholes where limited, predominantly continental deposition occurred. Thin Oligocene and Miocene sediments were deposited in topographic depressions (*i.e.* synclines; Andra 1998a).

A dramatic decrease in the level of the Mediterranean (>1500 m) occurred in the late Miocene at 5.8⁷ – 5.35 Ma due to restricted connection to the Atlantic (Beaudoin *et al.* 1999) and is commonly termed as the “Messinian salinity crisis”. Deep canyons developed in river valleys around the Mediterranean, and the incisions were several hundreds of kilometres long in some cases. In the region of interest, the canyons of the Rhône and of the Cèze rivers are of relevance (Figure 2.2-3). After the re-establishment of an unrestricted connection to the Atlantic, a marine transgression occurred (5.35 – 4.8 Ma, early Pliocene). At the same time, continental conditions prevailed in areas outside the

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⁷ A study in Cyprus applying high-resolution astrochronology yields a date of 5.96±0.02 Ma for the onset of the salinity crisis in the eastern Mediterranean (Krijgsman *et al.* 2002).
canyons, which were filled by clastic Pliocene deposits. The lower part contains coarse-grained clastic sediments, whereas the upper part consists of marine clays. At 3.0 Ma, the sea finally retreated. Since that time, the area has been uplifting and has been exposed to continental conditions and erosion.

*Diagenesis*

Maximum temperatures during diagenesis, based on fluid inclusion studies and the maturity of biomarkers, are only 35 – 50 °C (Buschaert *et al.* 2001). In spite of the limited maximum burial depth and temperature, partial carbonate cementation of the pore space occurred. Calcite is also the dominant mineral that seals fractures related to the Pyrenean compression in the Eocene (generally flat lying) and to the Oligocene distensive stage. Within the Couche Silteuse, the stable isotopic composition of fracture calcite is very similar to calcite in the rock matrix, indicating local buffering. One exception in borehole MAR501, spatially related to one of the penetrated faults (parts of the Bagnols fault system), where infiltration of meteoric water has been inferred (Buschaert *et al.* 2001).

*Implications for palaeo-hydrogeology*

In spite of several stages of emergence, the region was covered by the sea over much of the late Cretaceous, and the strata were essentially flat lying at that time. As a first approximation, it can be assumed that conditions in the aquifers embedding the Couche Silteuse de Marcoule were dominated by sea water, with small hydraulic gradients. The Pyrenean deformation, uplift and erosion of the topographic highs (anticlines) probably affected the flow system since the Eocene (*ca.* 50 Ma). The Cenomanian aquifer was exposed on the surface in the anticlines, and it is likely that it has been progressively flushed by fresh water since that time. The evolution of the lower Vraconian aquifer underlying the Couche Silteuse de Marcoule is more speculative, and its hydrogeology and hydrochemistry are less clear. Given the fact that it was also exposed on the surface to the west, fresh water may also have reached the area of interest. Conditions remained predominantly continental until the end of the Miocene.

The incision of deep canyons in the Rhône and Cèze valleys (up to 600 m below present surface in the area of interest; Beaudoin *et al.* 1999) during the Messinian crisis (5.8 – 5.35 Ma) had profound effects on the flow system, given the fact that aquifers were exposed and topography-driven hydraulic gradients were enhanced. Boreholes MAR203 and MAR501 are located at the edge of the Cèze canyon, while MAR402 lies *ca.* 2 km west of the Rhône canyon (Figure 2.2-3). The incision penetrated the Cenomanian aquifer and, at least locally, into the Couche Silteuse and the lower Vraconian aquifer. Possibly, the aquifers were drained and filled with fresh water. A last marine transgression in the early Pliocene (5.35 – 4.8 Ma) flooded the canyons, and this resulted in the lateral intrusion of sea water into the aquifers down to a depth of 700 m (Brulhet & Buschaert, pers. comm.). At deeper levels, *i.e.* below the deepest incision level, fresh water may have remained in the system. At the same time, the Pliocene canyon fills were deposited. These generally permeable clastic sediments provide hydraulic connections between different aquifer levels until the present day. The canyons remained under marine conditions until 3 Ma, when the sea finally retreated. The palaeo-hydrogeological evolution is summarised in Table 2.2-7.
Table 2.2-7: Reconstruction of the palaeo-hydrogeological evolution of the Couche Silteuse de Marcoule

<table>
<thead>
<tr>
<th>Event</th>
<th>Age [Ma]</th>
<th>Hydrogeological environment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deposition of the Couche Silteuse de Marcoule</td>
<td>100</td>
<td>Shallow marine</td>
</tr>
<tr>
<td>Late Cretaceous sedimentation (youngest recorded Cretaceous sediments: Santonian, 85 Ma, then erosional gap)</td>
<td>100 – 50</td>
<td>Predominantly marine</td>
</tr>
<tr>
<td>Pyrenean deformation: Formation of open folds, uplift, emergence, erosion in anticlines, exposure of aquifers to the surface</td>
<td>50</td>
<td>Continental</td>
</tr>
<tr>
<td>Tertiary, predominantly continental stage: Distensive tectonics, deep but local grabens in the region; little or no sedimentation in area of interest (lacustrine deposits in synclines, some marine episodes)</td>
<td>50 – 5.8</td>
<td>Mostly continental</td>
</tr>
<tr>
<td>Messinian crisis: Incision of deep canyons, drainage of aquifers</td>
<td>5.8 – 5.35</td>
<td>Continental</td>
</tr>
<tr>
<td>Marine transgression flooding the canyons but not areas outside canyons. Lateral intrusion of sea water into aquifers. Deposition of clastic canyon fills (coarse grained at the base, capped by a clay)</td>
<td>5.35 – 4.8</td>
<td>Continental outside canyons, mostly marine in canyons</td>
</tr>
<tr>
<td>Marine conditions prevail in canyons</td>
<td>4.8 – 3.0</td>
<td>Continental outside canyons, mostly marine in canyons</td>
</tr>
<tr>
<td>Regression, establishment of fully continental conditions, uplift and erosion</td>
<td>3.0 – 0</td>
<td>Continental</td>
</tr>
</tbody>
</table>

2.3 Opalinus Clay at Benken (Switzerland)

In contrast to some of the other sites considered in this report, the target formation with respect to waste disposal, i.e. the Opalinus Clay, is not directly embedded between aquifers at Benken but is part of a larger low-permeability sequence. Tracer profiles of stable water isotopes, Cl⁻ and δ³⁷Cl have already been modelled and interpreted in detail by Gimmi & Waber (2004) and Gimmi et al. (2007).

2.3.1 Structure and hydrogeology

The area where the Benken borehole was drilled is located in a tectonically quiet region between the northern boundary of the Swiss Molasse Basin and the Tabular Jura (Figure 2.3-1). A 3D seismic survey covering ca. 50 km² (Birkhäuser et al. 2001) indicated that the sedimentary rocks in that area are nearly horizontally bedded, and that no large faults are present. Similarly, in the Benken core materials, only a very limited number of shear planes were observed, and no faults were penetrated. Thus, the stratigraphic sequence encountered in the Benken borehole and shown in Figure 2.3-2 and Table 2.3-1 is representative for a wider area.

The Dogger (middle Jurassic) and Lias (early Jurassic) sedimentary rocks are dominated by clay-rich lithologies and, hydrogeologically, constitute a low-permeability sequence. Low permeabilities were also observed in the marls and limestones at the base of the overlying Malm (late Jurassic). The Dogger consists of about 200 m of marine claystones and marls with intercalated thin layers of limestones, calcareous sandstones and iron oolites. Opalinus Clay⁸, a 113 m thick sequence of dark grey, silty and calcareous claystones, is located at the base of the Dogger. In the footwall, the Lias comprises about 40 m of marine marls, silt- and claystones and thin limestone beds.

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⁸ Including the overlying Murchisonae Beds in Opalinus Clay facies.
The low-permeability Dogger/Lias sequence is sandwiched between two aquifers, namely the regional Malm (late Jurassic) aquifer in the hanging wall and the local Keuper (late Triassic) aquifer in the footwall:

- At Benken, the Malm aquifer comprises a 198 m thick sequence of limestone with thin marl intercalations. A period of erosion during late Cretaceous/early Tertiary times resulted in karstification and therefore in a spatially heterogeneous distribution of hydraulic conductivity. While, in other areas, this aquifer is being exploited, its hydraulic conductivity is relatively low at Benken ($\leq 1E-8$ m/s).

- The upper third of the 119 m thick Keuper (late Triassic) consists of a number of lithologies including shales, marls, sandstones and dolomites. Sandy lithologies and dolomite breccias of the Stubensandstein and Schilfsandstein formations contain zones of enhanced permeability. The permeable upper part of the Keuper is underlain by partly argillaceous anhydrite and gypsum beds and dolomites of the Gipskeuper.

Figure 2.3-1: Simplified tectonic map of northeastern Switzerland and southwestern Germany

Location of the Benken borehole is shown together with suggested ground-water flow paths in aquifers bounding the low-permeability sequence of the Dogger-Lias. M = Malm aquifer, K = Keuper aquifer. From Gimmi et al. (2007)
| Unit               | Lithology                                                                 | Hydrogeology | Depth [m b.g.] | $D_p$ @ 20 °C [m²/s] | $D_e$ @ 20 °C [m²/s] | $K_\perp$ [m/s] | $K_{||}$ [m/s] | $n$ [-] | $T$ [°C] |
|-------------------|---------------------------------------------------------------------------|--------------|---------------|---------------------|---------------------|----------------|---------------|--------|---------|
| Malm              | Limestone with thin marl intercalations                                  | Aquifer      | 199.0 – 397.0 | $1E-9 – 1E-8$       | $1E-8$              | $1E-9 – 1E-8$ | $1E-8$       | Water & anions: 0.18 | 21.6 |
| Lowest part of Malm | Limestone ± marl                                                        |              | 397.0 – 451.2 | $5.3E-11$ / $1.9E-11$ | $6.4E-12$ / $1.1E-12$ | $6E-15 – 6E-14$ | $6E-14$ | Water: 0.12 Anions: 0.06 | 24.5 |
| Upper and Middle Dogger | Marine claystones and marls with intercalated thin layers of limestones, calcareous sandstones and iron oolites |              | 451.2 – 538.8 | $5.3E-11$ / $1.9E-11$ | $6.4E-12$ / $1.1E-12$ | $2E-14 – 2E-12$ | $2E-13 – 2E-12$ | Water: 0.12 Anions: 0.06 | 28.7 |
| Opalinus Clay (incl. Murchisonae Beds) | Dark grey, silty and calcareous marine claystones                          | Low-permeability sequence | 538.8 – 652.0 | $5.3E-11$ / $1.9E-11$ | $6.4E-12$ / $1.1E-12$ | $6E-15 – 3E-14$ | $3E-14$ | Likely range 1E-14 – 6E-14, certainly <1E-13 | 34.5 |
| Lias              | Marine marls, silt- and claystones, and thin limestone beds              |              | 652.0 – 692.3 | $5.3E-11$ / $1.9E-11$ | $6.4E-12$ / $1.1E-12$ | $3E-15 – 3E-14$ | $3E-14$ | Likely value 3E-14, certainly <1E-13 | 39.3 |
| Keuper            | Various lithologies                                                       |              | 692.3 – 709.1 | $5.3E-11$ / $1.9E-11$ | $6.4E-12$ / $1.1E-12$ | $<1E-13$ | $<1E-13$ | Water: 0.12 Anions: 0.06 | 40.6 |
| Keuper aquifer (Stubensandstein) | Dolomite breccias                                                         | Aquifer      | 709.1 – 720.0 | $1E-8 – 1E-7$       | $1E-7$              | $1E-8$       | Water & anions: 0.10 | 41.4 |

See Table 1.8-1 for definitions of symbols. $\perp$ = normal to bedding, $||$ = parallel to bedding, $||/\perp$ = anisotropy factor. Values given in italics were not measured/estimated directly but are based on assumed analogy with measurements in other units. Diffusion coefficients from Nagra (2002), Van Loon et al. (2003), Van Loon & Soler (2004); other data from Nagra (2002). Shaded areas indicate aquifers.
2.3.2 \textit{Tracer distributions in the Dogger and Lias}

The pore-water data were obtained on core samples that were sealed immediately after recovery and kept under cool conditions until they were processed (within a few days) in the laboratory.

\textit{Stable water isotopes}

The stable isotope data are presented in Rübel & Sonntag (2000), Nagra (2002), Wafer \textit{et al.} (2003a), Gimmi & Waber (2004) and Gimmi \textit{et al.} (2007). The isotopic composition of pore water was determined using two different methods: the commonly used vacuum-distillation method and the newly developed diffusive-exchange method of Rübel \textit{et al.} (2002). In addition, two rock samples were squeezed at 512 MPa to obtain some pore water. A comparison between the diffusive-exchange, the squeezing, and the distillation methods clearly revealed that the last method consistently underestimates the $\delta^{18}\text{O}$ and $\delta^{2}$H values in the pore water. The distillation data were, on average, lower by $2.9 \pm 0.33$ \textperthousand in $\delta^{18}\text{O}$ and $10.7 \pm 1.9$ \textperthousand in $\delta^{2}$H compared to the diffusive-exchange data. This was explained by the incomplete removal and a Rayleigh-type fractionation of the pore water during distillation, leading to a depletion of heavy isotopes in the extracted water. Where available, data obtained from the diffusive-exchange technique were used by Gimmi & Waber (2004) and Gimmi \textit{et al.} (2007). For depths between about 570 and 650 m, no such data were available, and here distillation data that were shifted by the mean deviation between the two data sets were used. The errors obtained with the diffusive-exchange method were given by Gimmi \textit{et al.} (2007) as $\pm 0.4$ \textperthousand for $\delta^{18}\text{O}$ and $\pm 2.8$ \textperthousand for $\delta^{2}$H, those for the shifted distillation data as $\pm 0.5$ \textperthousand for $\delta^{18}\text{O}$ and $\pm 3.4$ \textperthousand for $\delta^{2}$H. No additional adjustments to the data of Gimmi & Waber (2004) and Gimmi \textit{et al.} (2007) were made for the present study.
Figure 2.3-3 shows profiles of $\delta^{18}$O and $\delta^2$H in the pore water across the low-permeability sequence, together with the values of the ground water in the bounding aquifers. Figure 2.3-4 displays the relations between the $\delta^{18}$O and $\delta^2$H data. The following observations can be made:

- The profiles of $\delta^{18}$O and $\delta^2$H have similar shapes. The values are highest near the centre and in the upper half of the low-permeability sequence and decrease towards the Keuper aquifer.
- The data obtained from ground-water samples match well with the adjacent values from the low-permeability sequence.
- The distillation data that have been adjusted by the mean deviation relative to the isotope diffusive-exchange data ($2.9 \pm 0.33 \%$ in $\delta^{18}$O and $10.7 \pm 1.9 \%$ in $\delta^2$H) fit well into the profiles of the data obtained from diffusive exchange.
- The $\delta^{18}$O and $\delta^2$H values in the low-permeability sequence are generally higher than those in modern meteoric waters but lower than those in present-day sea water.
- The data lie on the Global Meteoric Water Line at depths $>650$ m but are shifted to the right at shallower levels.
- One sample at 544.77 m depth falls out of the trend and is characterised by a more negative $\delta^{18}$O and, to a lesser degree, $\delta^2$H value. In the absence of geological and hydrogeological indications of permeable features at this depth, the values are attributed to a contamination by meteoric water and are not considered further.

Data obtained by vacuum distillation are corrected for for incomplete distillation (see text for details).

Data taken from Gimmi et al. (2007)
Cl\textsuperscript{-} contents and $\delta^{37}$Cl values in pore water are given in Nagra (2002), Waber et al. (2003a) and Gimmi & Waber (2004). The data were obtained from core samples by aqueous extraction and high-pressure squeezing and subsequent ion chromatography. Concentrations of Cl\textsuperscript{-} in the accessible pore water were calculated using water-content porosity (obtained from weight loss upon drying at 105 °C) and assuming a ratio of 0.5 between the Cl\textsuperscript{-}-accessible and water-content porosity. This ratio was based on porosities obtained from diffusion experiments with Cl\textsuperscript{-} and squeezing experiments with Benken and Mont Terri samples. Errors of ±10 % were given for the resulting Cl\textsuperscript{-} concentrations. The $\delta^{37}$Cl values were obtained directly from the aqueous extracts, and the analytical error was ±0.15 ‰.

Figure 2.3-5 shows profiles of Cl\textsuperscript{-} and $\delta^{37}$Cl in pore water at Benken. The following observations can be made:

- The Cl\textsuperscript{-} concentrations are well below those of modern sea water.
- The trend of the Cl\textsuperscript{-} data is similar to that of the stable water isotope data but less smooth.
- $^{37}$Cl is enriched towards the aquifers. The maxima of the $\delta^{37}$Cl values are found between the upper Dogger and the Malm, and in the lower part of the Opalinus Clay.

The reason for the increased scatter of the Cl\textsuperscript{-} data as compared to the stable water isotopes is not clear. It may partly be related to slight heterogeneities of porosity and, probably more importantly, to the uncertainty related to the Cl-accessible porosity. For the anion-accessible fraction of physical porosity, Waber et al. (2003a) used a constant value for the whole profile, because no detailed information on its dependence on other properties, such as mineralogy, was available. Regarding the errors of the $\delta^{37}$Cl values, Waber et al. (2003a) mention that analytical problems were encountered for aqueous extracts with high dissolved sulfate contents, such as in the Lias samples. Thus, the analytical error of ±0.15 ‰ may underestimate the total uncertainty of the data.
Profiles of chloride concentrations and $\delta^{37}$Cl values in pore and ground waters from the Benken borehole

Figure 2.3-5:

Cl$^-$ concentrations refer to the mass of chloride per volume of Cl$^-$-accessible pore water, assuming that 50% of the physical porosity is accessible to anions. Data from Gimmi & Waber (2004)

Noble gases

Noble-gas data from the Benken borehole are reported in Rübel & Sonntag (2000, pore- and ground-water data), Lehmann et al. (2001, rock data), Waber et al. (2002, ground-water data), Nagra (2002) and Waber et al. (2003a, pore-water data). Data are shown in Figure 2.3-6, and the following observations can be made:

- The He pore-water profile is flat, in contrast to the profiles of stable water isotopes and Cl$^-$.  
- He concentrations are well above those expected for water in equilibrium with air (4.56E-8 cm$^3$ STP/g water).
- The $^3$He/$^4$He ratios of pore and ground waters as well as of rocks are clearly higher than expected according to the in-situ neutron flux and average Li contents (about 2.8E-8 for a Li content of 100 ppm, about 1.4E-8 for a Li content of 45 ppm).

Excess He in the pore water most likely originates from in-situ production by decay of the U and Th chains and subsequent release into the pore water. Lehmann et al. (2001) calculated that 87% of the He produced since deposition has escaped from the system and that a production over 17 Ma would suffice to obtain the observed He concentrations (with an average He production rate of 5.31E-13 cm$^3$ STP/grock/a, or 1.05E-11 cm$^3$ STP/g water/a). According to Lehmann et al. (2001), the high $^3$He/$^4$He ratios of the ground and pore waters could result from the admixture of about 4% of mantle helium (with a $^3$He/$^4$He ratio of 1E-5) to the in-situ produced He (with a ratio of 1.4E-8 for an average Li content of 45 ppm). Increased ratios in the rock could then result from back diffusion of $^3$He from the pore water to the rock.

In Figure 2.3-7, the $^{40}$Ar/$^{36}$Ar data of ground and pore waters and of rocks are shown:

- The profile of the $^{40}$Ar/$^{36}$Ar ratios in the pore water has a curved shape, similar to the profiles of Cl$^-$ and stable water isotopes but unlike He.
The $^{40}\text{Ar}^{36}\text{Ar}$ ratios are higher than the atmospheric ratio of 295.5.

The increased $^{40}\text{Ar}^{36}\text{Ar}$ ratio of the ground and pore waters was explained by Lehmann et al. (2001) and Waber et al. (2003a) by in-situ production of $^{40}\text{Ar}$ from decay of $^{40}\text{K}$ and subsequent release of a small fraction to the pore water. The shape of the profile suggests a mostly diffusive transport of $^{40}\text{Ar}$ from the low-permeability sequence towards the confining aquifers, but it may also be influenced by inhomogeneous $^{40}\text{Ar}$ production and accumulation rates (Rübel & Sonntag 2000).

Figure 2.3-6: He contents and $^{3}\text{He}/^{4}\text{He}$ ratios of pore and ground waters from the Benken borehole

The dashed line in the right graph shows the value estimated for in-situ production based on a Li content of 100 ppm. Data from Rübel & Sonntag (2000) and Lehmann et al. (2001)

Figure 2.3-7: $^{40}\text{Ar}^{36}\text{Ar}$ ratios of pore and ground waters from the Benken borehole

The dashed line shows the ratio for water in equilibrium with air. Data from Rübel & Sonntag (2000)
Ground water from the Malm and the Keuper could be collected from packed-off intervals in the borehole. The research character of the deep borehole at Benken required the use of several different, traced drilling fluids, in order to maintain borehole stability and to minimise induced perturbations of the in-situ hydraulic and hydrochemical conditions (Nagra 2001). As a consequence, the obtained hydrochemical raw data had to be carefully examined for contamination by drilling fluid prior to their interpretation (Gimmi & Waber 2004). The stable water isotope values and the Cl⁻ concentration of the Malm ground water were corrected to account for a 23.3 % contamination by drilling fluid. For the chlorine isotopes in the Malm ground water, no correction was possible because the δ⁴³Cl value of the drilling fluid was not known. Gimmi & Waber (2004) mention that the in-situ δ⁴³Cl value of the Malm ground water is likely to be slightly more positive than the measured δ⁴³Cl = 0.31 ‰ because modern ground waters used for the drilling fluid preparation commonly have negative δ³⁷Cl values. For the Keuper ground water, the contamination by drilling fluid was below 1 % (and thus within analytical error) and so did not require any correction.

The stable water isotope values and the Cl⁻ concentration of the Malm ground water were corrected to account for a 23.3 % contamination by drilling fluid. For the chlorine isotopes in the Malm ground water, no correction was possible because the δ³⁷Cl value of the drilling fluid was not known. Gimmi & Waber (2004) mention that the in-situ δ³⁷Cl value of the Malm ground water is likely to be slightly more positive than the measured δ³⁷Cl = 0.31 ‰ because modern ground waters used for the drilling fluid preparation commonly have negative δ³⁷Cl values. For the Keuper ground water, the contamination by drilling fluid was below 1 % (and thus within analytical error) and so did not require any correction.

The chloride and the stable water and chlorine isotope values of the Malm and Keuper ground waters are given in Table 2.3-2. Ground waters from the Malm and the Keuper have similar total mineralisations of about 10 g/L but are of a different chemical type (Gimmi & Waber 2004). The Malm ground water is of the Na-Cl(SO₄) type with a Cl⁻ content of about 4 550 ± 455 mg/L. The Keuper ground water is of the Na-SO₄-(Cl) type with sulphate as the dominant anion and a Cl⁻ content of only about 520 mg/L. Both ground waters have an inline-measured reducing redox potential. For the Malm, estimated infiltration temperatures (10 – 20 °C) were clearly warmer than present-day values, whereas for the Keuper (about 7 – 9 °C) they are similar to present-day values.

The Malm ground water was interpreted as a mixture of a Tertiary sea-water component with meteoric water. Radiogenic and stable isotopes and noble gases suggest that infiltration of the meteoric component must have occurred during an interglacial period in the Pleistocene, if not even earlier, during late Tertiary times. Almost stagnant flow conditions appear to have prevailed since then.

The Keuper ground water has no measurable ³H and ¹⁴C, a high He content and a high ⁴⁰Ar/³⁶Ar ratio. All these data exclude the presence of a young ground-water component and indicate that recharge occurred well before the present climatic period, most probably during early Pleistocene times.

Table 2.3-2: Tracer data from ground waters in the aquifers embedding the Dogger and Lias at Benken

<table>
<thead>
<tr>
<th>Unit</th>
<th>Depth [m b.g.]</th>
<th>δ¹⁸O [%o V-SMOW]</th>
<th>δ²H [%o V-SMOW]</th>
<th>Cl⁻ [mg/L]</th>
<th>δ³⁷Cl [%o VSMOC]</th>
<th>He [cm³ STP/g water]</th>
<th>³He/⁴He</th>
<th>⁴⁰Ar/³⁶Ar</th>
<th>Remarks</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Malm</td>
<td>397.0</td>
<td>-5.46 ±0.1</td>
<td>-49.9 ±1</td>
<td>4 550 ±455</td>
<td>0.31 ±0.15</td>
<td>3.21E-4</td>
<td>3.66E-7</td>
<td>325.3 ±3.25</td>
<td>Corrected for contamination. Long residence time</td>
<td>Waber et al. (2003a), Gimmi &amp; Waber (2004)</td>
</tr>
<tr>
<td>Keuper</td>
<td>709.1</td>
<td>-9.53 ±0.1</td>
<td>-63.2 ±1</td>
<td>520 ±52</td>
<td>-0.92 ±0.15</td>
<td>2.07E-4</td>
<td>4.24E-7</td>
<td>306.4 ±0.45</td>
<td>³H and ¹⁴C below detection, high He and ⁴⁰Ar/³⁶Ar. Residence time &gt;&gt;25 ka, &lt;2.6 Ma</td>
<td></td>
</tr>
</tbody>
</table>
2.3.4 Transport parameters

Diffusion coefficients for water isotopes

Diffusion coefficients were determined for Opalinus Clay but not for the other low-permeability formations (i.e., the lower Malm, Upper Dogger, Lias, and the upper part of the Keuper). Within Opalinus Clay (depths of 564 m, 589 m, 636 m, and 651 m), Van Loon & Soler (2004) observed only a small heterogeneity of De for HTO and obtained a mean value of \((6.4\pm1.2)\times10^{-12}\) m\(^2\)/s for the direction normal to bedding. A very small dependence on confining pressure was observed in the range 4 – 15 MPa (Van Loon et al. 2003, Van Loon & Soler 2004). Diffusion coefficients parallel to the bedding are about a factor 5 larger. In the absence of data, the same values as for Opalinus Clay will be assumed for the other units of the low-permeability sequence. This assumption was already made by Gimmi and Waber (2004) and, based on the rather small heterogeneity of porosity (except in the lower Malm), appears justified as a first approximation. The data are listed in Table 2.3-1. Pore-diffusion coefficients were calculated using the listed values for accessible porosity.

Diffusion coefficients for anions

De measurements for Cl\(^-\) and I\(^-\) in Opalinus Clay from Benken are reported in Van Loon et al. (2003) and Van Loon & Soler (2004). The data were all obtained on samples from the lower, clay-rich part of Opalinus Clay. Higher rock capacities were obtained for I\(^-\) when compared to Cl\(^-\), and Van Loon et al. (2003) attribute this to a weak sorption. Due to this complication, data pertinent to I\(^-\) are not considered here, and the values shown in Table 2.3-1 refer to Cl\(^-\) only\(^9\). No diffusion data are available for the other units of the low-permeability sequence. As for water isotopes, it will be assumed that the values for Opalinus Clay are approximately applicable to those units as well.

Dp for Cl\(^-\) is about one third of the Dp value of water tracers. However, the laboratory diffusion experiments were performed with \(^{36}\)Cl at trace concentrations. Thus, the Cl\(^-\) diffusion coefficients obtained represent tracer diffusion coefficients. For transport of Cl\(^-\) at the field scale, charge balance constraints have to be fulfilled as well. Thus, the diffusion of Cl\(^-\) or another anion is influenced by the diffusion of other charged solutes (Gimmi & Waber 2004). In case of Opalinus Clay, co-diffusion of Na\(^+\), for instance, could increase the net diffusion of Cl\(^-\) as compared to tracer diffusion, and the relevant pore diffusion coefficients could be somewhat larger than the value given above. A salt diffusion coefficient for NaCl estimated from the tracer diffusion coefficients of Cl\(^-\) and Na\(^+\) in Opalinus Clay at Benken is about a factor of 1.9 larger than the tracer diffusion coefficient of Cl\(^-\). In the absence of pertinent data, no corrections were applied in Table 2.3-1.

Diffusion coefficients for He

In the absence of measured data, De(He) is estimated to be 3 times the value for De(HTO) according to the argument presented in Appendix A3.2.

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\(^9\) For the four samples on which Van Loon et al. (2003) performed their measurements, an average De value of 7.7E-13 m\(^2\)/s and an average rock capacity (Cl\(^-\)-accessible porosity) of 0.04 can be calculated, which yields a pore diffusion coefficient Dp of 1.9E-11 m\(^2\)/s, as listed in Table 2.3-1. The low Cl\(^-\)-accessible porosity in these samples (33 % instead of the usual 50 % of water-accessible porosity) is attributed to high anion exclusion due to their higher-than-average clay-mineral contents. De representative of the Opalinus as a whole (and listed in Table 2.3-1) is then calculated from the Dp value, using an anion-accessible porosity of 0.06 (average value for Opalinus Clay).
Hydraulic conductivity

Hydraulic conductivities of the low-permeability sequence at Benken and the bounding aquifers are reported in Nagra (2002) and are listed in Table 2.3-1. From laboratory and borehole tests, values parallel to bedding <1E-13 m/s were found for Opalinus Clay, Lias and uppermost Keuper, and 2E-13 to 2E-12 m/s for the overlying middle and upper Dogger. The likely range yields even smaller values for Opalinus Clay and Lias, as shown in Table 2.3-1. The low-permeability base of the Malm has a hydraulic conductivity parallel to bedding of 6E-14 m/s. The aquifers have hydraulic conductivities of 1E-8 m/s (Malm) and 1E-7 m/s (Keuper) parallel to bedding.

Hydraulic conductivity perpendicular to bedding was studied for Opalinus Clay only. On the basis of permeameter tests in the laboratory, two measurements of 6E-15 m/s and 3E-14 m/s were obtained, leading to approximate anisotropy ratios of 1 to 10 for these two samples. These ratios were used to estimate hydraulic conductivity perpendicular to bedding for those units for which no direct measurements are available. For Opalinus Clay, a reference value of 2E-14 m/s is used.

Porosity

Porosities were obtained using various methods and are documented in Nagra (2002). From the weight-loss porosities of Rübel & Sonntag (2000), an average value of 0.12±0.02 for the low-permeability sequence can be calculated. These data are in general agreement with values obtained by the diffusive-exchange method (Gimmi & Waber 2004). The weight-loss and diffusive-exchange porosities are shown in Figure 2.3-8, together with estimates from geophysical borehole logs (Nagra 2001). Porosities obtained from through-diffusion experiments (Van Loon & Soler 2004) are not considered here due to the lack of representativity and the sensitivity of the values to analytical artefacts. The geophysical borehole logs indicate a lower porosity in the lower Malm, with a value around 0.06 (range of about 0.04 to 0.08)\(^\text{10}\).

Anions are partly excluded from the pore space of Opalinus Clay. Van Loon and Soler (2004) found, for Cl\(^-\) and I\(^-\) and one sample from a single depth, anion-accessible pore fractions of about 0.3 and 0.5, respectively. It seemed that the latter value could be influenced by a slight sorption effect. The value for Cl\(^-\) is low compared to squeezing data (Gimmi & Waber 2004). For Opalinus Clay samples from Mont Terri, anion-accessible pore fractions in the order of 0.5 to 0.6 were found (Nagra 2002). Gimmi & Waber (2004) considered a value of 0.5, as supported by squeezing data, to be reasonable for the low-permeability sequence at Benken, even though some variations as a function of depth and mineralogy may occur. Here, we also assume an anion-accessible pore fraction of 0.5 as most reasonable, which leads to a generic anion-accessible porosity of 0.06. This value is used throughout the low-permeability sequence.

In-situ temperature

Current temperature is 25 °C at the top of the low-permeability sequence and 41 °C at the bottom (Nagra 2002), with a mean value of 33 °C. Average values for each unit are given in Table 2.3-1.

\(^{10}\) Due to the limited availability of representative porosity and diffusion-coefficient data outside Opalinus Clay, constant values are used for the whole low-permeability sequence for modelling purposes, \textit{i.e.} formation-specific properties are not considered.
Figure 2.3-8: Mineralogy and porosity for the Benken borehole

Left side: Mineralogy and gravimetric water content (assuming a water density of 1 g/cm³) calculated from geophysical borehole logs (Nagra 2001). All data in weight-%. Hatched area: no data available. Right side: Porosity (in volumetric units) from geophysical borehole logs (line) as well as weight-loss (open circles) and diffusive-exchange porosities (filled circles) for the samples for which the stable water isotope values were determined. From Gimmi & Waber (2004)

Figure 2.3-9: U and Th contents of rocks from the Benken borehole

Data points relate to laboratory analyses by Lehmann et al. (2001), gamma logs from Nagra (2001)
2.3.5  
**U and Th contents in rocks**

U, Th and K concentrations in rocks were obtained from gamma logs (Nagra 2001) as well as from rock samples (Lehmann et al. 2001) and are shown in Figure 2.3-9. Lehmann et al. (2001) calculated the following averages from the gamma logs for the depth range 437 – 811 m: [U] = 2.03±0.94 ppm, [Th] = 9.99±4.31 ppm, [K] = 1.87±0.70 %.

2.3.6  
**Hydraulic gradient**

The hydraulic gradient between the Keuper and Malm aquifers of about -0.2 m/m points to upward flow. With a hydraulic conductivity perpendicular to the layering of about 2E-14 m/s and a water-filled porosity of about 0.1, one calculates an advective velocity of 1E-13 m/s for water tracers that can spread over the whole water-filled pore space (Gimmi & Waber 2004). However, the fact that a slight overpressure is observed within the low-permeability sequence shows that this calculation is probably too simplistic. Considering the overpressures within the low-permeability sequence (estimated maximum gradient of 5 m/m) and the same hydraulic conductivity, maximum flow velocities up to 1E-12 m/s can be calculated. Note that these calculations assume Darcy’s law to be valid, which is not established for small gradients.

Figure 2.3-10:  
**Burial history for the Benken borehole**

USM = Lower Freshwater Molasse, OSM = Upper Freshwater Molasse. From Mazurek et al. (2006)

2.3.7  
**Geological and hydrogeological evolution**

The Mesozoic sedimentary pile in northeastern Switzerland underwent diagenetic overprints during two burial phases (Figure 2.3-10 and Mazurek et al. 2006). A first, continent-scale, long-lasting burial occurred during Cretaceous times, when Opalinus Clay was buried to a depth of about 1 100 m, after which about 600 m of Cretaceous and upper Malm were eroded during late Cretaceous and early Tertiary times. In the late Tertiary, the sedimentary pile was buried a second time below the Molasse (erosional debris of the rising Alpine mountain chain), and Opalinus Clay at Benken reached a depth of about 1 700 m at 10 Ma. In spite of deeper burial during this second stage, maximum temperature at Benken (85 °C on the level of Opalinus Clay) was reached in the Cretaceous (Mazurek et al. 2006).
Diagenetic cementation is generally weak and limited to silty-sandy beds and lenses. In the Benken drill core only a few open structures were observed in limestones, dolomites and sandstones, while the few identified veins are generally closed in the claystones, marls, and the gypsum-anhydrite units (Nagra 2002, p. 256ff).

**Malm aquifer**

Karstification of the Malm limestones during early Tertiary times resulted in a complex and heterogeneous flow regime characteristic of such environments. The present hydraulic conductivity of Malm limestones is regionally highly variable, with values between 1E-14 and 1E-4 m/s. In the Benken borehole, values of about 1E-9 and 1E-8 m/s were measured (Nagra 2002). The chemical evolution of Malm ground water has to be interpreted within the complex palaeo-hydrological history from Jurassic to present times. The original formation water was sea water and was diluted by meteoric water during karstification in the early Tertiary until ca. 34 Ma. The subsequent second burial stage (about 30 to 10 Ma) below Tertiary Molasse sediments in four alternating fresh-water and marine- to brackish-water cycles gave rise to a complex and probably spatially heterogeneous mixture of fresh- and marine-water components. Since 10 Ma, the region of interest has been uplifting and subject to erosion. Uplift was (and still is) stronger in the Black Forest to the northwest of Benken (Figure 2.3-1), which created surface exposures of the Malm. Differential uplift led to a change of the regional surface runoff system at the Pliocene-Pleistocene boundary (2.7 Ma) when the direction of surface discharge changed from north-east towards the river Danube to west towards the Aare river (Villinger 2003). The flow system within the Malm was most likely activated in the early Pleistocene (at about 1.8 – 2 Ma) when the river Rhine eroded into the Malm limestones and created a discharge zone. Since that time, infiltration into the Malm aquifer occurs in the outcrop areas in the foothills of the Black Forest (Figure 2.3-1). Indirect infiltration through the Molasse sediments takes place in the south. Discharge of the Malm aquifer in the Benken area occurs towards the Rhine river in the southwest but towards the river Danube for areas further east (Nagra 2002). The fact that an old and relatively saline ground water is found at Benken indicates that, at this location, flow has been and is very limited, and the hydrogeological situation is near-stagnant.

**Low-permeability Dogger-Lias sequence**

In the low-permeability sequence of the Dogger and Lias between the Malm and Keuper aquifers, very low hydraulic conductivities (in general below 1E-13 m/s, Nagra 2002) were measured. They resulted from the compaction of the marine, predominantly argillaceous sediments during the two burial events. Compaction was also related to the expulsion of major parts of the connate pore water. Compaction drastically reduced typical pore sizes as well as porosity. Only very small flow velocities (about 3 m/Ma) are estimated for these formations based on present-day hydraulic gradients and assuming Darcian behaviour.

**Keuper aquifer**

The connate water of the evaporite-bearing units of the Keuper is difficult to constrain. Given the shielding effect of the overlying low-permeability sequence, a dilution by meteoric waters during the erosional stage in the late Cretaceous and early Tertiary seems unlikely. Similar to the Malm aquifer, the infiltration area (surface outcrops in the foothills of the Black Forest) was exposed on the surface due to the differential uplift of the Black Forest postdating the second burial stage at 10 Ma (Figure 2.3-1). The discharge zones for the Keuper aquifer that are still active today were probably created by deep erosion in the Klettgau area (to the west of the study site) some 1.8 Ma ago following
the diversion of the Alpenrhein towards the Aare river, an event that occurred at about 2.7 Ma (Villinger 2003). The change in surface-flow direction also coincides with the exhumation of the Keuper and direct infiltration. It is concluded that flushing of the aquifer by meteoric water was initiated at 1.8 Ma and still continues.

In the Keuper aquifer, the hydraulic continuity within an individual stratigraphic bed is limited due to pronounced lateral differences in sedimentary facies and lithology. This is consistent with the observed lateral variability of hydraulic conductivity of any individual bed (1E-10 to 1E-7 m/s) and by the fact that different beds are water-conducting in different boreholes of the region (Pearson et al. 1991, Nagra 2002). On a regional scale, ground-water flow in the Keuper occurs via hydraulic connections of these individual beds. This means that the large-scale hydraulic conductivity is probably smaller than that measured in a specific permeable bed penetrated by a borehole.

A conceptual flow model suggests the foothills of the Black Forest east of the river Wutach as the major infiltration area (Figure 2.3-1). Discharge of ground water from the Keuper water-conducting zones occurs westwards in the river Rhine (Nagra 2002). In the study area, the water-conducting zone of the Keuper is the Stubensandstein Formation, which consists of sandy beds at the bottom and dolomite breccias (products of subsurface dissolution of gypsum that was originally present) at the top, with a hydraulic conductivity of about 1E-7 m/s (Nagra 2002).

2.4 Opalinus Clay at Mont Terri (Switzerland)

2.4.1 Structure and hydrogeology

Mont Terri is the most external anticline in the Folded Jura of northwestern Switzerland. Triassic and Jurassic rocks of the asymmetrical fold are exposed on the present surface of the Mont Terri (Figure 2.4-1). The formations of interest can be accessed underground from a reconnaissance gallery that was excavated for a motorway tunnel. The profile runs SE-NW through the core of the anticline (Figure 2.4-2, Figure 2.4-3). The rock laboratory was constructed from the reconnaissance tunnel in the Opalinus Clay section of the south-eastern part of the anticline (Figure 2.4-3), where structural complexity and deformation are limited.

According to Nussbaum et al. (2005), three fault systems can be distinguished:

1. SSE-dipping faults, subparallel to bedding (typical dip angles of 30 – 50°);
2. S- to SW-dipping faults, flat lying;
3. WNW- to W-dipping fault planes.

Systems 1 and 2 are thrust structures related to the folding of the Jura Mountains, and the near-vertical system 3 is related to transpressive movements of the Rhine Graben. The biggest structure cross cutting the laboratory, the so-called Main Fault (922 m along tunnel), belongs to system 1 and is considered to be an internal décollement (detachment) horizon within Opalinus Clay. The maximum overburden above the Rock Laboratory is about 300 m.

As shown in Figure 2.4-2, the rock laboratory cuts obliquely across the sedimentary sequence, and the bedding dips with angles between 22° (Lias – Opalinus Clay boundary) and 55° (Opalinus Clay – Dogger limestones boundary). In order to obtain distances orthogonal to bedding, distances along the tunnel were recalculated to the nearest distances from the Opalinus Clay – Dogger limestones boundary. They were obtained by a geometrical calculation taking into account the orientation of bedding as surveyed in the tunnel and assuming that the contact between Dogger
limestones and Opalinus Clay is a regular, planar feature with constant orientation. Using this method, the total thickness of Opalinus Clay was calculated to be 160 m (Pearson et al. 2003, Tab. 6.1). All tracer profiles shown below use orthogonal distance as the spatial axis, and, for simplicity, the graphs are rotated back to correspond to the original horizontal stratigraphic sequence.

The geological and hydrogeological subdivision of the profile at Mont Terri is listed in Table 2.4-1. The lower boundary of the low-permeability sequence is a water seepage in the Liassic Gryphaea limestone at 1 120 m along tunnel (orthogonal distance 205 – 208.5 m). The overlying Liassic units are predominantly shaly and are considered to belong to the low-permeability sequence. The overlying Opalinus Clay can be subdivided into five lithological sub-units, from bottom to top: shaly, sandy and carbonate-rich, sandy, shaly, and sandy facies (Pearson et al. 2003, Figure 2.6). The upper boundary of the low-permeability sequence is not easy to define. It is estimated to be located at -14 m orthogonal distance, i.e. about half way between the contact to Opalinus Clay and the first seepage with young, low-salinity water at 752 m (-23.8 m orthogonal distance). The resulting true thickness of the low-permeability sequence is 219 m. Note that while Opalinus Clay is lithologically quite similar at Mont Terri and at Benken, the embedding units are markedly different. For example, Opalinus Clay at Mont Terri is directly over lain by a limestone, whereas clay-rich units dominate at Benken. Therefore, the low-permeability sequence at Mont Terri is markedly thinner than the 312 m identified at Benken.

Figure 2.4-1: Geological map of the Mont Terri region

From Pearson et al. (2003)
Figure 2.4-2: Geological profile and erosion history across the Mont Terri anticline

Modified from Freivogel & Huggenberger (2003). Schematic representation of the erosion history according to discussion in Section 2.4.7

Figure 2.4-3: Arrangement of tunnels and niches in the vicinity of the Mont Terri rock laboratory
Table 2.4-1: Geometric properties and transport parameters of units at Mont Terri

<table>
<thead>
<tr>
<th>Unit</th>
<th>Lithology</th>
<th>Hydro-geology</th>
<th>Distance along tunnel [m]</th>
<th>Distance from Dogger limestone [m]</th>
<th>Dp @ 20 °C [m²/s]</th>
<th>De @ 20 °C [m²/s]</th>
<th>K⊥ [m/s]</th>
<th>K∥ [m/s]</th>
<th>n [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dogger limestone (ca. 168 Ma)</td>
<td>Sandy limestone</td>
<td>Aquifer</td>
<td>&lt;757</td>
<td>&lt; -14</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dogger limestone (ca. 168 Ma)</td>
<td>Sandy limestone</td>
<td></td>
<td>757 – 781</td>
<td>-14 – 0.0</td>
<td>HTO: 7.9E-11</td>
<td>Anions: 4.8E-11</td>
<td>4E-14</td>
<td>2E-13</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Anions: 4.6E-12</td>
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<td></td>
<td></td>
<td></td>
<td>1.4E-11</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Opalinus Clay (Dogger, ca. 174 Ma)</td>
<td>Shale</td>
<td></td>
<td>781 – 1 024</td>
<td>0.0 – 160.0</td>
<td>HTO: 7.9E-11</td>
<td>Anions: 4.8E-11</td>
<td>4E-14</td>
<td>2E-13</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Anions: 4.6E-12</td>
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<td></td>
<td></td>
<td></td>
<td>1.4E-11</td>
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</tr>
<tr>
<td>Jurensis Marl (Liassic, ca. 178 Ma)</td>
<td>Marl and marly shale</td>
<td>Low-permeability sequence</td>
<td>1 024 – 1 033</td>
<td>160.0 – 164.5</td>
<td>HTO: 7.9E-11</td>
<td>Anions: 4.8E-11</td>
<td>4E-14</td>
<td>2E-13</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Anions: 4.6E-12</td>
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<td></td>
<td></td>
<td></td>
<td>1.4E-11</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Posidonia Shale (Liassic, ca. 180 Ma)</td>
<td>Bituminous shale</td>
<td></td>
<td>1 033 – 1 061</td>
<td>164.5 – 178.5</td>
<td>HTO: 7.9E-11</td>
<td>Anions: 4.8E-11</td>
<td>4E-14</td>
<td>2E-13</td>
<td></td>
</tr>
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<td>Anions: 4.6E-12</td>
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<td></td>
<td>1.4E-11</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Obtusus Clay and Obliqua Beds (Liassic, ca. 185 Ma)</td>
<td>Shale</td>
<td></td>
<td>1 061 – 1 114</td>
<td>178.5 – 205.0</td>
<td>HTO: 7.9E-11</td>
<td>Anions: 4.8E-11</td>
<td>4E-14</td>
<td>2E-13</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Anions: 4.6E-12</td>
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<td></td>
<td></td>
<td></td>
<td>1.4E-11</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gryphaea Limestone (Liassic, ca. 192 Ma)</td>
<td>Limestone</td>
<td>Local aquifer</td>
<td>1 114 – 1 121</td>
<td>205.0 – 208.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

See Table 1.8-1 for definitions of symbols. ⊥ = normal to bedding, || = parallel to bedding, || / ⊥ = anisotropy factor. Values given in italics were not measured/estimated directly but are based on assumed analogy with measurements in other units. Data from Nagra (2002) Pearson et al. (2003), Van Loon et al. (2003, 2005) and Van Loon & Soler (2004). Shaded areas indicate aquifers.

2.4.2 Tracer distributions in the Dogger and Lias

The pore-water data are based on drillcore investigations and borehole samples originating from various locations across the low-permeability sequence (Gautschi et al. 1993, Rübel et al. 2002, Pearson et al. 2003). Water samples were obtained in situ at three locations in the Opalinus Clay (tunnel metres 864, 885 and 949) in packed-off borehole intervals into which small amounts of pore water seeped over periods of months.
Seepage waters were obtained from flows out of the tunnel wall in the Dogger limestone (tunnel metres 721 and 752), in the Posidonia Shale (tunnel metres 1 038 and 1 052) and in the Liassic Gryphaea limestone (tunnel metre 1 120). The seepages in the Dogger and Gryphaea limestones define the upper and lower boundaries of the low-permeability sequence. The seepage data of the Posidonia Shale show a decreasing salinity and decreasing δ²H and δ¹⁸O values over time, which indicates that fresh-water circulation in these seepages was only activated through the excavation of the tunnels at Mont Terri and so is not representative of the undisturbed system (Gautschi et al. 1993). For this reason, the seepage data from Posidonia Shale are screened out for the purposes of this report.

Stable water isotopes

The isotopic compositions of pore waters were determined by the vacuum-distillation method and the diffusive-exchange method of Rübel et al. (2002). Isotopic analyses were also made for in-situ water samples seeping into dedicated boreholes in the low-permeability sequence and for four pore-water samples extracted by squeezing at 70 to 512 MPa. In addition, seepages from the Dogger and Liassic limestone and Posidonia Shale were analysed. The resulting data are shown in Figure 2.4-4. All δ²H and δ¹⁸O values are negative, i.e. lower than values occurring in present-day sea water. The highest values are seen in the centre of the low-permeability sequence. The decrease towards the boundaries is steeper towards the underlying (Liassic) aquifer when compared to the trend towards the overlying Dogger limestones. This asymmetry could originate from activation of the bounding aquifers at different times, but also from heterogeneous initial concentrations or formation properties (even though the latter two alternatives are regarded unlikely). The δ²H data scatter somewhat less than the δ¹⁸O data.

All data obtained by vacuum distillation yielded clearly too low δ values when compared with data obtained by diffusive exchange and squeezing. A comparison yields a shift of about -2.1 ‰ in δ¹⁸O and -6.9 ‰ in δ²H for the vacuum distillation data (Pearson et al. 2003, ch. 3.3.4). The lower δ values were attributed to Rayleigh-type fractionation and incomplete removal of the pore water during distillation, leading to a depletion of heavy isotopes in the extracted water. This is also supported by the fact that in a plot of δ²H versus δ¹⁸O, the distillation data plot on the left side of the global meteoric water line (with a slope of about 5.5, typical for Rayleigh-type fractionation), whereas the data from all other methods plot close to the global meteoric water line. Accordingly, the diffusive-exchange data are considered to be more reliable. The available vacuum distillation data were corrected for incomplete distillation using the values indicated above. However, these data are used in this report only for samples where diffusive-exchange data are not available, whereas they are screened out if this is the case.

In Pearson et al. (2003), the errors of the δ²H data obtained by diffusive exchange, distillation and squeezing are given as ±3.0 ‰, ±3.0 ‰, and ±4.0 ‰, respectively, and those of normal analyses of the water samples as ±1.5 ‰. We attribute an increased error of ±4.0 ‰ to the corrected distillation data. For δ¹⁸O, errors of the diffusive-exchange data, the squeezing data, and the water samples are ±0.8 ‰, ±0.2 ‰, and ±0.2 ‰, respectively. For the distillation data, an error of ±0.4 ‰ is given in Pearson et al. (2003) but we increase it to ±0.8 ‰ here, in order to account for the uncertainty related to the correction procedure.
Anions

Chloride contents of pore waters were obtained by aqueous leaching and by squeezing. The aqueous leaching data were re-scaled by considering an anion-accessible pore fraction of 54% of the physical porosity. This fraction was suggested by Pearson (1999) on the basis of a comparison with the squeezing data. It is also consistent with data from independent diffusion experiments on Mont Terri samples with water tracers and anions (see below). Pearson et al. (2003) specify the errors of the Cl⁻ data as ±10%. Bromide and iodide data of the pore waters were only obtained from squeezed samples. The errors are specified as ±10% in both cases. Errors of ±0.2 ‰ are used for the $^{37}$Cl data, consistent with Figure A7.1 in Pearson et al. (2003), but ignoring the generally lower values reported in their Table A7.3.

The Cl⁻ profile (Figure 2.4-5 left) shows highest values (in the order of 14 g/L, that is, slightly lower than present sea water) at the interface of the Opalinus Clay and the Liassic. The values decrease towards both sides, with a much steeper slope towards the Gryphaea Limestone and the Keuper marls than towards the Dogger limestones, as in case of the stable water isotope profiles. The bromide data as well as the few iodide data (Figure 2.4-6) appear to follow the same trend as Cl⁻. The Br⁻/Cl⁻ ratio is very close to the value of sea water, whereas the I⁻/Cl⁻ ratio is clearly higher and is probably strongly affected by diagenesis. The $^{37}$Cl data (Figure 2.4-5 right) show a curved shape with maximum values shifted towards the Dogger limestones, and with a steeper decrease in this direction when compared to the decrease towards the Liassic and Keuper. The in-situ water samples from the Opalinus Clay have slightly lower values than the neighbouring pore waters. Note that no data are available for the Liassic Gryphaea limestone aquifer.
Figure 2.4-5: Profiles of chloride concentrations and $\delta^{37}$Cl values in pore and ground waters from Mont Terri

Cl$^-$ concentrations refer to the mass of chloride per volume of Cl$^-$-accessible pore water, considering that 54 % of the physical porosity are accessible to anions.

Figure 2.4-6: Bromide and iodide contents of pore and ground waters from Mont Terri

Br$^-$ and I$^-$ concentrations refer to the mass of chloride per volume of anion-accessible pore water, assuming that 54 % of the physical porosity are accessible to anions.

**Noble gases**

He contents and the $^{40}$Ar/$^{36}$Ar ratio of pore waters at Mont Terri are shown in Figure 2.4-7. The uncertainty of the He data is in the order of +30 %/-5 %. The He data describe a curved, approximately symmetric profile with decreasing values towards the aquifers. One outlier is observed.
in the Liassic Posidonia Shale, possibly due to the influx of old water activated by tunnel construction (Pearson et al. 2003, p. 252).

The maximum He concentrations in the centre of the low-permeability sequence are much lower than the total He that was produced since deposition. For the U and Th contents measured at five locations (see below), a mean He accumulation rate of 7.6E-13 cm³ STP/grock/a can be calculated. The ‘retention coefficients’ of He (measured concentrations divided by the calculated accumulated concentrations for a time of 174 Ma) are in the order of 3 to 6 % only.

The ⁴⁰Ar/³⁶Ar profile has an asymmetric shape, with the largest values in the Liassic and the adjacent Opalinus Clay. The uncertainty of the ⁴⁰Ar/³⁶Ar ratios is about ±6. The ⁴⁰Ar/³⁶Ar ratios in pore water are mostly higher than in water in equilibrium with air (ratio of 295.5).

![Figure 2.4-7: He contents and ⁴⁰Ar/³⁶Ar ratios of pore waters from the Mont Terri](image)

2.4.3 Upper and lower boundary

Seepage waters were collected from the aquifers above and below the low-permeability sequence (Gautschi et al. 1993, Pearson et al. 2003). In the upper aquifer, the seepage closest to Opalinus Clay is -23.8 m orthogonal distance away in the Dogger limestones. The next seepage is -49 m away from the contact to Opalinus Clay. No He and ⁴⁰Ar/³⁶Ar data are available for the Dogger limestones. As shown in Table 2.4-2, the salinity in both the upper and lower aquifer is very low, and δ values of water isotopes are more negative when compared to the low-permeability sequence.

---

11 In the model, the boundary is assumed to be at -14 m orthogonal distance.
Table 2.4-2: Tracer data from seepage waters of the aquifers embedding the low-permeability sequence at Mont Terri

<table>
<thead>
<tr>
<th>Unit</th>
<th>Distance from Dogger limestones [m]</th>
<th>δ¹⁸O [‰ v-SMOW]</th>
<th>δ³⁷S [‰ v-SMOW]</th>
<th>Cl⁻ [mg/L]</th>
<th>Br⁻ [mg/L]</th>
<th>I⁻ [mg/L]</th>
<th>δ³⁷Cl [‰ SMOC]</th>
<th>He [cm³ STP/g water]</th>
<th>⁴⁰Ar/³⁶Ar [–]</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upper aquifer: Dogger limestones</td>
<td>-49.0</td>
<td>-9.33</td>
<td>-65.8</td>
<td>4</td>
<td>b.d.</td>
<td>-0.35</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-23.8</td>
<td>-10.07</td>
<td>-72.5</td>
<td>97</td>
<td>0.3</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Lower aquifer: Gryphaea limestone</td>
<td>208.1</td>
<td>-9.34, -9.58</td>
<td>-65.3, -66.8</td>
<td>4, 10</td>
<td>b.d.</td>
<td>–</td>
<td>2.02E-6</td>
<td>293.5</td>
<td>He = 4.33E-5 cm³ STP/g water, ⁴⁰Ar/³⁶Ar = 297.7</td>
<td></td>
</tr>
</tbody>
</table>

Data from Pearson et al. (2003) and Gautschi et al. (1993). b.d. = below detection

2.4.4 Transport parameters in the Dogger and Liassic shales

Diffusion coefficients for HTO

Diffusion coefficients were determined for Opalinus Clay only and not for the Liassic shales or the lowermost part of the Dogger limestones, which are also part of the low-permeability sequence at Mont Terri. Effective diffusion coefficients De for HTO are reported in Nagra (2002), Pearson et al. (2003, Table A9.14), Van Loon et al. (2003) and Van Loon & Soler (2004). The first two references report partly on the same data obtained by various laboratories, but in Pearson et al. (2003) the ranges are given, whereas in Nagra (2002) mean values for the different laboratories are reported. Van Loon & Soler (2004) present data that were also published in other papers (Van Loon et al. 2003, Van Loon et al. 2004b, and Van Loon et al. 2005). For HTO, De perpendicular to bedding generally lies between 0.8E-11 and 2.3E-11 m²/s, and the average value of Van Loon & Soler (2004) of 1.4E-11 m²/s is given in Table 2.4-1. The porosity values obtained in the diffusion experiments for the different samples by the different laboratories varied somewhat. Using a typical porosity value of 0.177 (see below), we calculated a Dp of 7.9E-11 m²/s. According to this Dp, a geometry (or formation) factor D0/Dp of 29 was calculated with a self-diffusion coefficient of water D0 = 2.3E-9 m²/s (Mills 1973, cited by Cook & Herczeg 2000).

Diffusion coefficients parallel to bedding for Opalinus Clay samples from Mont Terri are about a factor 4 larger than those perpendicular to bedding (Van Loon & Soler 2004, Van Loon et al. 2004b). Field experiments at the Mont Terri rock laboratory (Wersin et al. 2004a, Van Loon et al. 2004a) confirmed the laboratory diffusion coefficients for diffusion parallel to bedding.

In the absence of formation-specific data, we attributed the diffusion coefficients for Opalinus Clay also to the Liassic claystones and to the lowermost part of the Dogger limestones.

Diffusion coefficients for anions

For I⁻ and Cl⁻, effective diffusion coefficients De are given in Nagra (2002), Pearson et al. (2003), Van Loon et al. (2003) and Van Loon & Soler (2004). The values for diffusion perpendicular to the bedding range (with one exception that is considered as influenced by artefacts) between 0.23E-11 and 0.48E-11 m²/s, with no significant differences between the values for I⁻ and Cl⁻. In Table 2.4-1, we
report the De value of 0.46E-11 m²/s determined for Cl⁻ by Van Loon & Soler (2004). The diffusion-accessible porosities varied in the reported experiments between 0.04 and 0.17, but the largest values seem to be unrealistic, presumably affected by artefacts of the experimental set-up. With a typical porosity value of 0.096 for anions (see below), we calculated a Dp of 4.8E-11 m²/s (Table 2.4-1).

It should be borne in mind that the reported Dp for Cl⁻ is a tracer diffusion coefficient. In case of movement of bulk Cl⁻, charge balance constraints are important and can affect the relevant diffusion coefficient. For instance, a salt diffusion coefficient for NaCl in Opalinus Clay at Mont Terri, estimated from the Cl⁻ and Na⁺ tracer diffusion coefficients, is about a factor of 1.6 larger than the ionic diffusion coefficient of Cl⁻ at trace concentrations. However, in the absence of relevant data, the values given in Table 2.4-1 were not corrected for the effect of co-diffusion of a cation.

Due to the lack of formation-specific data, the same De and Dp values as for the Opalinus Clay were also attributed to the Liassic claystones and the lowermost Dogger limestones.

**Diffusion coefficients for He**

In the absence of measured data, De(He) is estimated to be 3 times the value for De(HTO) according to the argument presented in Appendix A3.2.

**Hydraulic conductivity**

Based on packer testing, the hydraulic conductivity of Opalinus Clay lies around 2E-13 m/s (range: 2E-14 – 2E-12 m/s) parallel to bedding (see Table 2.4-1; Pearson et al. 2003, Nagra 2002). Values normal to bedding of about 0.6E-13 – 1E-13 m/s were derived from permeameter tests (Nagra 2002). Using an anisotropy factor of 4 (analogous to the diffusion coefficient), a typical hydraulic conductivity of 5E-14 m/s normal to bedding is calculated. It appears that there is no contrast in the hydraulic properties between the matrix rock and the Main Fault (Marschall et al. 2004).

In the absence of data for the other units of the low-permeability sequence, the same values as for Opalinus Clay are used.

**Porosity**

Porosities for the Opalinus Clay at Mont Terri were obtained by a number of different methods, notably by drying at 105 °C or other temperatures (weight-loss porosity), by pycnometric measurements, from diffusive exchange of water isotopes, or from diffusion experiments. The data are reported in Nagra (2002), Pearson (2003) and Van Loon & Soler (2004).

The biggest data set is available for weight-loss porosity at 105 °C, with an average value of 0.157 (Nagra 2002). Experience from Opalinus Clay at Benken indicates that porosity accessible for HTO in Opalinus Clay determined by various methods is ca. 1.13 times higher than water-loss porosity at 105 °C due to the incomplete removal of pore water at that temperature (Nagra 2002, p. 244). Using this relationship for Mont Terri leads to a diffusion-accessible porosity of 0.177 for HTO. Applying a value of 54 % for the fraction of HTO porosity that is accessible to Cl⁻ (Pearson 1999) leads to a Cl⁻-accessible porosity of 0.096, which is very close to the weighted average of the data given in Pearson et al. (2003, Tab. A10.4).
In-situ temperature

The current in-situ temperature at Mont Terri is ca. 14 °C.

2.4.5 U and Th contents in rocks

A limited number of analyses is available and indicates average values of 3.08 (range: 2.65 – 4) ppm for U and 13.8 (13 – 15) ppm for Th (Pearson et al. 2003, Tab. A5.3).

2.4.6 Hydraulic gradient

Ground-water pressures in the embedding flowing layers are not well characterised (the measurement points are located far from the contact to the low-permeability sequence; Marschall et al. 2004). Moreover, the interpretation of the pressure data is rendered difficult due to the effects of surface topography. Based on the limited data base, hydraulic gradients across the low-permeability sequence are certainly <1 m/m, more likely <<1 m/m and directed towards the Dogger limestone aquifer. Pore-pressure measurements in Opalinus Clay are available but cannot be used to reconstruct the conditions prior to the excavation of the tunnels (Marschall et al. 2004).

2.4.7 Geological and hydrogeological evolution

The Mesozoic evolution at Mont Terri is very similar to that of Benken (Section 2.3.7), as both locations were part of an epicontinental marine basin covering large parts of Europe. A stage of regional uplift and erosion followed in the early Tertiary. In the Oligocene, faulting and subsidence in the Rhine Graben left a structural imprint on the region (N-S oriented fracture set). Oligocene/Miocene Molasse deposits were thinner than at Benken due to the larger distance to the sediment source in the Alps, and so the underlying Mesozoic rocks did not receive an additional compaction at this time (Mazurek et al. 2006). According to Bossart & Wermeille (2003), the incision of the Doubs river started at 21.5 Ma (early Miocene).

The folding of the Jura Mountains occurred in the period 10.5 – 3 Ma (Berger 1996). Bossart & Wermeille (2003) implicitly assume that the folding of the Jura Mountains started in the proximal zone and proceeded to the distal parts over time. According to Bossart (pers. comm.), this contention is founded on the interpretation of a seismic profile across the Jura Mountains in the Vue des Alpes region (40 km SW of Mont Terri) published by Sommaruga & Burkhard (1997). It is also in line with evidence from similar settings in the Rocky Mountains and from analogue experiments (Pfiffner, pers. comm.). This would mean that the faulting and folding of the Mont Terri anticline, which is an external position, would be closer to 3 than to 10.5 Ma. On this basis, Bossart & Wermeille (2003) constrained the time at which the Hauptrogenstein of the Mont Terri anticline, i.e. the uppermost unit of the Dogger limestones, was exposed on the surface by erosion of the fold to the range 3.7 – 1.2 Ma. On the other hand, there is evidence in the Neuchâtel area that deformation started in the central part of the range and then proceeded to more external and internal regions (Pfiffner, pers. comm.). Burkhard (pers. comm.) stated that there are no arguments for clearly constraining the timing of faulting and folding at Mont Terri and that evidence from other parts of the Jura Mountains cannot be safely extrapolated due to lateral variability of the tectonic evolution.

12 In a more recent literature review, Becker (2000) obtained a similar range of 9 - 4 Ma.
The fact remains that deformation and thus the creation of topographic gradients, whether at Mont Terri or in more internal positions, started around 10 Ma, and this is considered as the maximum age for the activation of the limestone aquifer overlying Opalinus Clay. The minimum age is 1.2 Ma according to Bossart & Wermeille (2003). The aquifer underlying the low-permeability sequence were still undisturbed at this time.

The lower (Liassic) aquifer in the core of the anticline was most probably activated only after the Opalinus Clay above has been eroded away (Figure 2.4-2). According to Bossart & Wermeille (2003), this happened between 0.5 and 0.2 Ma.

As noted in Pearson et al. (2003), measured Cl\(^-\) contents and \(\delta\) values of water isotopes cannot be consistently explained as mixtures of sea water and a fresh-water component. The highest Cl\(^-\) measured indicates a marine component of ca. 72\%, whereas components of only 27/32\% are obtained for \(\delta^{18}O/\delta^{2}H\). Pearson et al. (2003, ch. 6.3.2) discuss various hypotheses and suggest on a qualitative basis that the higher diffusion coefficient for water when compared to chloride could explain the discrepant mixing ratios. Another hypothesis would be ultrafiltration of pore fluids from underlying formations, but this process cannot currently be quantified and appears unlikely (see also Section 4.2.3).

2.5 Opalinus Clay at Mont Russelin (Switzerland)

2.5.1 Structure and hydrogeology

The Caquerelle or Mont Russelin anticline is the neighbouring fold to Mont Terri, located ca. 5 km to the southeast, i.e. in a more internal position in the Jura Mountains. The anticline is penetrated by a motorway tunnel, which cross-cuts Opalinus Clay over more than one kilometre. The internal structure of the fold core in which Opalinus Clay occurs is more complex than at Mont Terri and contains several internal thrust faults (Figure 2.5-1). Based on detailed tunnel mapping (Bureau Technique Norbert 1993), a major fault zone is observed at 1 705 – 1 808 m along tunnel (138.1 – 166.4 m orthogonal distance; for definition of orthogonal distance see Section 2.5.2). This zone runs subparallel to the tunnel and close to the contact of Opalinus Clay and the underlying Liassic.

Opalinus Clay is overlain by Dogger limestones, from which seepages into the tunnel are observed. These limestones crop out on the surface and are considered to constitute an aquifer. Events of heavy rainfall result in higher discharges into the tunnel.

In contrast to Mont Terri, the Liassic underlying Opalinus Clay does not crop out on the surface. It occurs in the core of the anticline, is always overlain by Opalinus Clay and so has no evident hydraulic connection to the surface (Figure 2.5-1). Thus, while it may have an enhanced hydraulic conductivity, the water is likely stagnant, i.e. there is no clear lower hydraulic boundary for the Opalinus Clay (Table 2.5-1).
Table 2.5-1: Geometric properties and porosity of units at Mont Russelin

<table>
<thead>
<tr>
<th>Unit</th>
<th>Lithology</th>
<th>Hydrogeology</th>
<th>Distance along tunnel [m]</th>
<th>Orthogonal distance from Dogger limestone [m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dogger limestone (ca. 168 Ma)</td>
<td>Sandy limestone</td>
<td>Aquifer</td>
<td>&lt; 504.4</td>
<td>&lt; -45</td>
</tr>
<tr>
<td>Dogger limestone (ca. 168 Ma)</td>
<td>Sandy limestone</td>
<td>Low-permeability</td>
<td>1 504.4 – 1 552.7</td>
<td>-45 – 0</td>
</tr>
<tr>
<td>Opalinus Clay and Jurensis Marl (Dogger, ca. 174 Ma to Liassic, ca. 178 Ma)</td>
<td>Shale, marl and marly shale</td>
<td>&gt; 1 552.7</td>
<td>&gt; 0</td>
<td></td>
</tr>
</tbody>
</table>

Shaded area indicates the aquifer

Figure 2.5-1: Geological profile across the Mont Russelin anticline

Upper part: Predicted profile on the basis of surface mapping and borehole data. Lower part: Profile in the vicinity of the main tunnel according to actual findings. Sampling localities with orthogonal distances [m] to the Dogger limestones are also shown in green. Section highlighted in red indicates a major faulted zone. Adapted from Bureau Technique Norbert (1993)

2.5.2 Tracer distributions in the Dogger and Lias

Pore-water tracers were studied in the southeastern part of the Opalinus Clay section between tunnel metres 1 510 and 1 867.5, plus one sample from 2 065.5 (Koroleva et al., in prep.). The reasons for this choice were the following:

- At 1 867.5 m, an extensometer borehole drilled during tunnel construction yielded water from the Liassic that underlies Opalinus Clay. This water is affected by interaction with cement (pH = 11.9) but nevertheless provides information at least for conservative tracers. Measured Cl⁻ and Br⁻ contents of 18 400 and 65 mg/L are high and very similar to those of sea water. These values are even higher than the highest values identified at Mont Terri (Section 2.4). The same is true for water isotopes (δ¹⁸O = -4.9 ‰, δ²H = -28 ‰), even though these values are still well below those of sea water.
• A seepage with dilute and \(^3\)H-containing waters was observed in the Dogger limestones at 1 504.4 m. Further seepages occur at <1 504.4 m.

• These two points with contrasting water compositions are located 363 m apart along tunnel, which corresponds to about 220 m along a profile perpendicular to the contact plane between Opalinus Clay and Dogger limestones.

• The geometry in the chosen section is simpler when compared to that of the rest of the anticline, where the geometric definition of the aquitard-aquifer pattern is more difficult.

Samples for pore-water analysis were obtained from eighteen \(ca\). 4 m long boreholes drilled from the escape tunnel (which parallels the main tunnel) into the formation. For the purpose of understanding and modelling the tracer profiles, sampling locations measured in metres along tunnel were recalculated to orthogonal distances to the contact between Opalinus Clay and the overlying Dogger limestone (Blaukalk). Because this contact surface is curved (Figure 2.5-1), the recalibration does not follow a simple linear function. From the upper contact of Opalinus Clay to \(ca\). 1 715 m, the nearest contact plane to the overlying Blaukalk is located in the fold limb and dips steeply (\(ca\). 62°). At positions >1 715 m along the tunnel, the nearest contact plane is in the roof of the anticline, which dips with an angle of \(ca\). 12° only. In this range, the orthogonal distances increase only weakly with increasing distance along tunnel. The presence of tectonic slices of Dogger limestones even closer to the tunnel (Figure 2.5-1) is possible but not considered in the calculation of orthogonal distances because 1) their geometry is not sufficiently well constrained, and 2) the hydrogeological significance of these slices is unknown.

The one-dimensional representation of the tracer profile is a simplification, and modelling in 2 dimensions could potentially improve the accuracy. However, because the profile as shown in Figure 2.5-1 is subject to geometric uncertainties, the improvement is probably limited and not considered here.

**Stable water isotopes**

Data were obtained using the diffusiv-exchange technique. In addition, data points are available from extensometer borehole E4/2 at tunnel metres 1 867.5 (176.8 m orthogonal distance; water obtained from the Liassic in immediate contact to Opalinus Clay) and from the water seepage at 1 504.4 m (-45 m orthogonal distance; Blaukalk, part of the Dogger limestones overlying Opalinus Clay). All data are shown in Figure 2.5-2. Both O and H show an increase of the \(\delta\) values with increasing distance from the Dogger limestones, and the data from the seepage and borehole waters fit well into the pattern of the pore waters. The faulted interval 138.1 – 166.4 m orthogonal distance coincides well with a marked disturbance towards lower \(\delta\) values for both isotopes.

An additional sample taken at 2 065.5 m along the tunnel has \(\delta^{18}\)O and \(\delta^2\)H values of -7 and -49.3 ‰, \(i.e\). below the maximum observed in the vicinity of the extensometer borehole. Given the structural complexity (see Figure 2.5-1), an orthogonal distance to the nearest Dogger limestone contact cannot be well constrained for this sample, but it is most probably lower than in the region of the extensometer borehole.

**Anions**

A regular profile with Cl\(^-\) contents that increase with increasing distance to the Dogger limestones is found (Figure 2.5-3). Data obtained by leaching and squeezing are internally consistent when, analogous to the findings at Mont Terri (Section 2.4, Pearson *et al.* 2003), a fraction of 0.54 of
physical porosity is assumed to be accessible to anions. The Cl\(^-\) content in the water sample obtained from the extensometer borehole at 176.8 m is consistent with the pore-water data. In contrast to water isotopes, a disturbance in the faulted zone at 138.1 – 166.4 m is not identified. The sample at 2065.5 m along the tunnel has a Cl\(^-\) content of 11 561 mg/L, i.e. well below the maximum near the extensometer borehole. As for stable water isotopes, this value cannot be clearly interpreted.

Figure 2.5-2: Distribution of $\delta^{18}$O and $\delta^2$H at Mont Russelin

Data from Koroleva et al. (in prep.). Orange area shows the faulted zone at 138.1 – 166.4 m

Figure 2.5-3: Distribution of Cl\(^-\) at Mont Russelin

Data from Koroleva et al. (in prep.). Orange area shown the faulted zone at 138.1 – 166.4 m. No direct Cl\(^-\) analysis is available for the seepage water, but the low electrical conductivity of the water suggests a very low salinity
Noble gases

A limited number of analyses of He in pore water are available. Contents rise from low contents in the Blaukalk to 8E-4 cm$^3$ STP/g$_{\text{water}}$ in Opalinus Clay (Figure 2.5-4). A disturbance in the interval 138.1 – 166.4 m is evident (as for stable water isotopes) and characterised by heterogeneous He contents.

For Opalinus Clay at Mont Terri, Rübel et al. (2002) concluded that a distance of 3 m away from the tunnel is sufficient to obtain in-situ He contents that are unaffected by outgassing into the tunnel. For Mont Russelin, the situation is less clear, as He contents do not systematically increase with increasing borehole depth in all cases. The degree of brittle deformation is stronger than at Mont Terri, and this could result in localised He transport along natural fractures that were reactivated by tunnel construction. Boreholes drilled at Mont Terri were typically 4 m deep, and the data in Figure 2.5-4 show the maximum He concentrations observed in each borehole. In most but not all cases, this corresponds to the deepest sample. The uncertainty regarding the representativity of the He data for in-situ conditions has to be borne in mind for interpretation.

Figure 2.5-4: Distribution of dissolved He at Mont Russelin

Data from Koroleva et al. (in prep.). Orange area shows the faulted zone at 138.1 – 166.4 m

2.5.3 Upper and lower boundary

The upper boundary is defined by the water seepage in Blaukalk at -45 m orthogonal distance. Similar to Mont Terri, a zone within the Dogger limestones adjacent to Opalinus Clay is devoid of seepages and is considered as part of the low-permeability sequence. That is, the contact between Opalinus Clay and the overlying limestones is considered to have no hydrogeological significance.

The seepage at -45 m was investigated during tunnel construction, yielding a stable isotopic composition of $\delta^{18}$O = -9.4 ‰ and $\delta^2$H = -63.4 ‰ (Bureau Technique Norbert 1993). These values are
close to those of recent local recharge, which is confirmed by the $^3$H content of 20.2 TU. While the chemical composition of the water has not been studied, the low electrical conductivity (705 μS/cm) indicates that the water is very dilute.

Salinity, δ values of water isotopes as well as He contents increase towards the centre of the anticline until 176.8 m orthogonal distance. One sample taken well beyond this position (2 065.5 m along the tunnel) shows decreasing salinity and δ values, but the data are difficult to interpret due to the geometric complexity and due to the presence of structural discontinuities. In any case, a lower hydrogeological boundary (e.g. in the Liassic) is not observed.

2.5.4 Transport parameters in the Dogger and Liassic shales

Studies dedicated to samples from Mont Russelin are not available. Given the spatial proximity to Mont Terri and the analogy of the geological evolution at both locations, data from Mont Terri are considered as appropriate for Mont Russelin as well.

2.5.5 U and Th contents in rocks

In the absence of site-specific information, data from Mont Terri are taken as representative for Mont Russelin.

2.5.6 Hydraulic gradient

No data available.

2.5.7 Geological and hydrogeological evolution

No specific studies are available for Mont Russelin. However, the geological evolution can be assumed to be very similar to that at Mont Terri. With respect to hydrogeology, one difference to Mont Terri is the absence of a lower aquifer underlying Opalinus Clay, which is due to the fact that the Mont Russelin anticline has been less intensely eroded, and Liassic rocks are not exposed on the surface.

The highest Cl⁻ contents are close to that of sea water, whereas the highest δ values of water isotopes indicate a mixture of 50 % sea water and 50 % current recharge. Thus, the same observation is made as for Mont Terri that the pore waters cannot be consistently explained as mixtures of sea and meteoric water. In addition, unlike at Mont Terri and in the Liassic ground-water sample at Mont Russelin (1 867.5 m), the Cl⁻/Br⁻ ratio in pore waters is not constant and generally higher than that of sea water. The underlying processes are currently not well constrained.

2.6 Toarcian-Domerian at Tournemire (France)

2.6.1 Structure

The underground research laboratory at Tournemire, operated by IRSN, is located in the Causses Basin of southern France (Figure 2.6-1). This N-S oriented basin, containing Permian to late Jurassic sediments, is delineated by basement massifs (Constantin et al. 2002, 2004). The laboratory is hosted by an abandoned railway tunnel penetrating the upper part of a 200 m thick sequence of Toarcian-
Domerian marine shales (Boisson et al. 1998, 2001, Cabrera et al. 2001). The sequence of shaly and marly lithologies is flat-lying and sandwiched between limestone aquifers above (Aalenian) and below (Carixian) (Figure 2.6-2). A number of boreholes were drilled from the tunnel. Lithologically, the shaly-marly sequence shows some heterogeneity in the vertical dimension (Boisson et al. 2001). A number of sub-units with somewhat different properties are distinguished and are listed in Table 2.6-1.

Figure 2.6-1: Geological map of the Tournemire area

![Geological map of the Tournemire area](adapted_from_Cabrera_2002)

Figure 2.6-2: Geological profile across the Toarcian-Domerian at Tournemire

![Geological profile across the Toarcian-Domerian at Tournemire](adapted_from_Cabrera_2002)
### Table 2.6-1: Geometric properties and transport parameters of the Toarcian-Domerian at Tournemire

| Sub-unit                  | Lithology                        | Elevation [m a.s.l.] | Dp @ 20 °C [m²/s] | De @ 20 °C [m²/s] | K ⊥ [m/s] | K || [m/s] | n [-] | Anions1: | Anions2: | Anions3: | Anions4: | Anions5: | Anions6: |
|--------------------------|----------------------------------|----------------------|-------------------|-------------------|-----------|------------|-------|----------|----------|----------|----------|----------|----------|
| Aalenian aquifer         |                                  |                      |                   |                   |           |            |       |          |          |          |          |          |          |
| Middle and Upper Toarcian| Shaly unit, carbonate content 10 – 25 wt% | 377.6 – 554.3        | Anions1:          | Anions1:          | 1.0E-12    | 2.0E-12    |       |          |          |          |          |          |
|                           |                                  |                      | ⊥ 2.8E-11         | ⊥ 7.3E-13         |            |            |       |          |          |          |          |          |          |
|                           |                                  |                      | HTO:              | HTO:              |            |            |       |          |          |          |          |          |          |
|                           |                                  |                      | ⊥ 5.6E-11         | ⊥ 4.8E-12         |            |            |       |          |          |          |          |          |          |
|                           |                                  |                      | | / ⊥ = 2       | | / ⊥ = 2       |            |            |       |          |          |          |          |          |          |
|                           |                                  |                      |                   |                   |            |            |       |          |          |          |          |          |          |
|                           |                                  |                      |                   |                   |            |            |       |          |          |          |          |          |          |
| Lower Toarcian            | Carbonate content generally >30 wt% | 354.5 – 377.6        | Anions1:          | Anions1:          | 1.0E-12    | 2.0E-12    |       |          |          |          |          |          |
|                           |                                  |                      | ⊥ 2.1E-11         | ⊥ 5.7E-13         |            |            |       |          |          |          |          |          |          |
|                           |                                  |                      | HTO:              | HTO:              |            |            |       |          |          |          |          |          |          |
|                           |                                  |                      | ⊥ 4.2E-11         | ⊥ 2.3E-12         |            |            |       |          |          |          |          |          |          |
|                           |                                  |                      | | / ⊥ = 2       | | / ⊥ = 2       |            |            |       |          |          |          |          |          |          |
|                           |                                  |                      |                   |                   |            |            |       |          |          |          |          |          |          |
|                           |                                  |                      |                   |                   |            |            |       |          |          |          |          |          |          |
| Upper Domerian            | Shaly unit, carbonate content ca. 10 wt% | 325.0 – 354.5        | Anions1:          | Anions1:          | 1.3E-12    | 2.6E-12    |       |          |          |          |          |          |
|                           |                                  |                      | ⊥ 2.8E-11         | ⊥ 7.3E-13         |            |            |       |          |          |          |          |          |          |
|                           |                                  |                      | HTO:              | HTO:              |            |            |       |          |          |          |          |          |          |
|                           |                                  |                      | ⊥ 5.6E-11         | ⊥ 3.9E-12         |            |            |       |          |          |          |          |          |          |
|                           |                                  |                      | | / ⊥ = 2       | | / ⊥ = 2       |            |            |       |          |          |          |          |          |          |
|                           |                                  |                      |                   |                   |            |            |       |          |          |          |          |          |          |
|                           |                                  |                      |                   |                   |            |            |       |          |          |          |          |          |          |
| Lower Domerian            | Carbonate content decreasing from bottom (70 wt%) to top (10 wt%) | 296.9 – 325.0        | Anions1:          | Anions1:          | 1.3E-12    | 2.6E-12    |       |          |          |          |          |          |
|                           |                                  |                      | ⊥ 2.1E-11         | ⊥ 5.7E-13         |            |            |       |          |          |          |          |          |          |
|                           |                                  |                      | HTO:              | HTO:              |            |            |       |          |          |          |          |          |          |
|                           |                                  |                      | ⊥ 4.2E-11         | ⊥ 2.3E-12         |            |            |       |          |          |          |          |          |          |
|                           |                                  |                      | | / ⊥ = 2       | | / ⊥ = 2       |            |            |       |          |          |          |          |          |          |
|                           |                                  |                      |                   |                   |            |            |       |          |          |          |          |          |          |
|                           |                                  |                      |                   |                   |            |            |       |          |          |          |          |          |          |

Due to deep burial (Barbarand et al. 2001, Peyaud et al. 2005) and intense diagenetic cementation, the shales and marls of the Toarcian-Domerian are well consolidated, relatively massive rocks and show a more brittle deformation behaviour than many of the other formations considered in this study. The formation is penetrated by systems of brittle fractures, and some of these are weakly water conducting in the underground laboratory. Major fractures can represent at least local advective flow paths (Constantin et al. 2002, 2004).

Two E-W trending reverse faults, ca. 5 km apart and with several hundreds of metres offset, bound the area of the underground research laboratory (Cernon fault in the north, St-Jean-d’Alcapies fault to the south; Figure 2.6-1).
2.6.2 Tracer distributions

Tracers in pore waters were studied in core materials from several boreholes drilled from the railway tunnel or the underground rock laboratory. The horizontal distance between the boreholes is up to 200 m (Figure 2.6-2).

Anions

Tracer data are available from the Toarcian but not from the Domerian, which means that the lower part of the profile above the Carixian aquifer is not characterised at present.

Cl⁻ contents in pore water were analysed by an out-diffusion method by Patriarche (2001) and Patriarche et al. (2004a). For the calculation of Cl⁻ concentrations in free pore water, these authors assumed that the geochemical porosity (i.e. the porosity accessible to anions, see Pearson 1999) is 0.3 x physical porosity in the shales and marls and 1 x physical porosity in limestones of the aquifers. Savoye et al. (2006) measured Cl⁻-accessible porosity in samples from the Toarcian on the basis of radial out-diffusion experiments and concluded that the relationship geochemical porosity = 0.3 x physical porosity is appropriate for the middle and upper Toarcian. However, in the lower Toarcian, which is lithologically distinct (“schistes carton”, more calcareous), Savoye (pers. comm.) considers a value of 0.5 as a better choice. This higher geochemical porosity in the lower Toarcian has a significant effect on the shape of the Cl⁻ profile and is one of the differences in the data base of this study when compared to that of Patriarche et al. (2004a,b).

The spatial distribution of Cl⁻ in pore water is shown in Figure 2.6-3, and the following observations can be made:

- Cl⁻ contents are highest in the middle Toarcian and decrease towards both aquifers.
- Short boreholes TF1 and TF4 were drilled to study local heterogeneity due to the presence of faults and fractures. The observed variability of Cl⁻ contents is substantial. According to Savoye (pers. comm.), the variability is most likely an artefact caused by the partial evaporation of pore water prior to the measurement of water content. Savoye (pers. comm.) also relates the high Cl⁻ contents in boreholes VF2 and VF3 to difficulties with the determination of in-situ water content.
- Cl⁻ concentrations show a systematic variation between boreholes, which indicates lateral heterogeneity. Vertical borehole VF4 shows distinctly higher Cl⁻ contents when compared to borehole TN3 some 200 m further north.
- Some of the points <1 m away from fractures show Cl⁻ contents that do not fit the overall pattern. It appears that fracture flow affects Cl⁻ concentrations at least on the small scale (metres).
- Based on radial diffusion experiments, Savoye et al. (2006) obtained Cl⁻ contents compatible with those of Patriarche (2001) and Patriarche et al. (2004a).

Given the presence of lateral variability and local effects of fractures, only the data from boreholes TN1 and TN3 are used here for modelling Cl⁻ contents. In addition, all data from the vicinity of fractures (<1 m away) are screened out. Boreholes TN1 and TN3 were drilled vertically upward and downward from the same position in the tunnel and yield the most complete profile across the shaly to marly formations. This screening procedure is another difference to previous modelling efforts by Patriarche et al. (2004b) who used all available data.
Figure 2.6-3: **Spatial distribution of Cl\(^-\) in free pore water at Tournemire**

Solid symbols: Data points >1 m away from fractures; open symbols: data points <1 m from fractures. Elevations refer to boreholes TN1/TN3, and data from other boreholes are projected along strike. a: All data. b:Screened data used for modelling.

**Water isotopes**

δ\(^2\)H and δ\(^18\)O values of pore water were measured by several authors. Moreau-Le Golvan *et al.* (1997) and Patriarche (2001) used vacuum distillation at 60 °C and 50 °C, respectively. More recently, Savoye *et al.* (2006) and Altinier *et al.* (2007) applied the isotope exchange method. The spatial distributions of water isotopes are shown in Figure 2.6-4 and Figure 2.6-5:

- The δ\(^2\)H profile shows a well defined curved shape with an apex at ca. 400 m a.s.l., similar to what was found for Cl\(^-\). The δ\(^18\)O profile shows a similar shape, even though less well defined.
- The central and lower parts of the profiles yield well constrained trends of isotopic composition, while scatter is more substantial in the upper third. There is a gap in the Domerian where no data are available.
- In the uppermost ca. 30 m of the Toarcian, *i.e.* directly below the contact to the Aalenian aquifer, the δ\(^2\)H and, less clearly, the δ\(^18\)O data show a pronounced trend towards very low values. In the Aalenian aquifer, the values are higher. The possibility that the strong gradients in the isotopic composition of water are due to a geologically young (*e.g.* glacial) effect is explored in the modelling section below.
- When boreholes TF1 and TF4 (targeted at the identification of local disturbances due to faults) are disregarded, there is no identifiable lateral heterogeneity over 200 m horizontal distance. Also, data from samples located close to fractures do not show any conspicuous disturbances.
Figure 2.6-4: Spatial distribution of $\delta^2$H in pore water at Tournemire

Data from Patriarche (2001) and Savoye et al. (2006). All data are based on vacuum distillation, except those of boreholes DF1 and DF2 which were obtained by the isotope exchange method, and those of the ground waters in the aquifers. Elevations refer to boreholes TN1/TN3, and data from other boreholes are projected along strike. 
a: Uncorrected full data set. 
b: Screened data set used for modelling (boreholes TF1 and TF4 excluded), corrected for the effect of incomplete distillation.

Figure 2.6-5: Spatial distribution of $\delta^{18}$O in pore water at Tournemire

Data from Patriarche (2001) and Savoye et al. (2006). All data are based on vacuum distillation, except those of boreholes DF1 and DF2 which were obtained by the isotope exchange method, and those of the ground waters in the aquifers. Elevations refer to boreholes TN1/TN3, and data from other boreholes are projected along strike. a: Uncorrected full data set. 
b: Screened data set used for modelling (boreholes TF1 and TF4 excluded), corrected for the effect of incomplete distillation.
The δ²H and δ¹⁸O values obtained from vacuum distillation are internally consistent. However, they are lower by ca. 14 and 2.7 ‰ respectively when compared to the data obtained from the isotope exchange method used by Savoye et al. (2006). The latter method is currently preferred for the characterisation of water isotopes in pore waters, while the vacuum distillation technique at low distillation temperatures is known to be affected by incomplete distillation (see Appendix A2 and Rübel & Bath 2003). In order to account for incomplete distillation, the isotopic compositions derived from vacuum distillation are corrected by +14 and +2.7 ‰ for δ²H and δ¹⁸O, respectively. Altinier et al. (2007) derived similar corrections (+20 and +2.7 ‰) by measuring the fraction of the total pore water released during distillation at 50 °C and assuming a Rayleigh distillation process. Note that no correction was performed in the calculations of Patriarche (2001) and Patriarche et al. (2004b) because, at that time, the basis for such a correction was not yet established. It is noteworthy that the correction also results in near-identical isotopic compositions for pore and ground water in the Aalenian limestone (Figure 2.6-4, Figure 2.6-5), whereas the uncorrected values are lower than those of the ground water sample.

In a plot of δ²H vs δ¹⁸O, the data based on isotope exchange are close to the GMWL, slightly shifted to the right side. The data based on vacuum distillation show a substantial scatter, and many data points are left of the GMWL, indicating incomplete distillation. After the correction of the analytical bias, most data are on the right side of the GMWL. According to Savoye (pers. comm.), the δ²H data based on vacuum distillation can be, after correction, considered as reasonable, while the δ¹⁸O data are more uncertain for methodological reasons.

2.6.3 Upper and lower boundary

Ground waters in the Aalenian and Carixian aquifers have low salinities and stable isotopic compositions similar to that of recent recharge (Table 2.6-2).

Table 2.6-2: Tracer data from ground waters in the aquifers embedding the Toarcian-Domerian at Tournemire

<table>
<thead>
<tr>
<th>Borehole</th>
<th>Formation</th>
<th>Elevation [m a.s.l.]</th>
<th>Cl⁻ [mg/L]</th>
<th>δ¹⁸O [%o V-SMOW]</th>
<th>δ²H [%o V-SMOW]</th>
<th>Remarks</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CA</td>
<td>Aalenian</td>
<td>555.6</td>
<td>6.0</td>
<td>-7.7</td>
<td>-51.7</td>
<td>Contains ³H</td>
<td>Beaucaire et al. (2008)</td>
</tr>
<tr>
<td>DC</td>
<td>Carixian</td>
<td>295.3</td>
<td>73.1</td>
<td>-7.5</td>
<td>-49.2</td>
<td>³H below detection</td>
<td>Beaucaire et al. (2008)</td>
</tr>
<tr>
<td>Recent</td>
<td></td>
<td></td>
<td></td>
<td>-7.9</td>
<td>-50</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Elevations refer to boreholes TN1/TN3, and data from other boreholes are projected along strike.

In the Aalenian aquifer, tracer data exist both for pore water in the rock matrix and for ground water circulating in fractures:

- Cl⁻ contents in pore waters vary in the range 12 – 141 mg/L, whereas the ground water sample yields 6 mg/L (Figure 2.6-3). It appears that flushing of the aquifer by fresh water has not completely leached out the salinity in the matrix of the limestones.

- The stable isotopic composition of ground waters from both aquifers is characterised by substantially higher δ²H and δ¹⁸O values when compared to the uncorrected values in pore waters (Figure 2.6-4a and Figure 2.6-5a). On the other hand, the corrected pore-water values are consistent with the ground-water values in the Aalenian aquifer, and the ground-water value in the Carixian aquifer fits well the trend of the pore-water values in the Lower
Toarcian and Domerian (Figure 2.6-4b and Figure 2.6-5b). This good correspondence adds further credibility to the applied correction procedure of the isotope data based on vacuum distillation.

2.6.4 Transport parameters

Diffusion coefficient for anions

Pore-diffusion coefficients for Cl\(^-\) parallel to bedding were determined by Patriarche et al. (2004a) from out-diffusion experiments. The results are consistent with those based on radial out-diffusion experiments conducted by Savoye et al. (2006). Assuming that geochemical porosity is 0.3/0.5 x measured physical porosity (middle and upper Toarcian/lower Toarcian) and considering an anisotropy factor of 2 leads to the diffusion coefficients listed in Table 2.6-1. Data are only available for the Toarcian, and values shown in Table 2.6-1 for the Domerian are extrapolations based on lithological analogy.

Diffusion coefficient for HTO

A number of measurements normal to bedding are reported in Boisson et al. (2001) and Patriarche et al. (2004b), and the average values are given in Table 2.6-1. Most data (15) are available for the Middle and Upper Toarcian, one single for the Lower Toarcian, two for the Upper and none for the Lower Domerian. The shaly lithologies of the Middle/Upper Toarcian have very similar coefficients, whereas the more calcareous Lower Toarcian has a lower value. In the absence of data, it is assumed that the Lower Domerian has the same diffusion coefficient as the Lower Toarcian.

Hydraulic conductivity

A number of in-situ and laboratory determinations are documented in Boisson et al. (2001). The in-situ tests reflect hydraulic conductivity mainly in the direction parallel to bedding and vary in the range 1E-13 to 3E-11 m/s. Laboratory tests yield much lower values, typically in the range 1E-15 to 1E-13 m/s. Because the lab tests represent only properties of the unfractured rock matrix on a scale of centimetres, the in-situ tests are preferred, as they also include the potential effect of brittle discontinuities and refer to a larger scale. Geometric means of data derived from in-situ tests are listed in Table 2.6-1. The anisotropy of hydraulic conductivity is not well known. As an approximation, it is assumed that the values in the vertical dimension are half the values measured in in-situ tests. Due to the scarcity of data from the lower Toarcian and the lower Domerian, values from the respective upper parts of the formations are used.

The fact that limited water discharge from fractures is observed in the Toarcian shale in the underground research laboratory and the large difference between laboratory and in-situ measurements of hydraulic conductivity indicate that at least limited fracture flow occurs in the formation. On the other hand, the regular distribution of natural tracers suggests that, on the scale of the formation, advective transport is not of prime importance, probably due to a limited connectivity of the fracture network.

Porosity

A number of techniques were applied and are documented in Boisson et al. (1998, 2001) and Patriarche et al. (2004a). The data sets are consistent as long as data obtained from the same technique
are compared. Average water-accessible porosities listed in Table 2.6-1 are based on water-loss measurements by Patriarche et al. (2004a). Data are available for the Toarcian only, whereas values for the Domerian were assumed based on lithological analogy (see above). The fraction of physical porosity accessible to anions is discussed in Section 2.6.2.

**In-situ temperature**

The average temperature of water circulating in fractures is ca. 15 °C.

**2.6.5 U and Th contents in rocks**

U and Th contents in the Toarcian-Domerian are reasonably homogeneous with average values of 11 ppm Th and 2.5 ppm U.

**2.6.6 Hydraulic gradient**

The hydraulic potential in the Aalenian aquifer (443 – 463 m) is higher than that in the underlying Carixian aquifer (587 – 602 m), which is in line with the hydrogeological settings of these aquifers, i.e. the elevations of the in- and exfiltration areas. The resulting hydraulic gradient of slightly less than 0.5 m/m across the low-permeability sequence is directed downwards (Boisson et al. 2001). Heads within the low-permeability sequence lie broadly on a line connecting the values in the aquifers, i.e. no anomalous pressures are observed.

**2.6.7 Geological and hydrogeological evolution**

The Toarcian-Domerian was deposited at ca. 180 Ma (early Jurassic) in a shallow sea. The sedimentary sequence records continuously marine conditions between Triassic and late Jurassic (ca. 150 Ma). No younger deposits occur in the Causses Basin. Throughout the middle and late Jurassic (and probably the early Cretaceous), the basin was subjected to a number of episodes of extensional fracturing (normal faulting), which left their structural imprint in the Toarcian-Domerian shales (Constantin et al. 2004). Peyaud et al. (2005) and Barbarand et al. (2001) studied the thermal evolution of the basin using different indicators (apatite fission-track analysis, Rock-Eval, fluid inclusions) and proposed a maximum heating to ≥110 °C at 130 Ma (early Cretaceous), followed by cooling and uplift. Peyaud et al. (2005) calculated an eroded section (late Jurassic and early Cretaceous) in the Causses Basin of 1 000 – 1 600 m, and Barbarand et al. (2001) gave 2 000 – 2 500 m for the wider region. According to Simon-Coinçon & Schmitt (1999), continental conditions were established still in the early Cretaceous, even though the timing of this event is not well constrained. A last marine stage lasting ca. 10 – 15 Ma is possible around the Cretaceous/Tertiary boundary but is not clearly proven in the region of interest.

The Pyrenean compression (ca. 53 – 33 Ma) was the second relevant tectonic stage, during which existing structures were reactivated as reverse to strike-slip faults. Also, new compressional structures were created. A first stage of karstification of limestones is recorded from the middle Eocene (Lutetian/Bartonian, ca. 40 Ma), simultaneous with the peak of Pyrenean deformation.

Between 36 and 5 Ma, the Causses Basin was again subjected to slow extension. Karstification of limestone aquifers was initiated at 20 Ma (Ambert & Ambert 1995). Valley incisions started developing since 15 – 13 Ma. According to Cabrera (pers. comm.), the aquifers embedding the
Toarcian-Domerian shales were activated at ca. 10 Ma (uncertainty range: 6 – 15 Ma) because, at that time, the incision of valleys was substantial in the region.

Volcanic activity occurred between 5.1 and 3 Ma and is recorded by basaltic dykes cross cutting the sedimentary units in the region. Enhanced regional uplift has been ongoing since 3 Ma, triggering further deepening of valleys.

The geological and hydrogeological evolution of the Causses Basin is complex and not very well known. Moreover, the consequences of deformation and karstification events on the geochemical environment in and around the Toarcian-Domerian shale are somewhat hypothetical. Patriarche et al. (2004b) assume that marine conditions prevailed until the beginning of the Pyrenean compression at 53 Ma, at which time flushing of the system by meteoric water was initiated. However, the first meteoric effects could be older because continental conditions prevailed since the early Cretaceous, or younger because major hydraulic gradients triggering flow in the aquifers were probably only created during the incision of deep valleys at 15 – 6 Ma.

2.7 Boom Clay at Mol (Belgium)

2.7.1 Structure

Boom Clay at Mol is a flat-lying clay formation with a thickness of 103 m. Internally, it is largely homogeneous, with the exception of the lowermost 12 m where a coarsening of grain size is identified, which also has consequences for transport parameters. Based on minor lithostratigraphic differences, 4 sub-units were defined (Table 2.7-1). Boom Clay is sandwiched between 2 sandy aquifers, the Neogene aquifer above and the Lower Rupelian aquifer below. The hydraulic role of the silty/sandy Eigenbilzen formation that directly overlies Boom Clay is not entirely clear (see below).

A seismic reflection survey in and around the Mol–Dessel nuclear zone revealed numerous flexures on the regional scale in the Tertiary formations below Boom Clay, which itself remains unaffected (Ondraf/Niras 2001, Mertens 2001). Natural faults were not identified either by seismic methods (detection limit: 5 m vertical displacement) or in boreholes, shafts or tunnels. Even if undetected structures existed, their significance for flow and solute transport is likely negligible due to efficient self-sealing.

2.7.2 Tracer distributions

Anions

Water samples were collected from numerous piezometers, all from depths of -180 to -200 m a.s.l. and -220 to -235 m a.s.l. (level of the underground research laboratory). More comprehensive profiles were obtained from pore-water squeezing of core materials from boreholes HADES 2001/4, HADES 2003/9 and Mol-1. For the latter, only data set M-Cl is used in this report, while data set MTP, which was targeted at the identification of local variability due to lithological heterogeneity, is ignored. In summary, there is a good coverage of the whole profile through Boom Clay, except for the lowermost part (-237 to -264 m a.s.l.) where only few data are available. Key references to the raw data include De Craen et al. (2004a,b) and De Craen (2005).

The Cl⁻ and Br⁻ contents (shown in Figure 2.7-1) derived from piezometer samples and from core squeezing compare well. Cl⁻ concentrations increase from 15 – 25 mg/L in the upper part of Boom
Clay to 20 – 40 mg/L at -230 m a.s.l. The trend in the lowermost part is unclear due to lack of data. Br’ contents vary in the range 0.4 – 1.5 mg/L (with some outliers), and no depth trend is evident. I’ concentrations based on squeezing define a well shaped profile with highest values (ca. 600 µg/L) in the centre of Boom Clay. They decrease towards the top (240 – 460 µg/L) and in the lower third (360 – 520 µg/L at ca. -240 m a.s.l.). A similar trend is seen in the piezometer data, even though the values are systematically higher by a factor of ca. 1.5. The reason for this discrepancy is unknown.

In the central part of Boom Clay, Cl’ contents correspond to 0.001 – 0.002 times sea-water concentrations, demonstrating that the formation lost most of its salinity. Remarkably, I’ is enriched by one order of magnitude relative to sea water, most likely due to the release of I’ from organic matter during diagenesis.

Table 2.7-1: Geometric properties and transport parameters of Boom Clay at Mol

| Hydrogeologic unit | Formation                | Sub-unit                     | Elevation in Mol-I borehole [m a.s.l.] | Dp @ 20 °C [m²/s]  | De @ 20 °C [m²/s]  | K ⊥ [m/s] | K || [m/s] | n [-] |
|--------------------|--------------------------|------------------------------|--------------------------------------|--------------------|--------------------|-----------|-----------|------|
| Aquifer            | Voort / Berchem (Neogene)| -114.3 to -140.0             |                                      |                    |                    |           |           |      |
| Aquifer / aquitard | Eigenbilzen              | -140.0 to -161.2             |                                      | 1.8E-10            | 2.5E-10            |           |           |      |
| Aquitard           | Boom Clay (Rupelian)      | Transition zone              | -161.2 to -186.3                     |                    |                    |           |           |      |
|                    |                          | Putte Member                 | -186.3 to -232.3                     | Anions: 1.4E-10    | Anions: 2.2E-11    | 2.8E-12   | 5.2E-12   |      |
|                    |                          | Terhagen Member              | -232.3 to -247.9                     | || / ⊥ = 2         | || / ⊥ = 2         |           |           |      |
|                    |                          | Upper Belsele-Waas Member    | -247.9 to -251.8                     | Water isotopes: 2.3E-10 || / ⊥ = 2 | Water isotopes: 8.5E-11 || / ⊥ = 2 | 2.0E-12   | 4.8E-12   |      |
|                    |                          | Lower Belsele-Waas Member    | -251.8 to -263.8                     | Anions: 4.0E-10    | Anions: 6.4E-11    | 4.3E-11   | 2.9E-10   |      |
|                    |                          |                             |                                      | || / ⊥ = 2         | || / ⊥ = 2         |           |           |      |
|                    |                          |                             |                                      | Water isotopes: 4.6E-10 || / ⊥ = 2 | Water isotopes: 1.7E-10 || / ⊥ = 2 |           |          |      |
| Aquifer            | Lower Rupelian           | -263.8 to -288.6             |                                      |                    |                    |           |           |      |

See Table 1.8-1 for definitions of symbols. ⊥ = normal to bedding, || = parallel to bedding, || / ⊥ = anisotropy factor.
All depth data refer to m above sea level, and the Mol area has an elevation of 20 – 25 m a.s.l. Shaded areas indicate aquifers.
Water isotopes

There is one single data point available ($\delta^{18}O = -7 \, ^{\circ}V-SMOW$, $\delta^2H = -53 \, ^{\circ}V-SMOW$ at -227.6 m a.s.l.; Griffault et al. 1996, De Craen et al. 2004a).

2.7.3 Upper boundary

Located directly above the Boom Clay, the 21.2 m thick Eigenbilzen formation consists of silts and sands with surprisingly low hydraulic conductivities (Table 2.7-1; Wemaere et al. 2002, ch. 3.2.4.2). Nevertheless, it is regarded here as part of the overlying Neogene sandy aquifer. In the Mol-1
borehole, which provides the best data from the uppermost part of the profile, there is a systematic decrease of Cl$^-$ (and, less clearly, Br$^-$) contents with depth within the Neogene aquifer (Table 2.7-2). Close to the contact between the Eigenbilzen formation and Boom Clay, the lowest Cl$^-$ value of 18 mg/L (Br$^-$: 0.49 mg/L) is identified and is used as upper boundary condition. Ground water in the Berchem aquifer contains measurable amounts of $^3$H, indicating at least partial recharge in recent times. Stable water isotopes are very close to recent recharge (see Table 2.7-2; Marivoet et al. 2000).

Table 2.7-2: Tracer data from the aquifers embedding Boom Clay at Mol

<table>
<thead>
<tr>
<th>Aquifer</th>
<th>Borehole</th>
<th>Formation</th>
<th>Depth [m a.s.l.]</th>
<th>Cl$^-$ [mg/L]</th>
<th>Br$^-$ [mg/L]</th>
<th>$\delta^{18}$O [%V-SMOW]</th>
<th>$\delta^2$H [%V-SMOW]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upper</td>
<td>Mol-1</td>
<td>Berchem sands</td>
<td>-120.79</td>
<td>91.0</td>
<td>0.98</td>
<td></td>
<td></td>
<td>De Craen, pers. comm.</td>
</tr>
<tr>
<td></td>
<td>Mol-1</td>
<td>Berchem sands</td>
<td>-131.11</td>
<td>45.1</td>
<td>&lt;0.25</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mol-1</td>
<td>Eigenbilzen</td>
<td>-140.86</td>
<td>29.7</td>
<td>0.80</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mol-1</td>
<td>Eigenbilzen/Boom Clay</td>
<td>-160.27</td>
<td>18.0</td>
<td>0.49</td>
<td></td>
<td></td>
<td>De Craen, pers. comm.</td>
</tr>
<tr>
<td>Dessel-11c</td>
<td>Berchem</td>
<td>-7.4</td>
<td>-48.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Marivoet et al. (2000)</td>
</tr>
<tr>
<td>Boom Clay</td>
<td>Mol-1</td>
<td>Boom Clay</td>
<td>-260.23</td>
<td>32.9</td>
<td>0.85</td>
<td></td>
<td></td>
<td>De Craen, pers. comm.</td>
</tr>
<tr>
<td>Lower</td>
<td>Mol 15b</td>
<td>Lower Rupelian</td>
<td>27</td>
<td>3.4</td>
<td></td>
<td></td>
<td></td>
<td>Griffault et al. (1996)</td>
</tr>
</tbody>
</table>

Numbers shown in bold are selected as representative boundary values

**2.7.4 Lower boundary**

Boom Clay is directly underlain by the Lower Rupelian aquifer, which consists of a series of permeable sands separated by low-permeability clay layers. In the Mol-15b borehole, Cl$^-$ = 27 mg/L and Br$^-$ = 3.4 mg/L (Griffault et al. 1996, Beaucaire et al. 2000). However, these data are from a contaminated sample, and the correction procedure implies major uncertainties. In the absence of data, the deepest sample from Boom Clay at -260.23 m a.s.l., *i.e.* 3.6 m above the aquifer, is thought to best represent the anion concentrations at the lower boundary, with values of Cl$^-$ = 32.9 mg/L and Br$^-$ = 0.85 mg/L (Table 2.7-2). Reliable data for water isotopes are not available due to contamination (Marivoet et al. 2000).

The infiltration area of the Lower Rupelian aquifer is located *ca.* 20 – 30 km south of Mol, and the general flow direction is towards NNW (Marivoet et al. 2000). In boreholes close to the infiltration area, $^3$H is found in the ground water. Surprisingly, this is also the case at some distal locations, including Mol. Marivoet et al. (2000) argued that the modern ground-water components are due to artificial connections to the Berchem aquifer and so screened out these data from their analysis.

On a regional scale, the Lower Rupelian aquifer shows a consistent increase of salinity from the recharge area in the south towards the distal sampling points along the Belgian-Dutch border (*ca.* 50 km NNW; Figure 2.7-2, Beaucaire et al. 2000). The highest mineralisation was observed in the Essen borehole, with Cl$^-$ = 3 400 – 3 800 mg/L (De Craen et al. 2006). The regional trend is explained by the progressive admixture of infiltrating fresh water into an aquifer originally containing sea water.
Salinity is indicated by Cl⁻ contents [mg/L] in green (data from Marivoet et al. 2000, Griffault et al. 1996 and Beaucaire et al. 2000). Locations and numbers of existing boreholes are given in red.

2.7.5 Transport parameters

Diffusion coefficients for I⁻ (which is taken as representative for all anions) and ³H (taken as representative for all water isotopes) are given in Table 2.7-1, together with the species-specific accessible porosities. Hydraulic conductivities are also indicated. With the exception of the lower part of the Belsele-Waas Member, which has higher values for all transport parameters, there is little spatial variability. Diffusion coefficients for dissolved noble gases are not available.

In-situ temperature is 16.5 °C at the level of the underground research laboratory (Jeffries 1995).

2.7.6 U and Th contents in rocks

The spectral gamma-ray log in borehole Mol-1 provides the most comprehensive data set with a vertical resolution of 15 cm. Additional data, based on ICP-MS laboratory analyses of selected samples, yield consistent data for Th, while U contents are higher by a factor of ca. 1.5 when compared to the log data. Because the ICP-MS data are deemed more reliable when it comes to absolute values, the U contents based on log data were corrected by a factor of 1.5. The resulting U and Th contents in Boom Clay are shown in Figure 2.7-3.
2.7.7 Hydraulic gradient

A vertical hydraulic gradient of 0.02 m/m, resulting in downward flow, is considered as representative of the conditions over the last 20 years (Labat & Wemaere 2001). Due to the increasing exploitation of this aquifer, the gradient is increasing with time, and the current value is 0.04 m/m (Wemaere, pers. comm.).

2.7.8 Geological and hydrogeological evolution

Boom Clay is a shallow marine sediment deposited at 32 – 29 Ma (Rupelian). Diagenesis was only weak, including mainly the precipitation of glauconite and pyrite, and the formation of the septarian carbonate concretions. These diagenetic products are all related to the shallow burial realm (Van Keer & De Craen 2001). At the end of the Rupelian, a major stage of uplift caused the erosion of a large part of the Boom Clay (the Transition zone as well as the upper part of the Putte Member) in the region of Antwerp (about 50 km west of Mol). No erosion of Boom Clay occurred at Mol. After a period of non-deposition, more than 100 m of sands were deposited above Boom Clay in the last 8 Ma. Currently, Boom Clay at Mol is at the deepest burial level since deposition. A burial curve is shown in Figure 2.7-4 (Mertens et al. 2004).

Marine conditions prevailed in the region of Mol since deposition until about 2 Ma, when the area finally emerged from the sea (Kasse 1988, Van Keer 2000). Mol was never covered by glaciers but exposed to recurrent stages of permafrost. The current hydrogeological setting is shown in Figure 2.7-5.
Figure 2.7-4: Burial history of Boom Clay at Mol

From Mertens et al. (2004)

Figure 2.7-5: Hydrogeological setting of Boom Clay and surrounding aquifers in Belgium

From Wemaere et al. (2000)
Upper aquifer: Berchem sands

The aquifer overlying Boom Clay (Voort/Berchem sands, Neogene) contains \(^3\text{H}\) today (Marivoet et al. 2000), suggesting that there is a direct connection to the surface. Therefore, it can be assumed that meteoric recharge reaches the top of Boom Clay without any significant retardation, dilution or mixing. Fresh-water infiltration has probably occurred since emergence of the area from the sea at about 2 Ma.

Lower aquifer: Lower Rupelian

For the underlying Lower Rupelian aquifer, the situation is less straightforward. The retreat of the coast line from the area of interest was a complex, multi-stage process (Kasse 1988, Van Keer 2000), and the age of 2 Ma reported for the final emergence of the Mol region is a simplification. Another aspect to consider is the fact that the infiltration area of the Lower Rupelian aquifer is located farther inland than Mol (20 – 30 km to the south, see Figure 2.7-2) and so emerged well before 2 Ma. It is not known whether and to what degree meteoric infiltration into the aquifer occurred at the time when the Mol area itself was still marine, and whether the hydraulic gradients required for such flushing existed. The general flow direction is (and probably has been since emergence) towards the northwest. During advective/dispersive flow, infiltrated water mixes with sea water that was originally present in the aquifer. At Mol, the flushing of the Lower Rupelian aquifer by meteoric water is almost total today. Towards the north, salinity of the aquifer increases (Figure 2.7-2). The highest salinity, found in the Essen borehole, corresponds to a remaining proportion of sea water of 20 % (see Section 2.8).

2.8 Boom Clay at Essen (Belgium)

2.8.1 Structure

The deep borehole at Essen (location see Figure 2.7-2) was drilled in 2005/2006. Boom Clay at Essen is flat lying and 127 m thick, i.e. thicker than at Mol. Its internal subdivision as well as the presence of aquifers above and below (Table 2.8-1) is analogous to Mol.

2.8.2 Tracer distributions

Anions

Anion concentrations in pore waters squeezed from core samples were reported by De Craen et al. (2006). In the upper, Neogene aquifer, the values are near zero. With depth, the Cl\(^-\), Br\(^-\) and I\(^-\) contents increase regularly and reach values around 20 % of those of sea water in the underlying Lower Rupelian aquifer. Cl\(^-\)/Br\(^-\) ratios (range: 268 – 303) are very constant throughout the profile and correspond closely to that of sea water. A ground-water sample from the interval 285 – 383 m, covering the whole Lower Rupelian aquifer, shows a close correspondence of the anion concentrations to the values of the adjacent pore waters.

Water isotopes

\(\delta^{18}\text{O}\) and \(\delta^2\text{H}\) values in squeezed pore waters were determined in the same samples as described in the previous section (data from De Craen et al. 2006). The shapes of the \(\delta^{18}\text{O}\) and \(\delta^2\text{H}\) profiles (Figure 2.8-2) are very similar, showing a linear increase with depth. In contrast to the anion profiles,
the uppermost 20 m of Boom Clay show a sharp break in the general trend, with increasing values towards the overlying Neogene aquifer. All stable isotope data lie close to (slightly below) the meteoric water line. The enrichment in the heavy isotopes with depth can most likely be explained by an increasing sea-water component, consistent with the interpretation of the anion data (De Craen et al. 2006).

Figure 2.8-1: Anion concentrations in pore water squeezed from cores of the Essen borehole

Blue bar represents concentrations in ground water sampled from the test interval 285 – 383 m, corresponding to the full thickness of the Lower Rupelian aquifer. Data from De Craen et al. (2006)
Table 2.8-1: Geometric properties and transport parameters of Boom Clay at Essen

<table>
<thead>
<tr>
<th>Hydrogeological unit</th>
<th>Formation</th>
<th>Sub-unit</th>
<th>Depth [m b.g.]</th>
<th>$D_p$ (I-) @ 20 °C [m²/s]</th>
<th>$D_p$ (HTO) @ 20 °C [m²/s]</th>
<th>$K_\bot$ [m/s]</th>
<th>$n$ [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aquifer</td>
<td>Berchem (Neogene)</td>
<td>Transition zone</td>
<td>153 – 200</td>
<td>2.2E-10</td>
<td>2.2E-10</td>
<td>5.4E-12</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Putte Member</td>
<td>200 – 237.62</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Boom Clay (Rupelian)</td>
<td>Terhagen Member</td>
<td>237.62 – 260</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Upper Belsele-Waas Member</td>
<td>260 – 270</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aquitard</td>
<td></td>
<td>Lower Belsele-Waas Member</td>
<td>270 – 280.13</td>
<td>6.3E-10</td>
<td>4.4E-10</td>
<td>1.1E-10</td>
<td></td>
</tr>
<tr>
<td>Aquifer</td>
<td>Lower Rupelian (sandy sequence of several sand horizons separated by clays)</td>
<td></td>
<td>280.13 – 383</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

See Table 1.8-1 for definitions of symbols. $\bot = $ normal to bedding. Ground level at Essen is 14.88 m a.s.l. Stratigraphy according to Laga (2006), transport parameters from Maes (pers. comm. 2007). In the absence of measured data, transport parameters for the Lower Belsele-Waas Member are calculated from those obtained for Boom Clay at Mol (highlighted by italics in the Table). The parameter values for the Lower Belsele-Waas Member at Essen, $P(LBW, Essen)$, are related to those of the upper members, $P(T-U, Essen)$, according to $P(LBW, Essen) = P(T-U, Essen) \times P(LBW, Mol) / P(T-U, Mol)$. Shaded areas indicate aquifers.

Figure 2.8-2: Stable-isotope composition of pore water squeezed from cores of the Essen borehole

Data from De Craen et al. (2006)
Noble gases

Contents of dissolved He in pore waters were determined by Bigler & Mazurek (2006). The values are near those corresponding to air-saturated water in the Neogene aquifer but increase strongly with depth (Figure 2.8-3). In the lower part of the Belsele-Waa Member and in the Lower Rupelian aquifer, the profile becomes more irregular, with some data points with substantially lower He contents. Bigler & Mazurek (2006) consider these points as artefacts for the following reasons:

- The lower part of the Belsele-Waa Member and of the Lower Rupelian aquifer is dominated by weakly consolidated, sand-rich lithologies. The core material that was used for the analyses was very friable and may have lost He during the time of core recovery and conditioning.
- The He content in the ground water of the Lower Rupelian aquifer is higher than in all samples of Boom Clay. With the exception of sample 282.86, which fits well into the general trend, all He contents measured in pore waters are much lower than in the ground-water sample. It appears unlikely that this pattern could represent in-situ conditions.

If the sand-rich samples in the lower part of the profile are screened out, a profile with He contents increasing more or less linearly with depth emerges.

Figure 2.8-3: He concentrations in pore water from cores of the Essen borehole

Blue bar represents concentration in ground water sampled from the test interval 285 – 383 m, corresponding to the full thickness of the Lower Rupelian aquifer. Green points are considered as non-representative of in-situ conditions. Data from Bigler & Mazurek (2006)

2.8.3 Upper boundary

Ground water in the Neogene aquifer was not sampled in the Essen borehole. However, pore-water data based on two core samples taken in the aquifer show very low salinity, He contents close to that of air-saturated water and stable-isotopic composition of water close to that in recent
precipitation at the site (Figure 2.8-1, Figure 2.8-2, Figure 2.8-3, Table 2.8-2). These data indicate that the aquifer essentially contains modern fresh water. At Mol, the Neogene aquifer contains $^3$H, indicative of direct connection of this aquifer to the surface.

### 2.8.4 Lower boundary

A piezometer in the interval 285 – 383 m, covering the whole Lower Rupelian aquifer, was used for water sampling. It has to be borne in mind that the aquifer consists of 4 individual sandy, permeable beds, separated by clay-rich lithologies. It is not clear whether the aquifer is geochemically homogeneous or whether there are any differences among the different permeable beds. In the absence of specific information on ground water residing in the Ruisbroek sands, the uppermost part of the Lower Rupelian aquifer that is in direct contact with Boom Clay, data from the squeezed sample nearest to the contact are used as boundary condition (Table 2.8-2). The composition of this sample corresponds to a mixture of ca. 80 % fresh water and 20 % sea water.

<table>
<thead>
<tr>
<th>Hydrogeologic unit</th>
<th>Formation</th>
<th>Type</th>
<th>Depth [m b.g.]</th>
<th>Cl$^-$ [mg/L]</th>
<th>Br$^-$ [mg/L]</th>
<th>I$^-$ [mg/L]</th>
<th>$\delta^{18}$O [‰ V-SMOW]</th>
<th>$\delta^2$H [‰ V-SMOW]</th>
<th>Depth [m b.g.]</th>
<th>He [cm$^3$ STP/gwater]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recent precipitation (IAEA station Gilze/Rijen, ca. 35 km NE of Essen)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-7.2</td>
<td>-50.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Neogene aquifer</td>
<td>Berchem sands</td>
<td>Pore water</td>
<td>145.52</td>
<td>53.0</td>
<td>&lt;0.25</td>
<td>&lt;0.1</td>
<td>-6.07</td>
<td>-42.8</td>
<td>145.52</td>
<td>4.71E-8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pore water</td>
<td>150.37</td>
<td>31.2</td>
<td>0.4</td>
<td>&lt;0.1</td>
<td>-5.99</td>
<td>-42.6</td>
<td>146.89</td>
<td>2.52E-7</td>
</tr>
<tr>
<td>Uppermost part of the Lower Rupelian aquifer</td>
<td>Ruisbroek sands</td>
<td>Pore water</td>
<td>282.77</td>
<td>3400</td>
<td>11.7</td>
<td>0.90</td>
<td>-5.69</td>
<td>-39.1</td>
<td>282.86</td>
<td>4.89E-5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pore water</td>
<td>294.83</td>
<td>3700</td>
<td>12.8</td>
<td>0.99</td>
<td>-5.61</td>
<td>-37.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Data shown in bold (samples closest to the boundary) are used as boundary conditions. Data from De Craen et al. (2006) and Bigler & Mazurek (2006)

### 2.8.5 Transport parameters

A preliminary data set of hydraulic conductivities, diffusion coefficients and porosities is available (Maes, pers. comm. 2007) and is shown in Table 2.8-1. In comparison to Boom Clay at Mol, porosities are slightly higher, and the same is observed for hydraulic conductivity and for $D_p$ of anions. In the absence of measured data, De(He) is estimated to be 3 times the value for De(HTO) according to the argument presented in Appendix A3.2. In-situ temperature is assumed to be identical to that at Mol, i.e. an average of 16.5 °C is used.

### 2.8.6 U and Th contents in rocks

Five rock samples from Boom Clay were analysed by ICP-MS and yielded average contents of 3.4 ppm (range 3.0 – 4.2 ppm) for U and 10.4 ppm (8.0 – 12.7 ppm) for Th (Wemaere et al. 2006). Spectral gamma logs were also run in the borehole, but the resulting contents are inconsistent among runs and also with the laboratory data. Given the fact that the spatial variability of the U and Th
contents is limited, the averages of the laboratory data are considered as sufficient for the purpose of quantifying He production, and the logs are not considered.

2.8.7 Hydraulic gradient

According to preliminary data, the hydraulic heads in the upper and lower aquifers are identical within ±1 m, suggesting that the hydraulic gradient across Boom Clay is near zero (Wemaere, pers. comm.).

2.8.8 Geological and hydrogeological evolution

The geological and hydrogeological evolution of Boom Clay and its embedding aquifers at Essen can be considered identical to that at Mol until emergence from the sea. At Essen, this event probably happened later, at ca. 1.7 Ma, as opposed to ca. 2 Ma at Mol (L. Wouters, pers. comm., referring to information from the Geological Survey of Belgium). Since then, the area was exposed to recurrent stages of permafrost.

Neogene aquifer

Similar to Mol, it is likely that there is a good hydraulic connection between the top of Boom Clay and the surface. Therefore, water in the Neogene aquifer is considered to correspond directly to meteoric recharge.

Lower Rupelian aquifer

The Essen borehole is located ca. 25 km NNW of Antwerp and ca. 50 km NW of Mol (Figure 2.7-2). This location is closer to the sea and farther away from the infiltration area of the Lower Rupelian aquifer. Most of the statements on the palaeo-hydrogeology of the Lower Rupelian aquifer made for Mol (Section 2.7.8) also apply to Essen. The evolution of the Lower Rupelian aquifer since emergence is not fully clear. In particular, the details of the salinity decrease over time are not well constrained, including the precise timing of the onset of this process.

2.9 London Clay at Bradwell (UK)

2.9.1 Structure and hydrogeology

A sequence of Tertiary London Clay and underlying clays/silts/sands occurs at Bradwell at the north-eastern limb of the London Basin on the coast of eastern England. Below thin unconsolidated Quaternary deposits (mainly sand and gravel), the London Clay occurs near to the surface and comprises a stiff silty clay that was deposited in a marine environment in the Eocene at 55 – 49 Ma (Bloodworth et al. 1987). It is about 50 m thick and is underlain by a thin sandy layer (the Harwich Formation), which is a locally permeable horizon that separates London Clay from the underlying, about 30 m thick Lower London Tertiaries beds (Figure 2.9-1). The upper part of the Lower London Tertiaries is clay-rich and therefore has a low permeability, whereas the lowermost part is sandy and constitutes an aquifer continuous with the underlying Chalk. The latter is recharged at outcrop about 40 km NW of Bradwell, giving a very low upwards hydraulic gradient into the Lower London Tertiaries at the site. There is also a downwards and lateral hydraulic gradient for intrusion of sea
water into the top of the London Clay seawards from the coast. The hydrogeological conceptual model is shown in Figure 2.9-1.

Figure 2.9-1: **Geological setting and hydrogeological conceptual model of Bradwell on the coast of southeastern England**

The locations of the two boreholes (A=B101 and B=B102) from which pore waters have been obtained are also shown. From Bath et al. (1989)

Table 2.9-1: **System geometries and transport parameters that have been used for modelling the tracer profiles at Bradwell**

<table>
<thead>
<tr>
<th>Unit</th>
<th>Lithology</th>
<th>Depth in borehole B101 [m below surface]</th>
<th>Depth in borehole B102 [m below surface]</th>
<th>De (I') @ 20 °C</th>
<th>De (HTO) @ 20 °C</th>
<th>Hydraulic conductivity @ [m/s]</th>
<th>Porosity [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unconsolidated Quaternary sediments (aquifer)</td>
<td>Soil, sand, gravel</td>
<td>0 – 2.0 (Aquifer)</td>
<td>0 – 4.8 (Aquifer)</td>
<td>1.4E-10</td>
<td>2.8E-10</td>
<td>1.8E-11</td>
<td>high</td>
</tr>
<tr>
<td>London Clay</td>
<td>Clay</td>
<td>2.0 – 22.5</td>
<td>4.8 – 22.5</td>
<td>2.8E-10</td>
<td>1.6E-10</td>
<td>4.6E-12</td>
<td></td>
</tr>
<tr>
<td>Harwich Formation (heterogeneous small aquifer)</td>
<td>Sand</td>
<td>61.7 – 61.8</td>
<td>50.4 – 55.2 (Small aquifer)</td>
<td>8.0E-11</td>
<td>1.6E-10</td>
<td>5.0E-7</td>
<td>Water: 0.48</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Anions: 0.24</td>
</tr>
<tr>
<td>Lower London Tertiaries (upper part)</td>
<td>Clay, silt</td>
<td>61.8 – 73.5</td>
<td>55.2 – 67.6 (Aquifer)</td>
<td>8.0E-11</td>
<td>1.6E-10</td>
<td>4.6E-12</td>
<td>Water: 0.48</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Anions: 0.24</td>
</tr>
<tr>
<td>Lower London Tertiaries (lower part, aquifer)</td>
<td>Silt, sand</td>
<td>73.5 – 89.1 (Aquifer)</td>
<td>67.6 – 84.5 (Aquifer)</td>
<td></td>
<td></td>
<td>1.0E-8</td>
<td></td>
</tr>
<tr>
<td>Chalk (aquifer)</td>
<td>Chalk</td>
<td>&gt;89.1 (Aquifer)</td>
<td>&gt;84.5 (Aquifer)</td>
<td></td>
<td></td>
<td>1.0E-8</td>
<td></td>
</tr>
</tbody>
</table>

⊥ = normal to bedding. Values given in italics were not measured but are assumed to be identical to those in the lower part of London Clay. Note that the Harwich Formation is not considered to be an aquifer in B101 where it is only 10 cm thick. From Bath et al. (1989), Gilling et al. (1987), Bourke et al. (1993) and Halcrow (1988). Shaded areas indicate aquifers.
2.9.2 Tracer distributions

The drillcores were preserved by waxing and refrigeration on site and pore waters were subsequently extracted by squeezing in specially designed rigs at loads up to 70 MPa in the laboratory at British Geological Survey, Keyworth (Bath et al. 1989). Pore water was extracted in sequential fractions, and the reported chemical compositions are the weighted averages of data from individual fractions. All of the major solutes plus stable O and H isotope ratios were analysed. Data for pH, HCO$_3^-$ and SO$_4^{2-}$ may have been slightly perturbed in some samples due to oxidation of pyrite, though the fact that pH values were between 7 and 9.1 indicates that the effect was minimal (Bath et al. 1989). Two core samples were squeezed under anaerobic conditions giving pore waters which had similar compositions to the other samples. In addition, a limited number of pore-water data was obtained from centrifugation tests (heavy-liquid displacement).

Anions

The contrasting salinity profiles show that the palaeo-hydrogeological histories are dramatically different in the two cases, in spite of the proximity of the boreholes (Figure 2.9-2). Chloride analyses indicate that the rocks have been substantially flushed of their original marine depositional pore water. The profile of borehole B102, nearest to the present shoreline, has Cl$^-$ decreasing downwards from a maximum of 15 700 mg/L at 7.3 m depth, which suggests that this is the result of intrusion of sea water from the surface. The profile of borehole B101, further inland, has more dilute pore water with a slight peak of 432 mg/L Cl$^-$ at 14 m depth, which is thought to be the result of sea-water intrusion in the past. Bromide could only be analysed in extracted pore waters from profile B102. Cl$^-$/Br$^-$ ratios throughout are similar to the sea-water value, allowing for rather large uncertainties in Br$^-$ data. Towards the underlying Chalk aquifer, Cl$^-$ concentrations vary in both boreholes towards the range observed in ground water of that unit (543 – 739 mg/L).

Figure 2.9-2: Depth profiles of chloride in pore waters from boreholes B101 and B102 at Bradwell

Data from Bath et al. (1989)
Water isotopes

The stable isotope compositions of pore waters correlate with their salinities. The depth distributions are shown in Figure 2.9-3. In borehole B101, near-surface δ values correspond to those of recent recharge (represented by the superficial ground-water samples) and decrease to a minimum at ca. 20 m, with a slight increase below this depth. In profile B102, the most shallow samples analysed at ~7 m depth have isotopic compositions trending towards that of sea water. A minimum of δ values is observed at 35 – 40 m, then an increase to a local maximum in the Harwich Formation underlying London Clay at 50 – 55 m.

Figure 2.9-3: Depth profiles of water isotopes in pore waters from boreholes B101 and B102 at Bradwell

Data from Bath et al. (1989)
2.9.3 Upper and lower boundaries

In borehole B101, water samples were taken in the surficial deposits and reflect recent recharge (Table 2.9-2). In borehole B102, no information is available from the surficial deposits. The uppermost core sample, taken 2.5 m below the top of London Clay, contains a strong marine signal. The value at the boundary itself and its evolution over time remain uncertain. For modelling, the upper boundary in borehole B102 is assumed to be represented by normal sea-water composition (Table 2.9-2).

The composition of water in the Chalk aquifer is similar in both boreholes. The values for the uppermost sample are used as boundary conditions for borehole B101 (Table 2.9-2). For borehole B102, the sample from the Harwich Formation is used for the lower boundary.

<table>
<thead>
<tr>
<th>Unit</th>
<th>Borehole</th>
<th>Depth [m]</th>
<th>Cl [mg/L]</th>
<th>$\delta^{18}$O [‰ V-SMOW]</th>
<th>$\delta^2$H [‰ V-SMOW]</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surficial aquifer</td>
<td>B101</td>
<td>0 – 2.0</td>
<td>53</td>
<td>-6.6</td>
<td>-45</td>
<td>Cl: Squeezed sample; water isotopes: average of 3 ground-water and 1 squeezed sample</td>
</tr>
<tr>
<td>Basal Lower London Tertiaries and Chalk aquifer</td>
<td>B101</td>
<td>78.8</td>
<td>504</td>
<td>-7.2</td>
<td>-46</td>
<td>Uppermost squeezed core</td>
</tr>
<tr>
<td>Surficial aquifer</td>
<td>B102</td>
<td>0 – 4.8</td>
<td>19 350</td>
<td>0</td>
<td>0</td>
<td>Present sea water</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.3</td>
<td>15 700</td>
<td>-3.5</td>
<td>-26</td>
<td>Squeezed sample 2.5 m below top of London Clay</td>
</tr>
<tr>
<td>Harwich Formation</td>
<td></td>
<td>54.4</td>
<td>716</td>
<td>-6.5</td>
<td>-43</td>
<td></td>
</tr>
<tr>
<td>Basal Lower London Tertiaries and Chalk aquifer</td>
<td>B102</td>
<td>75.25</td>
<td>630</td>
<td>-6.8</td>
<td>-44</td>
<td>Uppermost squeezed core</td>
</tr>
</tbody>
</table>

From Bath et al. (1989)

2.9.4 Transport parameters

Diffusion coefficients

A substantial data set for $\Gamma$ in London Clay at Bradwell was collected from through- and some out-diffusion experiments by Gilling et al. (1987). The average value for De in the vertical direction (normal to bedding) is 1.2E-10 m²/s. A trend towards lower diffusion coefficients with increasing depth is observed, with an average value of 1.4E-10 m²/s in the upper half and 0.8E-10 m²/s in the lower half.

Only limited data are available on effective diffusion coefficients for water isotopes. For a sample set from ca. 30 m depth, Bourke et al. (1993) obtained 0.4E-10 m²/s for $\Gamma$ and 0.8E-10 m²/s for HTO. On this basis and in the absence of a spatially representative data set, diffusion coefficients for HTO are assumed to be 2 times higher than those for $\Gamma$. 

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No data are available for formations underlying the London Clay. For the purpose of tracer-transport modelling, the average values obtained for the lower part of London Clay are used. All data are summarised in Table 2.9-1.

Hydraulic conductivity

Hydraulic conductivity of London Clay was measured in the laboratory on samples using the same equipment as were used for through-diffusion tests (Gilling et al. 1987). The hydraulic gradient across the test samples was increased to switch from diffusion-controlled solute transport to advection control. Values for vertical permeability \( K_v \), range from 1.2E-12 to 1.1E-10 m/s. As for diffusion coefficients, the higher values occur in the upper 20 – 25 m of the sequence which has been affected by weathering, or are tests where the seals in the diffusion cell may have leaked. Therefore, values >5E-11 m/s are recommended to be discounted (Gilling et al. 1987). Average values for the upper and lower parts of London Clay are given in Table 2.9-1. A few measurements were also made of horizontal permeability, \( K_h \). These indicate a hydraulic anisotropy factor of about 3.

No data are available from the Lower London Tertiaries, and the same average value of hydraulic conductivity is assumed as for the lower part of London Clay. The sandy layer above the Lower London Tertiaries (the Harwich Formation) has a relatively high hydraulic conductivity of ~5E-7 m/s, and the value for the Chalk aquifer is 1E-8 m/s (Halcrow 1988).

Porosity

Water-loss porosities can be derived from water content data (based on drying to 105 °C) of Entwistle et al. (1989). The depth dependence is small, and the average is 0.48. This value compares well with that of Bourke et al. (1993), who obtained 0.5 from diffusion experiments, and with the range 0.39 – 0.51 reported by Dewhurst et al. (1999a). For \( \Gamma \), the diffusion experiments of Bourke et al. (1993) indicate that only half the water-accessible porosity is accessible to anions.

In-situ temperature

Data for in-situ temperatures are not available, but can be assumed to be close to 10 °C at the present-day. Temperatures would have been several degrees lower at the peak of the last glacial period.

2.9.5 U and Th contents in rocks

No data available.

2.9.6 Hydraulic gradient

Piezometer measurements indicated hydrostatic conditions in the upper part of unweathered London Clay, i.e. there is no detectable hydraulic gradient over this interval (Halcrow 1988). Deeper piezometric measurements indicate a low upwards gradient from the Chalk and the basal Tertiaries and a low downwards gradient of about 0.1 from the base of the London Clay into the more sandy facies at the top of the Tertiaries, the Harwich Formation, which appears to be a hydraulic ‘sink’. It has been suggested that these gradients are transient due both to natural processes and to man-made effects of abstraction from the fresh water zone up-gradient in the Chalk aquifer.
2.9.7 Geological and hydrogeological evolution

London Clay was deposited in the period 55 – 49 Ma. The marine sedimentary sequence at Bradwell was probably exposed subaerially, and therefore subject to meteoric water recharge, for the first time during the Neogene at ~20 Ma. This area is at the fringe of the present-day North Sea and probably remained terrestrial through the late Tertiary and into the Quaternary. The most significant changes during the Quaternary are assumed to have been those in relative sea level – due to both land subsidence (the eastern side of England is slowly going down whereas the western side is rising) and isostatic sea level. Glaciation by the youngest (Devensian) ice sheet did not extend this far south, but remote hydrological effects cannot be excluded. The geometric boundary conditions at Bradwell have not changed much over the past few tens of thousands of years. There are no indications of deep erosion or substantial sedimentation.

The Harwich Formation and the Chalk aquifer (including the lower part of the Lower London Tertiaries) have their infiltration areas tens of kilometres inland and so have not been affected by recent sea-level changes. In contrast, the surficial aquifer was subjected to drastic salinity changes during the Holocene. At the end of the Devensian glacial period, the area was subject to a marine transgression which began at around 9 000 a and lasted until 6 000 a (Falck et al. 1990). Since then, the coast line retreated to its current position. High-water maxima of 3 – 4 m above ordnance datum (AOD) have been recorded recurrently over the past decades, but even higher inundations may have occurred in periods predating the instrumental record. This means that the location where borehole B102 was drilled (1.3 m AOD) has been inundated recurrently throughout the Holocene. Borehole B101, with an elevation of 6 m AOD, is likely to have been affected mainly by meteoric water since 6000 a, with possible episodes of inundation (Bath et al. 1989).

It is possible that the upwards head gradient from the Chalk aquifer would have been greater in the past, prior to perturbation due to ground-water abstraction.

2.9.8 Existing models of tracer transport

The variations of chloride concentrations and stable isotope ratios in present-day pore waters were simulated with a 1-D finite difference model of diffusion-advection-dispersion with temporally changing boundary conditions (Falck & Bath 1989a,b, Falck et al. 1990). The modelling concluded that the most consistent agreement of model and observations was obtained when chloride transport was controlled by diffusion (Figure 2.9-4). The boundary conditions were adjusted to optimise the curve fit, and therefore the conclusions from this modelling are strongly conditioned by this, but they are consistent with likely variations of sea level and of salinity and isotopic compositions of meteoric recharge through the late Pleistocene and Holocene periods (Table 2.9-3). For example, the suggested transient maximum of 3 000 mg/L at the top of the profile of borehole B101 between 9 and 6 ka is consistent with a relative high of sea level from which intrusion of sea water accounts for the observed peak of Cl⁻ at 14 m depth. The minimum δ¹⁸O value of -8.0 ‰ at the upper boundary of both profiles from 40 to 9 ka is consistent with the recharge of ‘cold climate’ water during the peak of the Devensian glacial period.

However, modelling also showed that the profile shapes for Cl⁻ and δ¹⁸O could in principle be replicated by an advective model that is ‘tuned’ with different hydraulic gradients and diffusion properties. Therefore, the diffusive model is not definitive or unique, but it is the most straightforward explanation of what is observed.
Table 2.9-3: ‘Best fit’ temporal variations of boundary conditions of Cl\(^-\) and \(\delta^{18}\)O for diffusive models of profiles B101 and B102 at Bradwell

<table>
<thead>
<tr>
<th>Time period 0 - 6 ka</th>
<th>Time period 6 - 9 ka</th>
<th>Time period 9 - 16 ka</th>
<th>Time period 16 - 40 ka</th>
<th>Time period 40 - 70 ka</th>
<th>Time period 70 - 100 ka</th>
</tr>
</thead>
<tbody>
<tr>
<td>Profile B101 (800 m from present shore)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Upper boundary Cl(^-) [mg/L]</td>
<td>50</td>
<td>3000</td>
<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Upper boundary (\delta^{18})O [‰ V-SMOW]</td>
<td>-6.5</td>
<td>-6.0</td>
<td>-8.0</td>
<td>-7.0</td>
<td>-6.5</td>
</tr>
<tr>
<td>Lower boundary Cl(^-) [mg/L]</td>
<td>600</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lower boundary (\delta^{18})O [‰ V-SMOW]</td>
<td>-7.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Profile B102 (200 m from present shore)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Upper boundary Cl(^-) [mg/L]</td>
<td>16000</td>
<td>19350</td>
<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Upper boundary (\delta^{18})O [‰ V-SMOW]</td>
<td>-1.1</td>
<td>0.0</td>
<td>-8.0</td>
<td>-7.0</td>
<td>-6.5</td>
</tr>
<tr>
<td>Lower boundary Cl(^-) [mg/L]</td>
<td>600</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lower boundary (\delta^{18})O [‰ V-SMOW]</td>
<td>-7.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

From Falck & Bath (1989a,b)

Figure 2.9-4: Modelled profiles for Cl\(^-\) and \(\delta^{18}\)O in London Clay and Lower London Tertiaries at Bradwell according to Falck & Bath (1989a,b)

Top: borehole B101; bottom: borehole B102
3. OVERVIEW OF AVAILABLE INPUT DATA

3.1 Tracer concentrations in pore water – an overview

3.1.1 Chloride

As shown in Table 3.1-1, maximum Cl⁻ contents vary strongly among the sites considered between values close to that of sea water (Couché Silteuse at Marcoule – MAR203 and MAR402, Opalinus Clay at Mont Russelin) to contents of less than 1 % of that of sea water (Boom Clay at Mol). Many of the formations lost most of their original salinity. Maximum Cl⁻ contents are often found in the central parts of the low-permeability sequences, with negative concentration gradients towards both the underlying and the overlying aquifers (Table 3.1-1). Particularly high gradients for Cl⁻ are found in the Couché Silteuse at Marcoule, in the Opalinus Clay at Mont Terri and Mont Russelin and in London Clay at Bradwell and most probably indicate geologically young interactions with the aquifers and/or high transport resistance (in particular, low diffusion coefficients) in the low-permeability sequence. At some sites (e.g. Callovo-Oxfordian at Bure – EST311/312, Boom Clay at Essen), the Cl⁻ concentrations in the low-permeability sequence show linear trends connecting the values in the aquifers (i.e. the concentration gradient is negative towards one aquifer and positive towards the other). As a first hypothesis, such Cl⁻ distributions can be interpreted as steady-state diffusion profiles.

3.1.2 Water isotopes

All δ values are negative, indicative of some degree of interaction of the original sea water (with δ values close to 0) with isotopically lighter, presumably meteoric waters. The gradients of the δ values towards the embedding aquifers mostly have the same sign as those for Cl⁻, and the shapes of the profiles are often similar to those for Cl⁻. Exceptions are the Boom Clay at Essen and London Clay at Bradwell, where the shapes of the Cl⁻ and the stable isotope profiles differ due to Holocene climatic effects, which affect stable isotopic compositions but not Cl⁻ contents (see Appendix A4.1 for details).

Figure 3.1-1 shows the highest Cl⁻ contents observed in the low-permeability sequences in a plot against the highest δ¹⁸O values. It indicates that, at least in principle, pore waters at many sites could be explained as simple mixtures between sea water and meteoric waters with δ¹⁸O in the range of -5 to -12 ‰. Major exceptions to this are Opalinus Clay at Mont Terri and at Mont Russelin, and London Clay at Bradwell (B102). At least in these cases, a more complex evolution must be considered.

3.2 Overview of formation properties

An overview of geometric characteristics and transport parameters for all sites is given in Table 3.2-1. With the exception of Opalinus Clay at Mont Terri and at Mont Russelin, all sequences are near-horizontally bedded. Graphic representations of transport parameters are shown in Figure 3.2-1 to Figure 3.2-6 and are based on Table 3.2-1, but additional data from clays and shales compiled by Boisson (2005) were also included. Data on properties of other formations, including porosity, diffusion coefficients and hydraulic conductivity, are from Neuzil (1994) and Dewhurst et al. (1999b).
Table 3.1-1: Maximum tracer concentrations in the low-permeability sequences and gradients towards the aquifers

<table>
<thead>
<tr>
<th>Site</th>
<th>Max. content [mg/L]</th>
<th>Max. gradient towards upper aquifer [mg/L / 100 m]</th>
<th>Max. gradient towards lower aquifer [mg/L / 100 m]</th>
<th>Max. δ¹⁸O value [% v SMOW]</th>
<th>Max. gradient towards upper aquifer [% / 100 m]</th>
<th>Max. gradient towards lower aquifer [% / 100 m]</th>
<th>Max. δ²H value [% v SMOW]</th>
<th>Max. gradient towards upper aquifer [% / 100 m]</th>
<th>Max. gradient towards lower aquifer [% / 100 m]</th>
<th>Max. content [cm³ STP / kgwater]</th>
<th>Max. content [cm³ STP / kgwater]</th>
<th>Max. content [cm³ STP / kgwater]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Callovo-Oxfordian at Bure, URL site</td>
<td>2.166</td>
<td>-2.100</td>
<td>-700</td>
<td>-5.2</td>
<td>-3.0</td>
<td>-1.2</td>
<td>-33.8</td>
<td>-20</td>
<td>-7</td>
<td>6.29E-5</td>
<td>-9E-5</td>
<td>+1.5E-6</td>
</tr>
<tr>
<td>Callovo-Oxfordian at Bure, EST311 &amp; EST312</td>
<td>3.218</td>
<td>-2.700</td>
<td>+2.700</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Callovo-Oxfordian at Bure, HTM102</td>
<td>2.697</td>
<td>-1.000</td>
<td>+1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Couche Silteuse at Marcoule, MAR203</td>
<td>25.875</td>
<td>-16.000</td>
<td>-25.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Couche Silteuse at Marcoule, MAR402</td>
<td>17.428</td>
<td>-25.000</td>
<td>-22.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Couche Silteuse at Marcoule, MAR501</td>
<td>1.541</td>
<td>-9.000</td>
<td>-1.100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Opalinus Clay at Benken</td>
<td>7.331</td>
<td>-2.400</td>
<td>-6.600</td>
<td>-4.5</td>
<td>-1.5</td>
<td>-5.5</td>
<td>-41.8</td>
<td>-15</td>
<td>-40</td>
<td>1.95E-4</td>
<td>positive</td>
<td></td>
</tr>
<tr>
<td>Opalinus Clay at Mont Terri</td>
<td>13.853</td>
<td>-7.200</td>
<td>-30.000</td>
<td>-7.1</td>
<td>negative</td>
<td>-3.4</td>
<td>-46.6</td>
<td>-21</td>
<td>-40</td>
<td>1.31E-4</td>
<td>-1E-4</td>
<td>-1.5E-4</td>
</tr>
<tr>
<td>Opalinus Clay at Mont Russelin</td>
<td>21.716</td>
<td>-13.000</td>
<td>no lower aquifer</td>
<td>-4.4</td>
<td>-2.4</td>
<td>no lower aquifer</td>
<td>-27.3</td>
<td>-19</td>
<td>no lower aquifer</td>
<td>7.9E-4</td>
<td>-8E-4</td>
<td>no lower aquifer</td>
</tr>
<tr>
<td>Toarcian-Domerian at Tournemire</td>
<td>539</td>
<td>-320</td>
<td>-500</td>
<td>-4.8</td>
<td>-3.6</td>
<td>-1.2</td>
<td>-35</td>
<td>-46</td>
<td>-11</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Boom Clay at Mol</td>
<td>40</td>
<td>-35</td>
<td>unclear</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Boom Clay at Essen</td>
<td>3.100</td>
<td>-2.400</td>
<td>+2.400</td>
<td>-5.7</td>
<td>+2.3</td>
<td>+0.7</td>
<td>-39.3</td>
<td>+24</td>
<td>+8</td>
<td>3.36E-5</td>
<td>-3.5E-5</td>
<td>+3.5E-5</td>
</tr>
<tr>
<td>London Clay at Bradwell, B101</td>
<td>432</td>
<td>-3.300</td>
<td>unclear</td>
<td>-6.4</td>
<td>+4.4</td>
<td>small</td>
<td>-42</td>
<td>+43</td>
<td>small</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>London Clay at Bradwell, B102</td>
<td>15.700</td>
<td>+120.000</td>
<td>-1.000</td>
<td>-3.5</td>
<td>+23</td>
<td>+9</td>
<td>-26</td>
<td>+160</td>
<td>+60</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Maximum contents refer to the clay-rich unit within each low-permeability sequence; outliers were screened out. Gradients of tracer contents towards the aquifers are order-of-magnitude indications only. Negative gradient means decreasing concentration or δ value towards the aquifer. Empty fields = no data.
### Table 3.2-1: Comparison of geometric properties and of transport parameters for the low-permeability sequences considered in this report

<table>
<thead>
<tr>
<th>Site</th>
<th>Stratigraphy of low-permeability sequence</th>
<th>Total thickness of low-permeability sequence [m]</th>
<th>Thickness of shaly unit [m]</th>
<th>Pore diffusion coefficient for sodium ions in shaly unit @ 20 °C, [-] [m²/s]</th>
<th>Pore diffusion coefficient for HTO in shaly unit @ 20 °C, [-] [m²/s]</th>
<th>Effective diffusion coefficient for sodium ions in shaly unit @ 20 °C, [-] [m²/s]</th>
<th>Effective diffusion coefficient for HTO in shaly unit @ 20 °C, [-] [m²/s]</th>
<th>Anisotropy of Dp in shaly unit (A)</th>
<th>Hydraulic conductivity in shaly unit, [-] [m/s]</th>
<th>Hydraulic conductivity in shaly unit, [-] [m/s]</th>
<th>Physical porosity in shaly unit [-]</th>
<th>Fraction of physical porosity accessible to sodium ions in shaly unit [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Callovo-Oxfordian at Bure (URL site)</td>
<td>63 m limestone 130 m Callovo-Oxfordian shale 63 m limestone</td>
<td>256.0</td>
<td>130</td>
<td>5.6E-11</td>
<td>1.4E-10</td>
<td>5.0E-12</td>
<td>2.6E-11</td>
<td>&lt;2</td>
<td>5E-14 – 5E-13</td>
<td>n.d. (only minor anisotropy)</td>
<td>0.18</td>
<td>0.5</td>
</tr>
<tr>
<td>Couche Silteuse at Marcoule, borehole MAR203</td>
<td>404 m shaly siltstone</td>
<td>404</td>
<td>404</td>
<td>2.5E-11 – 6.9E-11</td>
<td>3.8E-11 – 1.1E-10</td>
<td>1.3E-12 – 3.6E-12</td>
<td>5.0E-12 – 1.4E-11</td>
<td>n.d.</td>
<td>n.d.</td>
<td>1.6E-12 – 1.8E-13</td>
<td>0.13 (0.09 – 0.18)</td>
<td>0.4</td>
</tr>
<tr>
<td>Couche Silteuse at Marcoule, borehole MAR402</td>
<td>246 m shaly siltstone</td>
<td>246</td>
<td>246</td>
<td>5.3E-11</td>
<td>8.8E-11</td>
<td>1.8E-12</td>
<td>7.0E-12</td>
<td>n.d.</td>
<td>n.d.</td>
<td>7E-14 – 4E-13</td>
<td>0.08</td>
<td>0.4</td>
</tr>
<tr>
<td>Couche Silteuse at Marcoule, borehole MAR501</td>
<td>163 m shaly siltstone</td>
<td>163</td>
<td>163</td>
<td>3.0E-11 – 7.0E-11</td>
<td>8.5E-11 – 1.9E-10</td>
<td>2.7E-12 – 6.3E-12</td>
<td>1.1E-11 – 2.5E-11</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>Opalinus Clay at Benken</td>
<td>54.2 m limestone ± marl 87.6 m claystone, marl ± sandstone, limestone 113.2 m Opalinus Clay³ 57.1 m marls, siltstones, shales ± other lithologies</td>
<td>312.1</td>
<td>113.2</td>
<td>1.9E-11</td>
<td>5.3E-11</td>
<td>1.1E-12</td>
<td>6.4E-12</td>
<td>5</td>
<td>6E-15 – 3E-14</td>
<td>1E-14 – 6E-14</td>
<td>0.12</td>
<td>0.5</td>
</tr>
<tr>
<td>Opalinus Clay at Mont Terri</td>
<td>14 m limestone 160 m Opalinus Clay⁴ 45 m Liasse shale</td>
<td>219.0</td>
<td>160.0</td>
<td>4.8E-11</td>
<td>7.9E-11</td>
<td>4.6E-12</td>
<td>1.4E-11</td>
<td>4</td>
<td>4E-14 (4E-15 – 4E-13)</td>
<td>2E-13 (2E-14 – 2E-12)</td>
<td>0.18</td>
<td>0.54</td>
</tr>
<tr>
<td>Opalinus Clay at Mont Russellin⁵</td>
<td>45 m limestone &gt; 177 m Opalinus Clay and Liasse shale</td>
<td>&gt; 222 (no lower boundary)</td>
<td>&gt; 177</td>
<td>4.8E-11</td>
<td>7.9E-11</td>
<td>4.6E-12</td>
<td>1.4E-11</td>
<td>4</td>
<td>4E-14 (4E-15 – 4E-13)</td>
<td>2E-13 (2E-14 – 2E-12)</td>
<td>0.18</td>
<td>0.54</td>
</tr>
</tbody>
</table>
Table 3.2-1 (continued)

| Site                                      | Stratigraphy of low-permeability sequence | Total thickness of low-permeability sequence [m] | Thickness of shale unit [m] | Porosity coefficient for anions in shale unit [20 °C, \( \perp \)] [m/a] | Porosity coefficient for CO\(_2\) in shale unit \([20 °C, \perp]\) [m/a] | Effective diffusion coefficient for anions in shale unit \([20 °C, \perp]\) [m/a] | Effective diffusion coefficient for HTO in shale unit \([20 °C, \perp]\) [m/a] | Anisotropy of Dp in shale unit (\( \perp/|| \)) | Hydraulic conductivity in shale unit \([\perp]\) [m/s] | Hydraulic conductivity in shale unit \([||]\) [m/s] | Physical porosity in shale unit [-] | Fraction of physical porosity accessible to anions in shale unit [-] |
|------------------------------------------|------------------------------------------|-----------------------------------------------|------------------------------|-------------------------------------------------------------------|-------------------------------------------------------------------|-------------------------------------------------------------------|-------------------------------------------------------------------|-----------------------------------------------------------------|---------------------------------------------------------------|---------------------------------------------------------------|---------------------------------------------------------------|---------------------------------------------------------------|
| Toarcian-Domerian at Tournemire           | 257.4 m Toarcian-Domerian shale          | 257.4                                         | 257.4                        | 2.1E-11 – 2.8E-11                                                  | 4.2E-11 – 5.6E-11                                                  | 5.7E-13 – 7.3E-13                                                  | 2.3E-12 – 4.8E-12                                                  | 2                                                  | 1.0E-12 – 1.3E-12                                               | 2.0E-12 – 2.6E-12                                               | 0.055 – 0.085                                                  | 0.3 – 0.5                                                      |
| Boom Clay at Mol                          | 102.6 m Boom Clay\(^a\)                 | 102.6\(^a\)                                    | 102.6\(^a\)                  | 1.4E-10 – 4.0E-10\(^b\)                                          | 2.3E-10 – 4.6E-10\(^b\)                                          | 2.2E-11 – 6.4E-11\(^b\)                                          | 8.5E-11 – 1.7E-10\(^b\)                                          | 2                                                  | 2.0E-12 – 4.3E-11\(^b\)                                         | 4.8E-12 – 2.9E-10\(^b\)                                         | 0.37 – 0.43                                                    |                                                              |
| Boom Clay at Essen                        | 127.1 m Boom Clay                       | 127.1                                         | 127.1                        | 2.2E-10 – 6.3E-10\(^b\)                                          | 2.2E-10 – 4.4E-10\(^b\)                                          | 5.5E-11 – 1.6E-10\(^b\)                                          | 9.5E-11 – 1.9E-10\(^b\)                                          | n.d.                                              | 5.4E-12 – 9.7E-11\(^b\)                                         | n.d.                                                          | 0.43 – 0.58                                                   |                                                              |
| London Clay at Bradwell                   | 59.7 m London Clay\(^a\)               | 59.7\(^a\)                                    | 59.7\(^a\)                   | 3.3E-10 – 5.8E-10\(^b\)                                          | 3.3E-10 – 5.8E-10\(^b\)                                          | 8.0E-11 – 1.4E-10\(^b\)                                          | 1.6E-10 – 2.8E-10                                                  | n.d.                                              | 4.6E-12 – 1.8E-11                                               | n.d.                                                          | 0.48 – 0.5                                                    |                                                              |

Data listed refer to the screened data sets used for modelling. Values in italics: Not directly measured but extrapolated/inferred from external evidence. Bold: Shaly target formations within low-permeability sequences. Diffusion coefficients refer to the original values obtained from laboratory experiments, *i.e.* they are not corrected for *in-situ* temperature. \( \perp \) = value normal to bedding, \( || \) = value parallel to bedding.

1 Values not measured but estimated from De(HTO).
2 2E-8 – 2E-9 in a silty-sandy bed.
3 Incl. Murchisonae Beds in Opalinus Clay facies
4 Opalinus Clay is tectonically thickened in the area of the rock laboratory. The primary thickness (*i.e.* the one prior to the formation of the anticline) is *ca.* 60 – 70 m less (Freivogel & Huggenberger 2003, Freivogel, pers. comm. 2003).
5 Transport parameters not measured; data are from Mont Terri.
6 The Eigenbilzen formation is considered as part of the overlying aquifer.
7 The latter value refers to the lowermost, sandier part of Boom Clay (Lower Belsele-Waas Member).
8 The latter value refers to the Lower Belsele-Waas Member and is extrapolated based on data from Mol, as described in Table 2.8-1.
9 Borehole B101
3.2.1 Diffusion coefficients

Effective diffusion coefficients for HTO for formations shown in Figure 3.2-1 span a range of 2 orders of magnitude. An empirical relationship between porosity and diffusion coefficient, known as Archie's law, can be formulated as

$$ \frac{D_e}{D_0} = n^m $$

(Boving & Grathwohl 2001),

where

- $n$ = porosity
- $m$ = empirical exponent
- $D_0$ = diffusion coefficient in free water.

According to Figure 3.2-1, data for the considered formations are consistent with empirical exponents of $2 - 3$ (HTO) and $2 - 2.5$ (anions).

Because porosity of argillaceous rocks is mainly a function of the maximum burial depth of the formation during geological basin evolution, there is also a regular variation of diffusion coefficients with maximum burial depth, as shown in Figure 3.2-2.
Figure 3.2-1: Diffusion coefficients for HTO and Cl\(^-\) in clays and shales as a function of porosity

Data are from Table 3.2-1 and from Boisson (2005) for formations not treated in this report. Diffusion coefficients in bulk water are from Atkins (1990) and Li & Gregory (1974). Blue curves represent Archie’s law relationships, and numbers indicate the empiric exponents.

Figure 3.2-2: Diffusion coefficients for HTO in clays and shales as a function of maximum burial depth during basin evolution

Data are from Table 3.2-1 and from Boisson (2005) for formations not treated in this report. Diffusion coefficient in bulk water from Atkins (1990). Maximum burial depths from Mazurek et al. (2006; Opalinus Clay), Peyaud et al. (2005) and Barbarand et al. (2001; Toarcian-Domerian at Tournemire), Mazurek (1999; Palfris Formation at Wellenberg), and Boisson (2005; all other formations).
Hydraulic conductivity

Overview

Hydraulic conductivity of the considered formations decreases with decreasing porosity, which reflects the closure of the pore space in response to mechanical compaction and to diagenetic cementation (Figure 3.2-3 and Figure 3.2-4). However, at porosities below 0.1, a sharp increase of hydraulic conductivity is observed and reflects the growing hydraulic role of fractures. The self-sealing capacity decreases at high degrees of compaction, and geomechanical properties approach those of hard, fractured rocks. The Boda Clay Formation (Hungary) and the Palfris Formation (Switzerland), which both experienced a maximum burial to depths of several kilometres before exhumation, are good examples of this. The Toarcian-Domerian at Tournemire occupies an intermediate position in this respect. This formation is fractured, and some minor moisture zones can be observed in the tunnel (Figure 3.2-5). Fractures also have a local influence on pore-water composition (Patriarche 2001). However, as a whole, the formation is still diffusion-dominated, given the still limited hydraulic conductivity of fractures and, more importantly, their poor larger-scale connectivity. It is noteworthy that in-situ measurements of hydraulic conductivity (reflecting the properties of fractures) cover the range 5E-14 – 1E-11 m/s, compared to the ca. 2 orders of magnitude lower values of 1.3E-16 – 1.6E-13 m/s for laboratory determinations (reflecting the properties of the matrix; Boisson et al. 2001). For less strongly consolidated formations, such as Boom Clay and Opalinus Clay, the discrepancy between the laboratory and in-situ determinations is smaller or even non-existent (see data compilation by Boisson 2005), which indicates the absence or limited hydraulic significance of fractures in these formations. The upscaling of hydraulic conductivity appears to be a straightforward process in higher-porosity units but becomes more demanding in units in which fracture flow plays a role. An in-depth discussion is provided in Neuzil (1994), including exceptions to the rule.

Effects of maximum burial depth

In Figure 3.2-6, hydraulic conductivity is shown as a function of maximum burial depth during basin evolution. Hydraulic conductivity decreases drastically with burial depth until ca. 2,000 m. Below this depth, it becomes increasingly controlled by fractures and less by the matrix as at shallower levels, and this is mirrored by the sharp increase of the values at greater depths. It needs to be noted that permeability may have been much lower in these formations at the time when they were located at maximum burial depth, and the enhancement may be related to processes during uplift to the present positions.

Effects of current depth

In a compilation of world-wide data, Appel & Habler (2002) identified a strong depth dependence of hydraulic conductivity (Figure 3.2-7). At shallow levels, the range of the data is enormous and covers about 10 orders of magnitude. This reflects the fact that, in over-consolidated formations, hydraulic conductivity is enhanced by fracturing in response to uplift and unloading, whereas very low values may be obtained in test intervals that do not contain fractures. Also, less or no fracturing is expected in normally consolidated formations (i.e. those that have never been buried more deeply). On the other hand, at depths below 200 m, hydraulic conductivity is always less than 1E-10 m/s (with two exceptions).

Considering a specific example, data from shallow boreholes through Opalinus Clay in southern Germany were evaluated by Hekel (1994), who identified a ca. 30 m thick, fractured decompaction
zone in which hydraulic conductivity is 5 – 6 orders of magnitude higher than at deeper levels (Figure 3.2-8). This zone also correlates with low pore-water salinity, which is another indicator of fluid circulation. Further observations documenting a decompaction zone a few tens of metres thick in Opalinus Clay are described in Mazurek et al. (1996). A contrasting example is the Palfris Formation at Wellenberg (Switzerland), where the zone with enhanced hydraulic conductivity is about 500 m thick (Figure 3.2-8; Nagra 1997). The much larger thickness of the decompaction zone at this site is probably due to the highly indurated nature of the Palfris Formation, resulting in the presence of a dense fracture network and a more limited self-sealing capacity (less swelling minerals). Even though the data base is limited, it appears likely that the thickness of the decompaction zone characterised by enhanced hydraulic conductivity depends on the geological evolution, in particular on the degree of induration (maximum burial depth).

Figure 3.2-3: **Hydraulic conductivity of clays and shales as a function of porosity**

Squares are geometric means, bars indicate variability. Data from Table 3.2-1 and from Boisson (2005) for formations not treated in this report.
Figure 3.2-4: Hydraulic conductivity of clays and shales as a function of porosity, including the data set of Neuzil (1994)

Squares are geometric means, bars indicate variability. Data from Table 3.2-1 and from Boisson (2005) for formations not treated in this report. Broken lines indicate ranges for clays and shales studied by Neuzil (1994)

Figure 3.2-5: Moisture zone along a fracture in the Toarcian-Domerian at Tournemire (tunnel wall)
Figure 3.2-6: Hydraulic conductivity of clays and shales as a function of maximum burial depth during basin evolution

Data are from Table 3.2-1 and from Boisson (2005) for formations not treated in this report. Maximum burial depths from Mazurek et al. (2006; Opalinus Clay), Peyaud et al. (2005) and Barbarand et al. (2001; Toarcian-Domerian at Tournemire), Mazurek (1999; Palfris Formation at Wellenberg), and Boisson (2005; all other formations).

Figure 3.2-7: Hydraulic conductivity of various clay and shale formations as a function of depth

Adapted from Appel & Habler (2002)
Figure 3.2-8: Hydraulic conductivity of Opalinus Clay (southern Germany) and of the Palfris Formation (Wellenberg, Switzerland) at near-surface levels

Adapted from Hekel (1994) and Nagra (1997). Equivalent depth at Wellenberg accounts for the fact that, due to the strong topographic relief, the depth-vertical stress relationship differs from that in a flat, planar surface.
4. MODELLING STRATEGY

4.1 Aims of modelling and modelling tool

The tracer data presented in this report were generally obtained in order to better characterise the hydraulic and transport properties of clay-rich aquitards. In particular, the interest is focussed on:

1. evaluating the dominant transport mechanisms;
2. estimating or delimiting transport parameters (such as hydraulic conductivity or diffusion coefficients) that are relevant at the formation scale;
3. understanding the evolution of the observed profiles over geologic time scales.

It is clear that these three aims are not independent of each other. Their interrelations become obvious when trying to model the tracer data.

All calculations were performed using the numeric code FLOTRAN (Lichtner 2004). The code, including the modifications made for the purpose of this report, as well as subsequent benchmarking, is documented in Appendix A5.

4.2 Processes considered

All simulations are based on a one-dimensional continuum-scale transport equation that includes advection, diffusion and dispersion and accumulation due to zero-order production\(^{13}\),

\[
\frac{n}{t} \frac{\partial C}{\partial t} = \frac{\partial}{\partial z} \left( n D_{p^*} \frac{\partial C}{\partial z} \right) - \frac{\partial}{\partial z} (v_a n C) + n \rho_w A
\]

where

\( C \) = concentration of a solute in pore water
\( n \) = porosity
\( D_{p^*} \) = pore dispersion coefficient
\( v_a \) = advective flow velocity
\( A \) = accumulation rate per mass of pore water due to zero-order production
\( \rho_w \) = water density
\( t \) = time
\( z \) = distance from the boundary of the aquitard.

For low advective velocities, \( D_{p^*} \) is equal to the pore diffusion coefficient \( D_p \), as the contribution of hydrodynamic dispersion to \( D_{p^*} \) becomes insignificant (see also equation in Section 4.3.4). See Section 1.8 for formal definitions of diffusion coefficients.

\(^{13}\) This source term is relevant for \(^{4}\)He and \(^{40}\)Ar that are continuously produced in the rock due to radioactive decay of U, Th and K.
4.2.1 Relative importance of advection and diffusion

In the general case, the flow velocity $v_a$ is related to the hydraulic gradient through the Darcy equation

$$v_a = \frac{q}{n} = -\frac{K}{n} \frac{\partial H}{\partial z}$$

where

$q = \text{Darcy velocity}$  

$K = \text{hydraulic conductivity}$  

$H = \text{total hydraulic head}$.

In argillaceous rocks, anions may not access all pore water. Then, the solute flow velocity may be different from the mean water flow velocity. Furthermore, the flow velocity of water and solutes may be slightly affected by osmotic gradients as discussed below.

The time that is required to propagate a perturbation by advection over a distance $z$ is

$$t_a = \frac{z}{v_a}.$$

For diffusion in one dimension and towards one side, a typical diffusive transport time can be given as

$$t_d = \frac{z^2}{D_p}.$$

The propagation time as given in the equation above refers to time at which about half of the total signal (i.e. half the concentration difference between the undisturbed aquitard and the boundary) reached a depth $z$ in the formation.

The relative significance of advective and diffusive transport can be estimated from a Peclet number $Pe$ defined as

$$Pe = \frac{t_d}{t_a} = \frac{v_a}{D_p} \cdot \frac{z}{L}.$$

If one is interested in the importance of the two transport mechanisms over the thickness $z = L$ of an aquitard, the relevant Peclet number is $Pe = v_a \cdot L / D_p$. Values below 1 indicate that transport is dominated by diffusion, whereas values clearly above 1 are characteristic of advection-dominated systems. Note that various definitions of Peclet numbers exist with somewhat different interpretations (Huysmans & Dassargues 2005). Note also that the Peclet number $Pe = v_a \cdot L / D_p$ is tracer specific because different tracers not only have different pore diffusion coefficients $D_p$ but also can access different parts of the pore water and thus may experience different flow velocities $v_a$. For instance, anions that can access only the larger pores may flow with higher average velocity as compared to water tracers that access all the pore water, and so are potentially more sensitive to advective flow at low hydraulic gradients. Unfortunately, the ratio of the average flow velocity of the anion accessible pore water to that of the total pore water is mostly unknown.
4.2.2 In-situ production and accumulation

The accumulation term $A$ in the transport equation is relevant in the case of He, which is produced in situ with a constant rate that depends on the $U$ and Th contents of the rock. Equations relating the $U$ and Th contents to the production rate of He in the rock and to the He accumulation in pore water are presented in Appendix A4.3, together with an outline of current understanding of He mobility in the Earth's crust. A discussion of the release efficiency of He from minerals to the pore water is also included.

Provided the boundary conditions remain constant over a sufficiently long period of time, the accumulation of He due to in-situ production equals the diffusive or advective loss of He across the boundaries, and a steady-state (i.e. time-invariant) He concentration profile develops. In general, it is very difficult to judge from the shape of the tracer profile alone whether a steady-state situation prevails. This can only be decided when additional information about relevant time scales and the palaeo-hydrogeological evolution is available, and by testing the steady-state assumption by a series of transient model runs.

4.2.3 Processes not considered: Chemical osmosis and ultrafiltration

In clay-rich rocks, the mobility of ions may be restricted by the charged surfaces and the narrow pore sizes. If solutes cannot freely move by diffusion or advection, these rocks may act as semi-permeable barriers, and salinity gradients will induce an osmotic potential, pulling water from the low-salinity regions towards the high-salinity regions. The corresponding water flow is typically expressed as being proportional to the osmotic gradient multiplied by the osmotic efficiency $\sigma$ (e.g. Soler 2001).

A perfect semi-permeable membrane has a $\sigma$ of 1, a material having no membrane effect a $\sigma$ of 0. In a rock with a high osmotic efficiency, a salinity gradient thus creates an additional water flow and solute flux that are independent of the hydraulic gradient. In geological systems, there are only few convincing examples related to the relevance of chemical osmosis. Marine & Fritz (1981) and Neuzil (2000) documented case studies in which hydraulic-head anomalies in shales correlate with pore-fluid salinity trends and interpreted the anomalies as due to osmosis.

For most of the low-permeability sequences considered here, no data on osmotic efficiency are available. For Opalinus Clay, a rather low value of less than 0.12 was reported (Nagra 2002). Recent in-situ experiments in the Callovo-Oxfordian at Bure indicate similarly low values (Rousseau-Gueutin et al. 2007). In view of these uncertainties and the small expected impact on solute transport, chemical osmosis is not explicitly considered in the transport modelling.

As chemical osmosis, ultrafiltration (or hyperfiltration or reverse osmosis) is a consequence of the membrane properties of argillaceous rocks. It is a coupled transport process in which high hydraulic gradients across a semi-permeable barrier mobilise water to a higher degree than ions, leading to a sieving effect of solutes. This process has been proposed as a mechanism to generate highly saline waters in sedimentary basins (e.g. Graf 1982). Indeed, the relevance of this process in clay-rich media has been demonstrated in laboratory experiments (e.g. Kharaka & Berry 1973). However, there is no compelling evidence that ultrafiltration across clay-rich matrices occurs in geological systems, and Hanor (1994) concluded that it is likely negligible in such systems. Therefore, it is not considered in this report as far as transport modelling in the low-permeability sequences is concerned. However, ultrafiltration must be kept in mind and may play a significant role for certain laboratory experiments in which high hydraulic gradients are applied, such as core squeezing (see Appendix A2.5) or advective-displacement experiments (see Appendix A2.8).
4.3 Concepts and parameters needed to quantify advection across low-permeability sequences

On the one hand, the possible effect of advection in the currently active system (measured head differences between the upper and the lower aquifer) is explored. On the other hand, calculations are made to study the effects of hypothetical higher hydraulic gradients that may have occurred in the past, and to place upper bounds on Darcy or advection velocities that are still consistent with the measured tracer distributions. Advection in the horizontal directions is not studied.

4.3.1 Validity of Darcy's law

Laboratory and in-situ hydraulic tests and experiments in low-permeability, clay-rich lithologies are conducted with hydraulic gradients of thousands and higher, where Darcy's law has been shown to be applicable. On the other hand, the behaviour of low-permeability rocks at natural gradients (typically <1 m/m) is not well explored. There are indications that Darcy's law is not applicable in argillaceous systems at hydraulic gradients <1 m/m (Nagra 2002, Marschall et al. 2004), in that the relation between flow and hydraulic gradient is non-linear or even a threshold gradient exists below which flow is very limited, if not absent (e.g. Lutz & Kemper 1959, Miller & Low 1963, Habib 1973, Dixon et al. 1992, 1999). Such a threshold gradient is typically motivated by considering the part of the pore water in the clay rocks close to the clay surfaces as partly bound, and becoming mobile only under larger hydraulic gradients. A review of real and apparent deviations from Darcy's law is provided by Horsemann et al. (1996, ch. 11). It has been argued sometimes that methodological difficulties (e.g. measuring very low flow velocities, or matching the chemistry of the pore water in the clay in order to avoid osmotic effects) could in some cases be the reason for the reported non-linearities.

Irrespective of these uncertainties, the formalism of transport processes as presented in Section 4.2 does not rely on the validity of Darcy's law at low hydraulic gradients, and the velocity \( v_a \) may or may not be linearly related to the hydraulic gradient. In the transport simulations targeted at the possible relevance of advection in the studied low-permeability sequences, \( v_a \) was varied systematically to identify maximum advection velocities that are still compatible with the observed tracer distributions, whereas higher velocities would contradict the data (see Chapter 5). These velocities do not depend on the validity of Darcy's law. Only when corresponding hydraulic gradients are calculated from these velocities, as is done in Section 7.9 below, Darcy's law comes into play. If it is not valid in the studied natural systems, then higher gradients would be required to induce the derived advection velocity. The calculated gradients, such as those in Table 7.9-1, are therefore considered as minimum values.

4.3.2 Significance of hydraulic gradients within low-permeability sequences

Slight overpressures were found in some low-permeability sequences, such as the Opalinus Clay at Benken or the Callovo-Oxfordian at Bure. In these units, salinity has its maximum values near the centres of the low-permeability sequences and decreases towards the over- and underlying aquifers (symmetric situation). These salinity gradients could create an osmotic potential that may pull water from the boundaries towards the centre of the low-permeability sequences and, with minute amounts of water transferred, create overpressures within the clay-rich rock. In the end, the resulting hydraulic pressures will balance the osmotic gradients, such that overall zero water flow occurs. Therefore, pressure excursions within the clay-rich rocks are neglected for modelling, and the natural gradients across the low-permeability sequences are defined by the heads in the embedding aquifers.
It follows that, in symmetric situations, osmotic flow and osmotic solute flux are relatively unimportant even if the osmotic efficiency is high. In asymmetric situations where salinity does not have an apex within the low-permeability sequence but in- or decreases steadily across the sequence (such as in Boom Clay at Essen), osmotic flow would not necessarily be counteracted by a pressure build-up. There, in principle, a steady-state osmotic flow could develop, provided the presence of a sufficient chemical gradient and a sufficiently high osmotic efficiency.

4.3.3 Effective hydraulic conductivity

The studied low-permeability sequences can be considered to consist of a number of distinct units with thickness $d_i$, each with a homogeneous hydraulic conductivity $K_i$. In the case of a horizontally bedded medium with total thickness $d$, the effective hydraulic conductivity in the vertical direction ($K_z$) can be obtained from

$$K_z = \frac{d}{\sum_{i=1}^{n} \frac{d_i}{K_i}},$$

which is the harmonic mean of the hydraulic conductivities of the individual beds, weighted for bed thickness (Freeze & Cherry 1979).

4.3.4 Dispersion length and dispersion coefficient

In aquifers, hydrodynamic dispersion has been recognised to be a function of the scale of observation. Gelhar et al. (1992) proposed that the longitudinal dispersion length is about 1 – 10% of the observation scale, whereas other studies propose non-linear relationships with exponents of 0.5 – 1.5 (Schulze-Makuch 2005, Neuman 2006). For low-permeability formations in which matrix flow dominates, little experimental knowledge is available on hydrodynamic dispersion. In principle, the process is linked to the scale at which heterogeneities occur in the medium. For the considered formations, this is most likely the scale of the maximum grain size.

The pore dispersion coefficient contains the contributions of diffusion and of hydrodynamic dispersion according to

$$D_p^* = D_p + a_L v_a$$

where

$D_p^*$ = pore dispersion coefficient (see advection-dispersion equation in Section 4.2)
$D_p$ = pore diffusion coefficient
$a_L v_a$ = hydrodynamic dispersion coefficient (dispersion length * advection velocity).

Considering a high (for low-permeability sequences) hydraulic conductivity of 1E-12 m/s, a high hydraulic gradient across the sequence of 10 m/m and a low flow porosity of 0.05 yields, according to Darcy's law (Section 4.2.1), an advection velocity of 2E-10 m/s. With a high dispersion length of 1E-2 m (i.e. about 10 times the maximum grain size), a hydrodynamic dispersion coefficient of 2E-12 m$^2$/s is obtained, which is considered to be a maximum due to the choice of the underlying parameter values. Nevertheless, the value of the calculated hydrodynamic dispersion coefficient is at least one order of magnitude below the pore diffusion coefficients listed in Table 3.2-1. It is concluded that hydrodynamic dispersion in sedimentary low-permeability sequences is of minor importance, and that the pore dispersion coefficient is dominated by molecular diffusion.
4.3.5 Flow porosity

Flow porosity characterises the fraction of the water-filled porosity that can be mobilised by applying a hydraulic gradient. Current knowledge about the relationship between water-accessible porosity and flow porosity in clay-rich rocks is limited, but typically not the whole accessible porosity can be hydraulically mobilised (Nagra 2002, ch. 5.4). Flow porosity also depends on the magnitude of the hydraulic gradient, on the structure of the diffuse double layer (and therefore on mineralogy and on pore-water salinity), on the geometry of the pore space and on species (water, anions, cations):

- If advection is slow (as is the case in clay-rich natural systems), diffusive exchange of species in free pore water and in bound water will occur. In this case, the whole water-accessible porosity must be attributed to flow porosity because, on a macroscopic scale, no distinction can be made between advective flow in free water and the “retardation” occurring via diffusive exchange with species in bound water. In practice, this applies to water itself, to cations and to neutral species. For these species, the whole water-accessible porosity is thought to best represent flow porosity.

- Diffusive exchange between flowing and bound water does not occur for anionic species due to anion exclusion. For the purpose of this report, flow porosity for anions is approximated by the anion-accessible fraction of porosity, typically 0.4 – 0.5 times the water-accessible porosity.

An in-depth discussion of these considerations for Opalinus Clay is available in Gimmi (2003).

4.4 Temperature dependence of diffusion coefficients

Laboratory determinations of diffusion coefficients typically refer to a temperature around 20 °C, whereas in-situ temperatures may be slightly lower to significantly higher. Because the mobility of solutes strongly increases with rising temperature (the decreasing viscosity of water being one reason), the temperature dependence needs to be considered in modelling. According to Fick’s laws, diffusion coefficients appear in the equations as products \( D \times t \), with \( t \) = diffusion time. Thus, the consideration of the temperature dependence of diffusion coefficients affects the modelled evolution times of the tracer profiles. If long evolution times are considered, the in-situ temperature may change over the modelled period. For example, temperature decreased markedly at Mont Terri due to uplift and erosion over the last few Ma. In such cases, a time-dependent temperature correction was applied. The formalism of the temperature correction is presented in detail in Appendix A3.1. Note that while temperature corrections were made for modelling, the original laboratory values of diffusion coefficients are reported in Chapters 2 and 3.

4.5 Temperature dependence of \( \delta^{18}O \) and \( \delta^2H \) in precipitation

At many of the study sites, the isotopic composition of water \( (\delta^{18}O, \delta^2H, \hat{^3}H) \) in the embedding aquifers indicates that the water represents recent recharge. Palaeo-hydrogeological arguments suggest that frequently the boundaries of the low-permeability sequence were defined by young, locally infiltrated meteoric water over long periods of time in the past. The complication in this simple scenario is the fact that \( \delta^{18}O \) and \( \delta^2H \) in precipitation vary with surface temperature, which changed over time in response to climate fluctuations (for example during glacial cycles). In general, there is no direct method to constrain the isotopic composition of precipitation in the geological past because these waters have long been flushed away. Therefore, an indirect approach is used here, based on the (reasonably well known) surface temperature variation over time. A detailed description is provided in Appendix A4.1.
4.6 Sea-water composition over geologic time

All sedimentary sequences considered here originated from marine environments, and some were affected by several stages of emergence and transgression since the time of deposition. In certain cases, it is justified to consider sea water as the initial condition for modelling the observed tracer profiles, and in other cases this is simply assumed as a working hypothesis without independent confirmation. The question how constant sea-water composition was over geologic time is addressed in Appendix A4.2.

4.7 Systematics of $\delta^{37}Cl$

A short documentation of fractionation processes of $^{35}Cl$ and $^{37}Cl$, their relative mobility and the approaches to modelling profiles of $\delta^{37}Cl$ is provided in Appendix A4.4.

4.8 General modelling approach

We attempt to reach the aims presented in Section 4.1 by simulating the development of tracer profiles within the aquitards and comparing the simulation results with the measured data. In general, we follow a forward modelling strategy. That is, we use boundary conditions inferred from the palaeo-hydrogeological evolution and transport parameters determined in laboratory or field experiments to reproduce the observed concentration profiles. A good match between data and simulations is taken as evidence that the considered processes and chosen input parameter values could be appropriate. In cases where the evolution of the boundary conditions over time is uncertain, an inverse approach may also be used. Here, initial or boundary conditions, or parameter values are adjusted until the simulated profiles match with the observed data. In view of the large number of unknowns, this is clearly a difficult task. Thus, we have always tried to constrain the input data as much as possible by independent evidence.

Ideally, one would like to perform a "complete" simulation starting at the time of deposition of the sediment and running it until today. Whereas such a procedure may be feasible and promising in the case of young deposits such as glacial tills, it is considered to be very difficult, if not impossible, in the case of formations with ages of tens of millions of years or more. In such formations, diagenetic processes (e.g. compaction, cementation) occurred and affected relevant formation properties, such as porosity and transport behaviour. A complete calculation would require a fully coupled modelling of thermal, mechanical, hydraulic, and geochemical transformation processes over very long time scales, with varying parameters and under varying boundary conditions, both of which are essentially unknown.

In practice, it is difficult to characterise reasonably the palaeo-hydrogeological evolution and notably the precise boundary conditions at a site beyond ca. 10 Ma before present, or even less. Thus, it is of limited use to embark on modelling efforts over longer time scales. The fact that the effects of older events on a tracer profile may be largely obliterated by the younger evolution is an advantage because it limits the degree of detail to which the older evolution must be known for the purpose of modelling. For example, a long lasting marine transgression at some stage may lead to total equilibration of pore water in the aquitard with the sea water circulating in the bounding aquifers. In such a case, the transgression can be taken as the initial condition for modelling the younger evolution, without the need to know anything of the long history prior to the transgression. Another potential simplification lies in the fact that the effects of oscillatory events, such as glacial cycles, may average out and need not be characterised in full detail. In order to estimate what type of averaging or which simplifications are permissible, one can calculate relaxation times (or distances) and propagation times.

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(or distances) for various types of disturbances at the boundaries. We illustrate this in the next section.

4.9 Temporal variation of the boundary conditions

A perturbation of a solute concentration at the boundary propagates through the aquitard with time. In case of advection, the propagation velocity equals the flow velocity

\[ v_a = \frac{q}{n} = -\frac{K}{n} \frac{\partial H}{\partial z} \]

and is constant (assuming constant hydraulic conductivity K, hydraulic head H and porosity n). In case of one-dimensional and one-sided diffusion, the propagation velocity decreases with time t or distance z travelled. The average propagation velocity up to a distance z can be estimated as

\[ v_d = \frac{D_p}{z} = \sqrt{\frac{D_p}{t}} \]

where \( D_p \) = pore diffusion coefficient (assumed to be constant).

Conversely, we can estimate times required to propagate a perturbation from one boundary through an aquitard of a given thickness, as outlined in Section 4.2.

Table 4.9-1 lists examples of propagation velocities and propagation times for advection and diffusion calculated for parameters that are typical for moderately indurated argillaceous formations. It is evident that for short distances, diffusion is a more efficient transport process than advection, and vice versa (a statement inherent in the Peclet number as defined above).

Table 4.9-1: Propagation velocities and propagation (or relaxation) times for the propagation of a perturbation at the boundary through an aquitard

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>Z = 1 m</th>
<th>Z = 10 m</th>
<th>Z = 100 m</th>
<th>Z = 200 m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Advective velocity ( v_a )</td>
<td>m/ka</td>
<td>0.032</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diffusive velocity ( v_d(z) )</td>
<td>m/ka</td>
<td>3.2</td>
<td>0.32</td>
<td>0.032</td>
<td>0.016</td>
</tr>
<tr>
<td>Advevtive propagation time ( t_a(z) )</td>
<td>ka</td>
<td>32</td>
<td>320</td>
<td>3 200</td>
<td>6 300</td>
</tr>
<tr>
<td>Diffusive propagation time ( t_d(z) )</td>
<td>ka</td>
<td>0.32</td>
<td>32</td>
<td>3 200</td>
<td>12 700</td>
</tr>
</tbody>
</table>

Parameters used for the calculations: \( K = 1E-13 \) m/s, \( \partial H/\partial z = -1 \), \( n = 0.1 \), \( D_p = 1E-10 \) m²/s

4.9.1 Stepwise changes in the boundary condition

The velocities and propagation times of Table 4.9-1 are relevant for constant boundary conditions, as shown schematically by the blue line in Figure 4.9-1. If the boundary condition varies stepwise over time, we can compare the calculated propagation times with the duration of the intervals with constant values at the boundary:

- If the propagation time is smaller than the intervals of constant boundary conditions (green line in Figure 4.9-1), averaging of boundary conditions over time is not possible, but probably also not required. The tracer concentration at the boundary during the most recent interval is the most important one for the considered profile in the aquitard. The concentrations at the boundary of
the second-but-last and possibly the previous interval have to be considered in the assignment of
the initial conditions only. All older intervals are obliterated and did not leave any resolvable
traces in the present tracer profile.

- If the propagation time for diffusion or advection is much longer than the intervals of constant
values at the boundary (red line in Figure 4.9-1), one has to consider the time sequence of
boundary values. However, using averaged concentrations at the boundary may be possible in
certain cases (i.e. when diffusion dominates) and leads to approximately correct results for large
parts of the aquitard.

**Figure 4.9-1: Schematic representation of tracer propagation time in the aquitard and evolution of the
boundary condition in the bounding aquifer**

These considerations are illustrated in Figure 4.9-2 in a more quantitative way. There, generic
calculations are shown for a 200 m thick aquitard with the same properties as those used in
Table 4.9-1. The initial condition is zero tracer concentration, and it is assumed that the bottom of the
model does not influence the concentrations in the overlying aquitard (semi-infinite system).
Simulations are shown for diffusion induced by either a constant boundary condition with a nominal
concentration of 0.75 g/L, or for a boundary condition changing stepwise between 0.5 and 1 g/L, i.e.
with an amplitude of 0.25 g/L. For the latter case, periods $t_p$ for the oscillations at the boundary of
10 ka (Figure 4.9-2a), 100 ka (Figure 4.9-2b) and 1 Ma (Figure 4.9-2c) were chosen, and the shapes of
the resulting tracer profiles in the aquitard are shown for different times. For the given parameters, the
diffusive propagation time $t_d$ for the 200 m thick aquitard is about 13 Ma (Table 4.9-1). For a period of
10 ka (Figure 4.9-2a), which is clearly smaller than the diffusive propagation time, the alternating
values at the boundary affect only the uppermost about 10 m. For most of the profile, neglecting the
temporal variation and using a constant average value at the boundary leads to results nearly
indistinguishable from those for alternating values at the boundary. For a period of 100 ka
(Figure 4.9-2b), the situation is still similar, with a slightly larger region – about the uppermost 40 m –
affected by the periodically changing boundary values. Only when the period is approaching the
diffusive propagation time of about 13 Ma (Figure 4.9-2c, $t_p = 1$ Ma), averaging the boundary values
over time is no longer permissible. In this case, a large part of the profile is influenced or even
dominated by the latest values at the boundary. However, a reasonably close approach to the real
situation is to use a constant average value for most of the simulation time but consider the last change
(or the last two changes) in the boundary explicitly. This means that in this case the last change in
boundary conditions is dominant, and earlier changes can well be averaged (except for the region very close to the boundary). From the computational standpoint, this is equivalent to starting the simulation only at the time of the last change and use the average value as an initial condition.

Figure 4.9-2: Simulations of diffusive transport of a tracer across a 200 m thick aquitard with $D_p = 1E-10$ m$^2$/s, considering a step function for the evolution of the upper boundary

The initial concentration is 0, and a semi-infinite system was considered. Solid lines refer to a constant upper boundary condition of 0.75 g/L. Dashed lines refer to an upper boundary condition that varies stepwise between values of 0.5 and 1 g/L, with a period $t_p$ of 10 ka (top), 100 ka (centre) and 1 Ma (bottom).
More smoothly changing boundary conditions may be approximated by a sinusoidal function. Such a simplification allows extracting some typical features of the propagation of the boundary values into the aquitard. A temporal sine wave of the concentration with amplitude \(A_0\) and period \(t_p\) at the upper boundary creates (neglecting the initial phase) a spatial concentration wave that propagates down through the aquitard. This depth wave has a wavelength \(\lambda\):

\[
\lambda = 2 \sqrt{\pi D_p t_p}
\]

and a depth-dependent, damped amplitude \(A\) of

\[
A = A_0 \exp \left( -z \frac{\pi}{\sqrt{D_p t_p}} \right)
\]

(Carslaw & Jaeger 1959). Over a distance of one wavelength \(\lambda\), the amplitude \(A_0\) is reduced to 0.0019 times its value at the boundary; a damping to 10% of \(A_0\) is reached within a distance \(z_{0.1}\) of

\[
z_{0.1} = \frac{\lambda}{2} \frac{\ln(10)}{\pi} = \frac{\ln(10)}{2} \sqrt{\frac{D_p t_p}{\pi}}.
\]

The concentration fluctuations, that is the maximum and minimum concentrations, are propagated into the aquitard with a velocity \(v_d(t_p)\)

\[
v_d(t_p) = 2 \sqrt{\frac{\pi D_p}{t_p}}.
\]

These equations show, similarly to the calculations made in Section 4.9.1, that oscillations of the boundary concentration with a short period are very efficiently attenuated with depth, whereas those with longer periods penetrate further into the aquitard. Also, shorter periods at the boundary lead to short wavelengths, that is, create short-distance concentration variations in the aquifer, whereas long periods lead to variations over longer distances. Figure 4.9-3a shows the damping of the amplitude with depth for a \(D_p = 1E-10\) m²/s. In Figure 4.9-3b, the wavelength \(\lambda\) and depths \(z\) for an attenuation of the amplitude to 1% or 10% of the surface value are shown as a function of the period \(t_p\) of the boundary oscillation for the same \(D_p\):

- For a period \(t_p\) of 10 ka, 100 ka, and 1 Ma, the corresponding wavelengths for the distribution of tracer concentration with depth are about 20 m, 63 m, and 200 m, respectively.
- The penetration depth of an oscillation (expressed as the damping to 1% of the boundary value) with a period of 10 ka is only about 15 m, depths for periods of 100 ka and 1 Ma are about 50 m and 150 m for the chosen \(D_p\) value. Thus, we see the same behaviour as in Figure 4.9-2 for the stepwise constant boundary condition\(^\text{14}\).

\(^\text{14}\) We note in passing that the stepwise changing of the boundary conditions shown in Figure 4.9-2 is actually a square wave that can be represented by a series of sine waves. The period of the square wave is determined by the lowest harmonic and the sharp changes are due to the higher harmonics (with shorter periods). Because the higher harmonics with shorter periods are more strongly attenuated with depth than the lower harmonics, their effect disappears more quickly and the square wave becomes gradually a sinusoidal wave with depth. Also, in general, any periodic boundary condition can be represented as a Fourier series, that is, it can be decomposed in a series of harmonic functions.
4.9.3 Conclusion

Periodic boundary conditions represent only a special and idealised situation for the evolution of aquifers embedding aquitards. Nevertheless, consideration of such idealised situations allows drawing some general conclusions. Clearly, when simulating the evolution of tracer profiles, times much larger than the estimated propagation times for a given aquitard need not be considered explicitly. Instead, one can take their effects into account when defining the initial conditions. Loosely speaking, one can say that an aquitard has a detailed memory only for about the estimated propagation time. Older events leave their traces in a more diffuse form, which may be captured in terms of the initial condition for subsequent events. For a 200 m thick aquitard with a Dp of 1E-10 m\(^2\)/s and insignificant advection, overlain by an aquifer, the propagation time is in the order of 13 Ma (Table 4.9-1), and it is very likely that events that occurred at times before 10 Ma ago left only a diffuse background signature but no distinct peaks or concentration patterns. This means that it is permissible to limit the modelling efforts to times somewhat longer than the propagation time and not consider the older evolution explicitly.

Near-periodic boundary conditions may be appropriate to represent the situation during the ice ages. The generic calculations presented above indicate the degree to which such perturbations should be considered explicitly. For an aquitard with properties given as in Table 4.9-1, periods of 10 ka and 100 ka are expected to leave their signatures only in the upper about 15 and 50 m of the aquitard.

4.10 Vertical heterogeneity of parameters

4.10.1 Variation of porosity

Clay-rich aquitards, as any other sedimentary rocks, may have been deposited under variable conditions and so may exhibit a vertical heterogeneity with respect to mineralogy, porosity, permeability and diffusion coefficients. Heterogeneities at very small scale are averaged out in the definition of the representative elementary volume (REV) that is the basis for the continuum-scale
transport equations and which is typically two or more orders of magnitude larger than the pore scale. Parameter heterogeneities beyond the REV scale need to be considered explicitly in the modelling of the tracer profiles. However, similarly as in case of temporal variations at the boundary, spatial parameter variations over distances clearly (i.e. more than one to two orders) smaller than the total thickness of the aquitard affect the simulations only slightly so that average parameters can be used. We illustrate this in Figure 4.10-1 with two simulations for $\delta^2$H data in Opalinus Clay at Benken. In one case, we assumed a constant porosity of 0.12 throughout the formation, in the other case we took into account variable porosities as estimated from various geophysical borehole logs (Nagra 2001) and shown on the left side of the Figure. In both cases, the simulations were performed for pure diffusion with a diffusion coefficient $D_p = 7.7E-11 \text{ m}^2/\text{s}$ (15) and constant boundary conditions on both sides. At locations with relatively large changes in the estimated porosity, e.g. at depths of about 440 m and about 660 m, some deviations between the two simulations occur. There, the development of the profile is somewhat slowed down. However, the differences are small compared to the errors of the data. Also, the uncertainty of the porosity estimated from the borehole logs is rather large; the values may be affected by local borehole collapse, and some of the heterogeneity may be due to artefacts. It is concluded that, while spatial heterogeneity of transport parameters should be considered if the scale of the heterogeneity is a significant fraction of the total formation thickness and the variability of the parameter in question is substantial, small heterogeneities can generally be averaged out without a major loss of precision.

Figure 4.10-1: Tracer profile of $\delta^2$H at Benken (from Figure 2.3-3) and simulations for 0.7 Ma considering constant (base case, same parameters used as in Figure 5.3-1), or heterogeneous porosity in the low-permeability sequence

![Tracer profile of $\delta^2$H at Benken](image)

Left: Porosity from geophysical logging (grey line; Nagra 2001, 2002), laboratory analyses (red diamonds) and values used for modelling (blue and orange lines)

15 Laboratory value of 5.3E-11 m$^2$/s multiplied by a factor of 1.45 accounting for the in-situ temperature of 33 °C.
4.10.2 Variation of temperature

In case of thick aquitards, temperatures may vary and notably increase with depth. Temperature gradients can act as an additional driving force and induce solute transport, and they certainly affect the values of the pore diffusion coefficients. We use the situation at Benken, where the thermal gradient is particularly elevated, for a scoping calculation. The temperatures along the borehole (Nagra 2002) are shown on the left side of Figure 4.10-2. For Opalinus Clay at Benken, Van Loon et al. (2005) determined the temperature dependence of $D_p$ for water tracers, as discussed in Appendix A3.1. Using a reference value of 7.7E-11 m$^2$/s for a depth of 570 m (corresponding to the value at 33°C), we calculated temperature-corrected $D_p$ values for the whole profile. On the right side of Figure 4.10-2, simulations for $^2$H are presented for both a constant $D_p$ value of 7.7E-11 m$^2$/s and for the temperature-dependent values. The simulations for variable $D_p$ do not consider any additional driving force for solute transport. There is only a small difference between the two simulations, indicating that the effects of the temperature variations considered in this simulation are minor.

4.10.3 Conclusion

The general strategy to be followed is of course to take into account the heterogeneity of transport parameters if it is well known or can be estimated reliably, and if the values are considered as relevant over the whole time period of the simulation. If no reliable estimates about the vertical heterogeneity of porosity, permeability, and pore diffusion coefficient are available, it appears that the use of constant, average parameters often introduces only a relatively small error in the simulations compared to the typical uncertainties of the measurements.

Figure 4.10-2: Tracer profile of $^2$H at Benken (from Figure 2.3-3) and simulations for 0.7 Ma considering a constant (base-case, same parameters used as in Figure 5.3-1) or a temperature-dependent pore-diffusion coefficient in the low-permeability sequence

Left: Borehole temperature from Nagra (2001) and temperature-dependent relative pore-diffusion coefficient calculated using the experimental data of Van Loon et al. (2005)
4.11 Gaps and challenges

At many sites, only one single borehole is available, and little is known about the lateral heterogeneity of tracer profiles and boundary conditions. Even in situations where data were obtained from several boreholes, it may be difficult to obtain a full three-dimensional picture. Also, the bounding aquifers may be heterogeneous, and the evolution of the boundaries at different location may be different. Thus, lateral heterogeneity remains an issue that, due to the current lack of relevant information, cannot be rigorously addressed at the present stage.

Having data on several different tracers at one location is definitely an advantage when trying to interpret the observations. The data can provide complementary information that helps to constrain the modelling. However, care must be taken because the evolution of boundary conditions may be quite different for different tracers. For example, varying surface temperatures as occurring during glacial cycles may substantially affect water isotopes but not necessarily anions.
5. RESULTS OF MODEL CALCULATIONS

Model runs are called “base-case” calculations if the simulations explain the measured data reasonably well with input parameters and scenarios that are within the independently derived ranges. All base cases consider diffusion as the only transport process—not by definition but due to the observation that adding advection does not improve the model fits to the data. In contrast, “scoping” or “alternative” models refer to cases that purposely deviate from known palaeo-hydrogeological scenarios and ranges of input parameters, or to cases that are not sufficiently well constrained by independent information and therefore remain on a hypothetical level.

5.1 Callovo-Oxfordian at the Site Meuse/Haute Marne (Bure), France

5.1.1 Anions

URL site: boreholes EST211 and EST212

The profiles of boreholes EST211 and EST212, based on rock leaching by Waber (2005), squeezing and direct sampling yield the most clearly defined, curved Cl⁻ profiles at the URL site (Figure 2.1-5). In EST211, maximum Cl⁻ contents are observed in the centre of the low-permeability sequence, with decreasing concentrations towards the aquifers. Unfortunately, there are no tracer data from the Dogger limestone in EST211 and EST212, so some uncertainty remains in the lower part of the profiles. Nevertheless, the regularity and curvature of the profiles suggests that diffusion may be the most relevant transport process. When trying to quantify this hypothesis and using the aquifer concentrations observed at present as boundary conditions, two unknowns remain, namely 1) the initial Cl⁻ content in the low-permeability sequence before flushing of the aquifers started and 2) the evolution time. Due to the limited knowledge of the palaeo-hydrogeological evolution and the absence of well characterised and dated events, there are no clear constraints on these parameters. Figure 5.1-1 shows the results of model calculations for EST211, considering diffusion as the only transport process and assuming the synchronous activation of both aquifers at a specific time. The chosen Cl⁻ initial concentrations range between the highest value currently observed in the centre of the formation (2150 mg/L) and the sea-water value (19350 mg/L). Figure 5.1-1 shows that for all initial concentrations, good fits to the data can be found when the evolution time is used as a free parameter. The best-fit evolution time is 1.2 Ma for Cl_{init} = 2150 mg/L and increases with increasing Cl_{init}. The model curves for Cl_{init} = 5000, 10000 and 19350 mg/L are identical within line thickness in the graph, and the evolution times are 5.3 – 11 Ma. Figure 5.1-2 shows the same type of calculation for EST212. Similarly, good model fits are obtained, but evolution times for a given Cl_{init} are slightly longer than for EST211 because the curvature in the spatial distribution of the data is smaller.

The assumption of spatially constant initial conditions as made in the previous simulations can be justified by the long interaction and diffusion times since deposition of the sediments. However, other initial concentration distributions may also be considered. A linear increase of the concentrations with depth before the flushing of the lower aquifer, similar to that (still?) observed in EST311/312, is also conceivable. Accordingly, we made simulations starting from a linearly increasing concentration distribution with depth, with a maximum value of 3960 mg/L (value measured in the Dogger aquifer...
of EST312) or 5,000 mg/L at the lower boundary. For the former, the fits are somewhat worse in EST211, for the latter they are similar to those obtained with uniform initial concentrations. The calculated best-fit evolution times are about 1.2 and 2 Ma, respectively, for EST211, and about 5 and 6 Ma, respectively, for EST212 (Figure 5.1-3). We note that these times are within the range obtained for the low or high uniform initial conditions.

The Cl⁻ data of EST211 and EST212 differ considerably at larger depths, with lower values for EST212. Because EST211 is an inclined borehole (Figure 2.1-4), there is a lateral distance of about 240 m to 560 m between the locations of the Callovo-Oxfordian samples of the two boreholes at a specific depth below surface. The question arises whether 1) the data could reflect lateral variability, and, if so, 2) a 1D approach for modelling Cl⁻ is appropriate. The inclination of the borehole means that the data of EST211 may possibly not represent the 1D vertical situation correctly. Assuming an increase of concentrations with distance from borehole EST212, Cl⁻ concentrations in EST211 at greater depths could be higher than those that would be obtained for a vertical profile. In principle, one could try to calculate back a vertical profile from the data of both boreholes, assuming a linear trend in Cl⁻ concentrations with distance. Because of the relatively small number of samples, however, we did not attempt to correct for this effect.

Lateral concentration heterogeneities are expected to smooth out over time by diffusion, and the question arises over which time this would occur. As a rough estimate, we can calculate the diffusive propagation time defined in Section 4.2 as \( t_d = \frac{x^2}{D_p} \), which indicates the time until the centre of a step change would reach a distance \( x \). The front of this step change would propagate about a factor 2 faster. Using a \( D_p \) parallel to bedding two times larger than that perpendicular to bedding, we obtain times between about 8 to 45 Ma (front) or 16 to 90 Ma (centre) for distances between 240 and 560 m. From this estimation we see that, (a), lateral concentration heterogeneities could persist over quite long times, and, (b), 1D approaches for the two profiles may be a reasonable approximation for evolution times lower than about 8 Ma, but are probably inappropriate for evolution times larger than 8 to 16 Ma.

It is concluded that the observed data can be well reproduced considering diffusion as the only transport process. Because of the limited knowledge of the palaeo-hydrogeological evolution, a range of combinations of initial Cl⁻ concentrations and evolution times fit the data equally well, and so it is not possible to define a single base case.

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16 Vinsot (pers. comm.) argues that it is currently not clearly established whether the different Cl⁻ contents at the same stratigraphic level in EST211 and EST212 are indeed significant and so represent lateral heterogeneity. While the same laboratory protocols were used for samples from both boreholes and the same procedures were followed to calculate in-situ Cl⁻ contents, differences exist in drilling techniques and other procedures. Future drilling campaigns are expected to shed light on this issue.
Figure 5.1-1: Model for Cl\(^-\) in borehole EST211 at the Bure URL site considering a constant initial Cl\(^-\) concentration

Blue bars indicate ground waters. Only diffusive transport is considered. \(t\) = evolution time since activation of the aquifers.
Model runs COX BUR A1 (Cl\(_{\text{init}}\) = 2 150 mg/L), COX BUR A2 (Cl\(_{\text{init}}\) = 5 000 mg/L), COX BUR A3 (Cl\(_{\text{init}}\) = 10 000 mg/L), COX BUR A4 (Cl\(_{\text{init}}\) = 19 350 mg/L)

Figure 5.1-2: Model for Cl\(^-\) in borehole EST212 at the Bure URL site considering a constant initial Cl\(^-\) concentration

Blue bars indicate ground waters. Only diffusive transport is considered. \(t\) = evolution time since activation of the aquifers.
Model runs COX BUR A5 (Cl\(_{\text{init}}\) = 1 432 mg/L), COX BUR A6 (Cl\(_{\text{init}}\) = 2 500 mg/L), COX BUR A7 (Cl\(_{\text{init}}\) = 5 000 mg/L), COX BUR A8 (Cl\(_{\text{init}}\) = 10 000 mg/L), COX BUR A9 (Cl\(_{\text{init}}\) = 19 350 mg/L)
Figure 5.1-3: Models for Cl⁻ in boreholes EST211 and EST212 at the Bure URL site considering initial Cl⁻ concentrations increasing with depth

Blue bars indicate ground waters. Linearly increasing initial condition as shown by straight lines, from value in Oxfordian aquifer to 3 960 mg/L (blue) or 5 000 mg/L (green) in Dogger aquifer before activation of the latter. Only diffusive transport is considered. Model curves are shown for evolution times $t$ that best fit the data. Model runs COX BUR A10 ($C_{\text{in},\text{max}} = 3 960 \text{ mg/L, 1.2 Ma [EST211] and 5 Ma [EST212]}$), COX BUR A11 ($C_{\text{in},\text{max}} = 5 000 \text{ mg/L, 2 Ma [EST211] and 6 Ma [EST212]}$)

Regional boreholes EST311/312 and HTM102

Data sets for several of the regional boreholes are incomplete and/or scattered (Figure 2.1-6). The only borehole that appears suited for quantitative treatment is EST312, even though the tracer profile is also incomplete. The interesting point is that the Dogger aquifer is more saline than at any other location of the Bure region and contains about 4 g/L Cl⁻. The Oxfordian aquifer has been sampled in borehole EST311 drilled from the same platform. The Cl⁻ data in the low-permeability sequence show a linear increase with depth and roughly connect the ground-water concentrations in the bounding aquifers. In principle, they could record a steady-state diffusion profile. Model calculations for different initial Cl⁻ contents are shown in Figure 5.1-4. The evolution times for a steady-state profile vary between about 10 – 15 Ma ($C_{\text{in}} = 3 960 \text{ mg/L, the current value in the Dogger aquifer}$) and 20 – 25 Ma ($C_{\text{in}} = 19 350 \text{ mg/L, the sea-water value}$). These evolution times are comparatively long to those obtained at the URL site. Only when considering initial Cl⁻ concentrations below the current value in the Dogger aquifer, would shorter evolution times be obtained.

The data for the borehole HTM102, which is located about 3 km to the southeast of the URL site, are rather scattered and incomplete. We nevertheless considered them for modelling, because $\delta^{37}\text{Cl}$ data are also available. The Cl⁻ concentrations tend to increase slightly with depth within, and more strongly below the Callovo-Oxfordian shale. Unfortunately, neither the location of the Dogger aquifer is known, nor are the Cl⁻ concentrations in ground waters from any of the aquifers available. For the simulations, we assumed a thickness of 54 m of the low-permeability Dogger limestone above the aquifer. We considered a low Cl⁻ concentration of 83 mg/L (value of HP1 at the Bure URL site) for the Oxfordian aquifer, and 2 176 mg/L for the Dogger aquifer (approximated by the deepest pore-water sample in the low-permeability sequence) and as initial condition. The simulated profiles approach the measured data for minimum evolution times of about 6 to 15 Ma, i.e. when approaching steady state.
Nevertheless, given the scatter of the data, the match is not convincing. An improved match and shorter evolution times could be obtained by assuming a lower initial concentration, but this appears unlikely from a palaeo-hydrogeological perspective because it would imply a salinity increase over time at the lower boundary. Using higher initial concentrations, the times to approach the steady state would become longer. It is concluded that while scenarios exist that reasonably well reproduce the data, the calculations remain on a hypothetical level because several parameters are essentially unknown, so the choices made for the calculations cannot be defended.

Figure 5.1-4: Models for Cl\(^-\) in borehole EST312, 13 km northeast of the Bure URL

Blue bars indicate ground waters. Only diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the aquifers. Model runs COX 312 A1 (Cl\(_{\text{init}}\) = 3,960 mg/L), COX 312 A3 (Cl\(_{\text{init}}\) = 19,350 mg/L)

Figure 5.1-5: Scoping models for Cl\(^-\) in borehole HTM102, 3 km southeast of the Bure URL

Only diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the upper aquifer. Model run COX 102 A3 (Cl\(_{\text{init}}\) = 2,176 mg/L)
5.1.2 Water isotopes

Stable-isotope data are only available from boreholes at the URL site (Figure 2.1-7). δ values increase in the upper half of the low-permeability sequence and reach a maximum approximately in the centre (disregarding some outliers). There is a trend towards more negative values in the lower half of the profile, but the data are more scattered, especially for δ2H. Taking the highest δ values observed in the low-permeability sequence as initial values (again disregarding some outliers) and assuming the simultaneous activation of both aquifers, characterised by present-day δ values, leads to model calculations shown in Figure 5.1-6. The upper half of the profile can be roughly represented by a diffusion time around 1 Ma, i.e. similar to the 1.2 – 2 Ma derived for Cl- for the same scenario.

On the other hand, the lower half is not well reproduced by the model due to the complexity of the data. In particular, the relative minimum of δ values at ca. 520 m depth is not captured by the model. The origin of this local excursion in the data is not clear. In principle, this excursion could record a stage of lower δ values in the Dogger aquifer in the past. Based on this working hypothesis, a number of model calculations considering various parameter combinations were made and clearly indicate that it is impossible to reproduce the sharp excursion of the data just by varying the lower boundary condition over time. In particular, the signal of a stage with low δ values in the Dogger aquifer will be damped when it propagates into the low-permeability sequence over time. When the signal reaches the depth where the data show a relative minimum, it has already lost most of its amplitude and so does not yield a noticeable relative minimum (see also discussion in Section 4.9).

As long as the system geometry, in particular the depth of the Dogger aquifer, is not disputed, the lower part of the profile cannot be satisfactorily reproduced by model calculations. The fact that the data, in particular those for δ2H, show a significant local scatter suggests that problems related to sample preparation and analysis may be important. Moreover, almost no tracer data are available from the Dogger limestone overlying the aquifer horizon.

As for Cl-, the initial condition is not well constrained, and the δ values could have been higher than the currently observed maxima in the centre of the low-permeability sequence. The data points from the deep Dogger indicate δ values increasing with depth (Figure 5.1-6), and underlying Triassic brines in the central/eastern Paris Basin have δ18O up to 0 ‰ and δ2H of about -25 ‰ (Dewonck 2000). In Figure 5.1-7, δ18O = δ2H = 0 ‰ is assumed as the initial condition. As for Cl-, the shape of the best-fit model curve is near-identical to the case where negative initial δ values were assumed, but the evolution time increases to about 4 Ma. At the present stage, it is not possible to judge which case represents the more realistic situation. However, it appears unlikely that the initial δ values were >0 ‰, which means that, in the framework of the assumptions that were made, the evolution time of 4 Ma can be considered as a maximum. Because the available data are scattered (and so model fits based on simple scenarios cannot well explain them) and because the palaeo-hydrogeological evolution is not known well enough to justify well-defined scenarios, the uncertainty is substantial, and modelling remains on the level of scoping calculations.

5.1.3 Helium

A He profile is available from boreholes EST211 and EST212 at the Bure URL site. The in-situ production rate of He within the Callovo-Oxfordian of about 6.5E-12 cm³ STP/gwater/ a can be calculated from the U and Th contents given in Table 2.1-5. Multiplying this number by the time since deposition of the sediment (155 Ma) leads to a pore-water concentration of roughly 1E-3 cm³ STP/gwater. This value can be considered as the maximum He concentration that could be reached in the pore water, assuming that no loss from the formation had occurred (which is unlikely)
and that all the He produced had been released from the rock to the pore water (a good assumption, see Bigler et al. 2005). Comparing this number with the maximum concentrations of about 6E-5 cm³ STP/gwater in the lower part of the profile, it becomes clear that most of the He that has been produced since the deposition of the sediments has left the low-permeability sequence. However, the details of when and how this loss occurred and to what extent He was added to the system from underlying units are not known. Thus, it is not possible to define well-supported initial conditions for He.

Figure 5.1-6: Model for water isotopes at the Bure URL site, assuming maximum observed δ values as initial condition

Blue squares indicate ground waters. Only diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the aquifers. Model run COX BUR W1

Figure 5.1-7: Model for water isotopes at the Bure URL site, assuming δ¹⁸O = δ²H = 0 as initial condition

Blue squares indicate ground waters. Only diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the aquifers. Model run COX BUR W2
As a second uncertainty, it is not clear whether the profile observed today represents a transient state as in case of Cl⁻ or the stable water isotopes, or whether a steady state where production balances the (advective or diffusive) loss was established. In the case of steady state, the profile does not contain information about the evolution time, except that it has to be long enough to allow stationarity.

In this report, only the profile between the Oxfordian and Dogger limestones is considered. Bigler et al. (2005) also included three points below the Dogger aquifer in their modelling. These points show a strong increase of He concentrations with depth (Figure 2.1-8). However, the system below the Dogger aquifer is not well constrained (transport parameters, existence of deeper aquifers or other boundaries, etc.) and therefore not treated here. The prominent change of the depth gradient of He contents at the level of the Dogger aquifer suggests that He currently diffusing upwards from depth is removed laterally via flow in this aquifer.

Steady-state calculations

The simulated steady-state concentrations using diffusion parameters given in Section 2.1.4 (Dp three times that of water tracers, see Appendix A3.2) are shown in Figure 5.1-8. The simulated steady-state profile (shown in blue in Figure 5.1-8) underestimates the measured He concentrations. This means that either the He data do not represent a steady state, or that some of the used parameters are incorrect. A better match between the data and a steady-state situation can be obtained by decreasing the diffusion coefficient in the Oxfordian limestone, or by increasing it in the Dogger limestone. Figure 5.1-8 shows simulations providing good fits to the data when using a diffusion coefficient for the Oxfordian limestone 2.2 and 2.9 times smaller than the independently estimated value of the first case. A steady-state simulation for a 4.6 times higher diffusion coefficient in the Dogger limestone is also shown. In spite of the significant deviation of Dp from the first case, the fit is still not satisfactory. We conclude that the measured profile can be interpreted as a steady state only when some of the independently estimated parameters, notably the diffusion coefficient in the Oxfordian limestone, are substantially changed.

The time to reach a profile close to steady state varies depending on the assumed initial condition.

Transient calculations

Alternatively, the profile may represent a transient state that started from higher initial conditions than the maximum values observed. Figure 5.1-9 shows simulations for various combinations of initial concentrations and evolution times. Times in the range 0.6 – 4.3 Ma were obtained for 6.42E-5 < C_{initial} < 1E-3 cm³ STP/g_water. All these initial conditions can lead to a good match with the data. In fact, the simulations for 0.6 Ma and C_{initial} = 6.42E-5 cm³ STP/g_water, 1.5 Ma and C_{initial} = 1E-4 cm³ STP/g_water, or 4.3 Ma and C_{initial} = 1E-3 cm³ STP/g_water match within the thickness of the line.
Diffusive transport and production are considered. Model runs COX BUR N8 (Dp according to Section 2.1), COX BUR N3 (Dp in Oxfordian limestone decreased by factor 2.2), COX BUR N4 (Dp in Oxfordian limestone decreased by factor 2.9), COX BUR N7 (Dp in Dogger limestone increased by factor 4.6).

Both aquifers are assumed to have been activated at the same time in the past. Diffusive transport and production are considered. Model runs COX BUR N8 (C_{init} = 6.42 \times 10^{-5} \text{ cm}^3 \text{ STP/g water}), COX BUR N9 (C_{init} = 1 \times 10^{-4} \text{ cm}^3 \text{ STP/g water}), COX BUR N10 (C_{init} = 1 \times 10^{-3} \text{ cm}^3 \text{ STP/g water}).
Conclusions

- The He profile at EST211/212 can be interpreted as resulting from He production within the low-permeability zone and diffusion to the bounding aquifers. Some He data (with higher He concentrations) are also available from units below the Dogger aquifer but have not been modelled here. Whether all He ascending from deeper levels is removed laterally in the Dogger aquifer is currently uncertain.

- The profile may represent a transient or a steady-state situation; the modelling does not allow to make a definite statement in this respect because there are uncertainties regarding the diffusion coefficients for He and the initial condition.

- Interpreting the data as a steady-state profile would require some of the independently estimated parameters to be adjusted, for instance, to reduce the diffusion coefficient in the Oxfordian limestone by a factor 2 to 3.

- When interpreting the data as a transient profile, no adjustment of the parameters is required. In this case, evolution times are not well constrained; they vary within a rather broad range, depending on the assumed initial condition. An evolution time around 4 Ma can be obtained for an initial concentration of about 1E-3 cm$^3$ STP/g water.

- All calculations were made under the assumption that there is no upward transport of He across the Dogger aquifer and that all He originating from depth is transported away laterally in this aquifer. This assumption is supported by the prominent change in slope of the measured He profile at the depth of the Dogger aquifer (Figure 2.1-8) and by the fact that the He concentration in the sample just below the aquifer is near-identical to that in the lowermost sample of the Callovo-Oxfordian, so there is currently no concentration gradient that would suggest upward diffusion of He to be important. However, it has to be admitted that the data base is limited in the lower part of the profile, in particular in the Dogger aquifer and the overlying limestones below the Callovo-Oxfordian. A more complete data set from a recently drilled borehole is currently being collected and may reduce the existing uncertainties.

5.1.4 Cl isotopes in borehole HTM102

Parameters for modelling (such as $R_{\text{std}}$, the standard Cl isotope ratio, and the Dp ratio for $^{35}\text{Cl}$ and $^{37}\text{Cl}$) were chosen according to the discussion in Appendix A4.4. As for Cl, there are no data from the bounding aquifers, and the data from the low-permeability sequence show a scatter that is large compared to the overall variability over the whole profile. This means that model calculations remain on a hypothetical level and do not add truly independent insights. The simulations rely on the same assumptions as those for Cl in borehole HTM102 (see Section 5.1.1), i.e. an initial Cl concentration of 2 176 mg/L and boundary conditions of 83 (top) and 2 176 (bottom) mg/L. Positive initial $\delta^{37}\text{Cl}$ values of 0.3, 0.6 or 1.0 ‰ were assumed that may have resulted from older processes. At the upper boundary, a $\delta^{37}\text{Cl}$ value of 0 ‰ (as can be found in meteoric water) was assumed. For the lower boundary, values of -1 ‰ or -0.5 ‰ were considered, in analogy to the typically negative values observed in other boreholes in the area (Table 2.1-3). In the absence of independent constraints, these assumptions are not well supported. In Figure 5.1-10, simulation results are shown for times ≥6 Ma, which are required to obtain an approximate match of the Cl data (see Figure 5.1-5). As can be seen, the fit of the modelled curves for the different scenarios is not overly convincing. For an evolution time of 6 Ma, the lower part of the measured profile is roughly approximated by the model, but the $\delta^{37}\text{Cl}$ values in the upper part are over-predicted. The choice of a negative $\delta^{37}\text{Cl}$ value at the upper boundary, based on the range of -2 – 0 ‰ observed in other boreholes (Table 2.1-3) would somewhat
improve the fit for 6 Ma. No good fits at all are obtained for longer evolution times, for which too low $\delta^{37}\text{Cl}$ values are predicted. Figure 5.1-10 also shows that evolution time strongly affects the simulated profiles, whereas the choice of the initial condition or the lower boundary condition have comparatively minor effects.

**Figure 5.1-10: Simulations for $\delta^{37}\text{Cl}$ in borehole HTM102, 3 km southeast of the Bure URL**

Both aquifers are assumed to have been activated at the same time in the past. Numbers adjacent to model curves indicate evolution times since activation of the aquifers. Only diffusive transport is considered. Left: $\delta^{37}\text{Cl}_{\text{bottom}} = -1$‰, right: $\delta^{37}\text{Cl}_{\text{bottom}} = -0.5$‰. Model runs COX 102 37Cl 8 ($\delta^{37}\text{Cl}_{\text{bottom}} = -1$‰, $\delta^{37}\text{Cl}_{\text{init}} = 0.3$‰), COX 102 37Cl 9 ($\delta^{37}\text{Cl}_{\text{bottom}} = -1$‰, $\delta^{37}\text{Cl}_{\text{init}} = 0.6$‰), COX 102 37Cl 12 ($\delta^{37}\text{Cl}_{\text{bottom}} = -1$‰, $\delta^{37}\text{Cl}_{\text{init}} = 1$‰), and COX 102 37Cl 10 ($\delta^{37}\text{Cl}_{\text{bottom}} = -0.5$‰, $\delta^{37}\text{Cl}_{\text{init}} = 0.3$‰).

From the simulations of the $\delta^{37}\text{Cl}$ values, we conclude the following:

- The $\delta^{37}\text{Cl}$ data have a considerable scatter, which may hint at large analytical errors that possibly mask the main trend of the data.
- The quantitative description of the data is very uncertain. It depends not only on the (unknown) Cl$^-$ contents at the boundaries, but also on the unknown initial and boundary conditions for $\delta^{37}\text{Cl}$. The latter may be strongly influenced by older processes, because $\delta^{37}\text{Cl}$ signatures evolve more slowly than those for Cl$^-$. Thus, the system has many degrees of freedom and cannot be well constrained.
- The negative $\delta^{37}\text{Cl}$ values in the lower part of the profile could be explained by Cl$^-$ diffusion from the Dogger aquifer into the low-permeability sequence, i.e. an upward propagation of the negative $\delta^{37}\text{Cl}$ of the Dogger aquifer.
- The positive values in the upper part could result from out-diffusion of Cl$^-$ from the low-permeability sequence towards the upper aquifer. However, for the long times required to obtain a good match of the Cl$^-$ data, the simulations assuming a negative $\delta^{37}\text{Cl}$ in the Dogger aquifer tend to underestimate the $\delta$ values.

Lavastre (2002) interpreted the $\delta^{37}\text{Cl}$ signature across the low-permeability sequence of HTM102 in a semi-quantitative way as being mostly inherited from older processes, notably from ultrafiltration
during compaction. She concluded that fractionation by diffusion alone is insufficient or even inconsistent with the observed $\delta^{37}$Cl and Cl$^-$ data. Our modelling shows that, depending on the choice of boundary and initial conditions, the general $\delta^{37}$Cl pattern could also originate from diffusive processes. However, the uncertainty of the assumed modelling scenarios is so large that no definitive statement can be made.

Lavastre et al. (2005a) modelled the Cl$^-$ and $\delta^{37}$Cl data of the Tithonian to Oxfordian limestones of HTM102 between the surface and a depth of about 400 m. No attempt was made there to model the data in the underlying low-permeability sequence. A match to the observed Cl$^-$ and $\delta^{37}$Cl data in the upper part of the profile was achieved by assuming uniform properties and fitting the product of diffusion coefficient and evolution time, as well as the fractionation coefficient Dp$_{35\text{Cl}}$/Dp$_{37\text{Cl}}$. For the latter, a value of 1.0014 was obtained for the HTM102 data, and 1.0022 for the few data available for borehole EST311. The parameters that were fitted appear to be reasonable, but because of the scarcity of the Cl$^-$ and $\delta^{37}$Cl data close to the interface between shale and limestone, it remains unclear how well supported some of the assumptions (e.g. homogeneous conditions) are.

### 5.1.5 Considering vertical advection

In boreholes at the Bure URL site, slight overpressures of 40 – 60 m with respect to the over- and underlying aquifers were measured within the Callovo-Oxfordian shale (Section 2.1.6, Figure 2.1-14). The currently preferred explanation of this feature are salinity gradients that induce an osmotic potential (Andra 2005b). In such a case, the small pressure anomalies just balance the osmotic potential, so that the hydraulic gradient across the shale remains near zero and no water flow occurs (see Section 4.3).

The influence of vertical advection on the simulated Cl$^-$ profiles was tested at EST211 and EST311/312. Models considering advection were limited to cases with evolution times not much larger than about 4 to 6 Ma, because (a), the results for the stable water isotopes indicate that longer times are not likely and (b), for much longer times lateral diffusion also needs to be considered. These constraints on the maximum evolution time restrict the spectrum of initial Cl$^-$ concentrations to 2 150 – 5 000 mg/L in the case of borehole EST211 (Figure 5.1-1).

In Figure 5.1-11, results for simulations for EST211 starting from an initial concentration of 2 150 mg/L with upward fluxes corresponding to advection velocities of -1.1E-13, -5.6E-13 and -1.1E-12 m/s in the Callovo-Oxfordian shale are shown. For an upward advection velocity of -1.1E-13 m/s, the differences to the purely diffusive case are small. For values of -5.6E-13 m/s or more, no satisfying fits can be obtained, as the simulations always overestimate the data in the upper part. For downward advection, the definition of the maximum advection velocity that is still in broad agreement with the data is difficult due to the absence of data below the Callovo-Oxfordian shale and due to the unexplained high Cl$^-$ value in the Dalle Nacrée. A flux corresponding to an advection velocity of 5.6E-12 m/s in the Callovo-Oxfordian can be tentatively considered as a maximum because the fit is becoming poor in both limbs of the profile at higher velocities. For downward advection, best-fit evolution times decrease with increasing velocity.

In Figure 5.1-12, the simulations with advection starting from a higher initial concentration of 5 000 mg/L are shown. Approximate fits can be obtained for upward or downward Darcy fluxes of 2E-14 m/s, corresponding to an advection velocity of 2.2E-13 m/s in the Callovo-Oxfordian, with either a somewhat larger (upward advection, 5.5 Ma) or somewhat smaller (downward advection, 5.0 Ma) evolution time as compared to pure diffusion (5.3 Ma). However, fits for advection velocities ≥5.6E-13 m/s in both directions are no longer compatible with the data. In the case of downward
advection, the maximum advection velocity is 1 order of magnitude smaller than in the case with the lower initial Cl⁻ concentration of 2150 mg/L (Figure 5.1-11). This is because the evolution time is longer for higher initial concentrations, and this increases the effects of advection on the shape of the profile. This means that maximum advection velocities for even higher initial concentrations are expected to be lower than those derived from Figure 5.1-12.

As mentioned above, the data for boreholes EST311/312 appear to indicate steady-state diffusion. When including advection, the simulated steady-state profiles would bend in the direction of the water flow. Accordingly, for upward advection with a Darcy flux of -2E-14 m/s (advection velocity of -2.2E-13 m/s in the Callovo-Oxfordian) and higher, no good match could be obtained at any time (Figure 5.1-13). For downward advective flux, a wide range of velocities and evolution times yields fits that are equally good or even slightly better than for diffusion alone. Given the fact that data are only available from the centre of the low-permeability sequence, a threshold velocity beyond which downward advection is contradicted by the data cannot be defined.

Figure 5.1-11: Influence of advection on simulations for Cl⁻ in borehole EST211 at the Bure URL site, considering an initial Cl⁻ concentration of 2150 mg/L

Blue bars indicate ground waters. Both aquifers are assumed to have been activated at the same time in the past. Advective-diffusive transport is considered, with Cl\textsubscript{init} = 2150 mg/L. Upward Darcy flux corresponding to advection velocities of -1.1E-13 m/s (COX BUR A14), -5.6E-13 m/s (COX BUR A13) and -1.1E-12 m/s (COX BUR A12) in the Callovo-Oxfordian shale. Downward flux corresponding to advection velocities of 5.6E-13 m/s (COX BUR A15), 1.1E-12 m/s (COX BUR A25) and 5.6E-12 m/s (COX BUR A26). Positive sign refers to downward flow.
Figure 5.1-12: **Influence of advection on simulations for Cl⁻ in borehole EST211 at the Bure URL site, considering an initial Cl⁻ concentration of 5 000 mg/L**

Blue bars indicate ground waters. Both aquifers are assumed to have been activated at the same time in the past. Advevtive-diffusive transport is considered, with Clinit = 5 000 mg/L. Darcy flux corresponding to advection velocities of -2.2E-13 m/s (COX BUR A16 [upward], COX BUR A17 [downward]) and -5.6E-13 m/s (COX BUR A18 [upward], COX BUR A19 [downward]) in the Callovo-Oxfordian shale. Positive sign refers to downward flow.

Figure 5.1-13: **Influence of advection on simulated Cl⁻ concentrations in borehole EST311/312, 13 km northeast of the Bure URL**

Blue bars indicate ground waters. Both aquifers are assumed to have been activated at the same time in the past. Advevtive-diffusive transport is considered. Advection velocities are specified for the Callovo-Oxfordian shale. Advevtive-diffusive transport is considered for Clinit = 3 960 mg/L. Model runs COX 312 A1 (v_a = 0 m/s), COX 312 A4 (v_a = -2.2E-13 m/s), COX 312 A5 (v_a = 2.2E-13 m/s), COX 312 A8 (v_a = 5.6E-13 m/s), COX 312 A9 (v_a = 1.1E-12 m/s), COX 312 A10 (v_a = 2.2E-12 m/s), COX 312 A11 (v_a = 5.6E-12 m/s). Positive sign refers to downward flow.
5.1.6 Conclusions

- At the URL site, good data sets for Cl⁻ are available for boreholes EST211 and EST212 and define curved profiles. Good and near-identical model fits can be obtained for a range of initial Cl⁻ contents and evolution times. In the absence of independent constraints, a specific base case cannot be defined, but it can be concluded that diffusion alone explains well the data using geologically sensible combinations of input parameters.

- Borehole EST312, northeast of the URL site, provides another data set suited for quantification. The high salinity in the underlying Dogger aquifer underpins the importance of lateral heterogeneity, which is also seen in the Cl⁻ data from the low-permeability sequence. As a first approximation, these data can be interpreted to represent a steady-state diffusion profile, even though the scatter is substantial and no data are available from the limestone units within the low-permeability sequence. In such a case, minimum evolution times of about 10 – 25 Ma can be calculated, assuming that the initial Cl⁻ concentration was that observed today in the Dogger aquifer, or higher.

- Water-isotope data are only available from boreholes at the URL site. The profiles are curved and similar to that for Cl⁻, but the scatter of the data is substantial, namely in the lower half. Depending on the assumed initial condition, evolution times for acceptable fits to the data in the upper limb of the profile in the range 1 – 4 Ma are obtained. However, the uncertainties in the data and in the evolution scenarios are so substantial that not much weight is attributed to these results.

- In HTM102, Cl⁻ and δ⁷Cl data are available. Simulations assuming a Cl⁻ concentration at the lower boundary equal to the maximum observed value within the Callovo-Oxfordian (neglecting the value in the Dalle Nacrée) can lead to approximate steady-state fits of the Cl⁻ data. However, for the long times required to reach steady state for the chosen initial condition (about 10 Ma), the δ⁷Cl simulations do not match the measured data. The trend to negative values in the lower part can be captured by using a negative δ⁷Cl value at the lower boundary, but the positive values in the upper part are mostly underestimated. Unfortunately, the boundary and initial conditions are not well constrained, and data from the aquifers are not available. Improving the match by choosing specific initial and constant or time-dependent boundary conditions is possible but not independently supported, so does not lead to a better understanding of the processes acting in the system.

- The He profile of boreholes EST211/212 can be interpreted as originating from production and diffusion towards the aquifers. However, we cannot decide whether it represents a steady or a transient state. If independently estimated transport parameters are used, the simulated steady state underestimates the measured concentrations. Only a decrease of the diffusion coefficient in the Oxfordian limestone by a factor of 2 to 3, for instance, would lead to an acceptable match. Simulated transient profiles that started from various initial concentrations match the measured data equally well without the need to adjust transport parameters. The evolution times are ≤4 Ma for He_{initial} ≤1E-3 cm³ STP/g water.

- The small observed hydraulic overpressure in the Callovo-Oxfordian was not considered for calculations of vertical advection because it may represent a counter gradient to the osmotic potential and so does not lead to flow. Only an additional gradient between the two embedding aquifers would induce flow, and such cases were explored.

- Considering constant upward or downward advection for the Cl⁻ data of borehole EST211, in no case could an improvement of the match be obtained when compared to the diffusion-only cases. For upward flow, advection velocities in excess of -5.6E-13 m/s in the Callovo-Oxfordian lead to simulated profiles that do not reproduce the data well. In the case of
downward flow, the corresponding threshold value is about 5.6E-12 m/s, i.e. acceptable model fits are obtained for a much larger range of velocities compared to upward flow. The reason is the absence of data in the Dogger limestone, which means that the lower part of the modelled profiles is not constrained. This uncertainty propagates into the estimation of the maximum advection velocity.

5.2 Couche Silteuse at Marcoule (Gard, France)

The Couche Silteuse was penetrated by 3 boreholes, among which the formation thickness varies substantially (see Section 2.2). Anion contents are highest in borehole MAR203, where the formation is 404 m thick, and lowest in borehole MAR501, where the formation is 163 m thick. In borehole MAR203, maximum Cl\(^-\) contents in the centre of the Couche Silteuse are slightly higher than in present-day sea water.

5.2.1 Anions

First, the hypothesis is tested whether the differences in formation thickness alone could explain the contrasting Cl\(^-\) concentrations in the boreholes. Due to the proximity (few km) of all boreholes, the hydrogeological evolution of the aquifers was assumed to be similar at all locations. The maximum observed Cl\(^-\) content of 25 875 mg/L was taken as the initial condition for all boreholes\(^{17}\), and a simultaneous activation of both aquifers was considered, assuming present-day Cl\(^-\) concentrations at the boundaries since then. Present-day diffusion coefficients (including a temperature correction) were considered in the calculation. As shown in Figure 5.2-1, good fits to the data are obtained for diffusion times of 3 Ma (MAR203), 1.5 Ma (MAR402) and \(\geq 3\) Ma (MAR501). It is remarkable that this very simple palaeo-hydrogeological scenario results in diffusion times within a factor of 2, in spite of the highly contrasting tracer contents. Moreover, the time of 3 Ma corresponds to the final emergence of the region from the sea, so there is also a reasonable consistency with the actual palaeo-hydrogeological evolution. This calculation is therefore considered as the base case.

Analogous calculations for Br\(^-\) are shown in Figure 5.2-2 and lead to the same conclusions as those for Cl\(^-\), even though the scatter of the data is somewhat larger. In MAR501, diffusion times in excess of 3 Ma would be consistent with the data. However, only two data points are available, one of which has a Br\(^-\) content below detection. Due to the substantial analytical errors in determining very low Br\(^-\) contents, these data points are not interpreted further.

In the next step, the full hydrogeological evolution of the site as shown in Table 2.2-7 is explored. After deposition at 100 Ma, the formation remained marine until 50 Ma. Between 50 and 5.35 Ma, it was exposed on the continent, even though some marine incursions occurred. Due to this long continental period, it is possible that all marine signatures were obliterated and that fresh-water conditions prevailed in the whole sequence. Therefore, the model calculation was started at 5.35 Ma and assumed zero anion concentrations as the initial condition. Between 5.35 and 3 Ma, i.e. after the Messinian salinity crisis, the area was exposed to marine conditions until final emergence at 3 Ma. For the marine stage, the highest observed anion contents (Cl\(^-\) = 25 875 mg/L, Br\(^-\) = 65.1 mg/L) were considered as boundary conditions. Figure 5.2-3 and Figure 5.2-4 show the model results for Cl\(^-\) and Br\(^-\). The fits to the observed tracer distributions are good for MAR501 but unacceptable for the other boreholes. The reason for the misfit is the fact that the relatively short marine period (5.35 – 3 Ma)

\(^{17}\) An initial Cl\(^-\) concentration slightly higher than that in current sea water is conceivable due to the salinity excursions during the Messinian salinity crisis (5.8 - 5.35 Ma).
was insufficient to raise the salinity in the Couche Silteuse to marine values, leading to predicted anion contents that are lower than those observed.

In principle, the calculated salinity in the Couche Silteuse at 3 Ma could be maximised by assuming:

1) a higher salinity in the embedding aquifers between 5.35 and 3 Ma (a possible hypothesis given the fact that the Mediterranean was still a restricted water body), and/or

2) a longer period during which in-diffusion of salinity into the Couche Silteuse occurred.

Ad 1). In Figure 5.2-5, a scoping calculation is shown in which the salinity in the embedding aquifers during the last marine period (5.35 – 3 Ma) is taken as 4 times that of sea water. In spite of this high salinity at the boundaries, the marine period is still not long enough to transport sufficient quantities of Cl\(^-\) into the central parts of the Couche Silteuse in borehole MAR203. Thus, the predicted present-day concentration profile does not fit the measured, substantially higher Cl\(^-\) contents. In contrast, the model over-predicts the current Cl\(^-\) concentrations in borehole MAR501. This is due to the fact that the Couche Silteuse is much thinner in this borehole and the in-diffusion of Cl\(^-\) during the marine period is almost complete (i.e. the concentrations in the centre of the formation are almost as high as those of the boundaries), whereas the continental period since 3 Ma is not sufficiently long to lower the high concentrations to the currently observed values. Only for borehole MAR402 does the model correspond reasonably well with the observations. It is concluded that Cl\(^-\) concentrations much higher than those of sea water cannot consistently explain the observed profiles in the 3 boreholes.

Ad 2). During the Messinian crisis (5.8 – 5.35 Ma), the embedding aquifers were intersected by the canyons of the Rhône and Cèze rivers and so were probably hydraulically active containing fresh water. However, this period is too short to lead to a substantial out-diffusion of salinity from the Couche Silteuse, at least in boreholes MAR203 and MAR402 where formation thickness is substantial. The earlier history (i.e. before 5.8 Ma) is less clear, and so the assumption made in the previous calculations that anion concentrations were 0 throughout the Couche Silteuse at 5.35 Ma cannot be rigorously defended. The region was located close to the marine shoreline over geological periods of time, so the possibility exists that salinity was elevated. In conjunction with the in-diffusion during the last marine stage (5.35 – 3 Ma), it is conceivable that anion contents were similar to those of sea water at 3 Ma, which would correspond to the situation considered in Figure 5.2-1 and Figure 5.2-2.
Figure 5.2-1: Base-case model for the out-diffusion of Cl\textsuperscript{-} at Marcoule considering an initial concentration of 25875 mg/L (max. observed value). Only diffusive transport is considered. Numbers indicate evolution times in Ma since activation of the aquifers. Model runs G203 A5, G402 A5, G501 A5.

Figure 5.2-2: Base-case model for the out-diffusion of Br\textsuperscript{-} at Marcoule considering an initial concentration of 65 mg/L (max. observed value). Only diffusive transport is considered. Numbers indicate evolution times in Ma since activation of the aquifers. Model runs G203 A5, G402 A5, G501 A5.
Figure 5.2-3: Scoping model for Cl⁻ at Marcoule considering the full hydrogeological evolution

Only diffusive transport is considered. Numbers indicate evolution times in Ma since activation of the aquifers. Model runs G203 A6, G402 A6, G501 A6

Figure 5.2-4: Scoping model for Br⁻ at Marcoule considering the full hydrogeological evolution

Only diffusive transport is considered. Numbers indicate evolution times in Ma since activation of the aquifers. Model runs G203 A6, G402 A6, G501 A6
Figure 5.2-5: Scoping model for Cl⁻ at Marcoule considering the full hydrogeological evolution and assuming a high salinity during the marine stage.

Only diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the aquifers. Model runs G203 A7, G402 A7, G501 A7.
5.2.2 Cl isotopes

Cl isotope data are only available for borehole MAR203. As shown in Figure 2.2-5, $\delta^{37}\text{Cl}$ increases from ca. -0.75‰ at the base of the Couche Silteuse to ca. +1.3‰ near the top but then decreases to ca. 0.5‰ adjacent to the upper aquifer. In the aquifers themselves, $\delta^{37}\text{Cl}$ values do not all fit into the overall pattern and, more importantly, there are differences larger than 1‰ between ground-water samples and data obtained from rock leaching in the same interval. It is not clear whether this heterogeneity is real or due to analytical artefacts, and in any case renders the definition of boundary conditions difficult. In the light of these uncertainties (augmented by the lack of knowledge concerning the initial $\delta^{37}\text{Cl}$ value and the temporal evolution of the boundaries), only scoping calculations of possibly limited relevance can be made.

In a first calculation, the simple out-diffusion scenario of case A5 (Figure 5.2-1) is considered. A sea-water initial value ($\delta^{37}\text{Cl} = 0$) is used. $\delta^{37}\text{Cl}$ values of samples from the Couche Silteuse immediately adjacent to the aquifers (0.54 and -0.77‰) are taken as boundary conditions, which are assumed to be time-invariant. The resulting distribution of $\delta^{37}\text{Cl}$ after a diffusion time of 3 Ma is shown in Figure 5.2-6. The upper part of the model profile shows a reasonably good fit to the data, while the lower part of the model does not capture well the near-linear trend of the data. Out-diffusion of Cl always results in an enrichment of the heavier isotope (and therefore $\delta^{37}\text{Cl}$) in the external parts of the low-permeability formation, but this is not the case in the measured data. Either processes other than diffusion played a role, or the parameterisation of the model calculation is inadequate.

Figure 5.2-6: Scoping model for $\delta^{37}\text{Cl}$ in borehole MAR203 at Marcoule considering a marine initial condition ($\delta^{37}\text{Cl} = 0$)

The simple out-diffusion scenario of model run A5 (Figure 5.2-1) and time-invariant boundary conditions, corresponding to present values, are considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the aquifers. Model run G203-Cl 5
The simple out-diffusion scenario of model run A5 (Figure 5.2-1) and time-invariant boundary conditions, corresponding to present values, are considered. The initial $\delta^{37}$Cl is $+1 \%_{\text{V-SMOW}}$ at the top and decreases linearly to $-2 \%_{\text{V-SMOW}}$ at the bottom. Numbers adjacent to model curves indicate evolution times in Ma since activation of the aquifers. Model run G203-Cl 9

In a second calculation, a heterogeneous initial condition is considered, decreasing from $\delta^{37}$Cl = $+1$ at the top of the Couche Silteuse to $\delta^{37}$Cl = $-2$ at the bottom. Such an initial distribution could be achieved if, at a stage before out-diffusion was initiated (i.e. at $>3$ Ma), a gradient of CI$^{-}$ concentrations existed in the Couche Silteuse and led to a diffusive re-distribution. If at that time CI$^{-}$ concentrations were higher in the lower part of the formation, upward diffusion of CI$^{-}$ would have led to a depletion of $^{35}$Cl in the lower part and to an enrichment in the upper part. The results of the calculation are shown in Figure 5.2-7. The model curve shows a reasonable fit to the data and even reproduces the bulge towards positive $\delta^{37}$Cl values in the upper part of the formation, before decreasing again at the very top. It is concluded that, in principle, diffusion alone can explain both the CI$^{-}$ and the $\delta^{37}$Cl profiles in borehole MAR203. However, in order to obtain good fits to the data, a heterogeneous initial distribution of $\delta^{37}$Cl must be assumed for which independent palaeo-hydrogeological evidence is lacking. Thus, the calculation remains on a hypothetical basis.

5.2.3 Considering vertical advection

The fact that the CI$^{-}$ and Br$^{-}$ profiles in boreholes MAR203 and MAR401 are symmetric, with the highest ion concentrations in the centre of the Couche Silteuse, strongly suggests that transport is dominated by diffusion (unless complex and unsupported scenarios are constructed). The current hydraulic gradient is small ($<0.01$ m/m), so advection is not relevant at present. The effect of advection in the past on the base case, which considers out-diffusion since $2 - 3$ Ma, is shown in Figure 5.2-8. The case without advection yields the best fit to the data, and vertical advection distorts the symmetry. Based on Figure 5.2-8, it is concluded that the vertical upward component of advection cannot exceed an advection velocity of ca. $-5.5E-13$ to $-1.1E-12$ m/s because the resulting tracer profiles would become inconsistent with the observations. Using the same argument, the maximum
downward velocity is 5.5E-13 m/s. These velocities result in relatively high Peclet numbers of 5 – 10. The reason for these high numbers is the fact that the substantial scatter of the data is propagated into the definition of velocities that yield clear misfits with the data. With a hydraulic conductivity of 1E-13 m/s, the derived velocity range corresponds to hydraulic gradients of 0.3 – 0.5.

**Figure 5.2-8:** Effect of vertical advection on the Cl’ profile of borehole MAR203 at Marcoule

![Figure 5.2-8](image)

Advevtive-diffusive transport is considered. Left: Evolution time = 2 Ma; right: evolution time = 3 Ma. Base case without vertical flow shown in black, corresponding to Figure 5.2-1. Model runs G203-A9 ($v_a = 1.1E-12$ m/s), G203-A10 ($v_a = 5.5E-13$ m/s), G203-A12 ($v_a = -1.1E-12$ m/s), G203-A13 ($v_a = -5.5E-13$ m/s). Positive sign refers to downward flow.

5.2.4 Conclusions

In spite of the complex hydrogeological evolution of the region, the shapes of the observed tracer profiles are simple and consistent with out-diffusion of salinity from the Couche Silteuse initially containing marine or only slightly higher Cl’ contents, starting at the time of final emergence at 3 Ma (Figure 5.2-2). The fact that a shorter time for out-diffusion of 1.5 Ma (i.e. a more recent activation of the aquifers) is predicted for MAR402 can be explained by the deeper position of the Couche Silteuse when compared to the other sites (see Figure 2.2-2) and by the fact that this borehole is farther from the Rhône and Cèze rivers which contain deep canyons originating from the Messinian crisis, filled with Quaternary sediments thereafter. It is concluded that the regular profiles observed in all boreholes can be consistently explained by diffusive loss of salinity since final emergence and opening of the aquifers to fresh water, and thus the model calculations shown in Figure 5.2-1 are considered as the most likely scenario.

Some uncertainty remains regarding the salinity in the Couche Silteuse at 3 Ma. The model calculations indicate that Cl’ contents at this time must have been elevated, probably close to those of sea water. From a palaeo-hydrogeological point of view, this is possible but not straight-forward to substantiate.

Cl isotopes show a complex profile in borehole MAR203. The out-diffusion over 3 Ma as suggested by the modelling of the Cl’ profile can only be reconciled with the $\delta^{37}$Cl profile if a heterogeneous initial distribution of $\delta^{37}$Cl is assumed, for which independent evidence is not available.
Model cases considering diffusion only yield better fits to the data than models combining diffusion and vertical advection. The symmetry of the anion profiles is an argument for the insignificance of advective transport.

5.3 Opalinus Clay at Benken (Switzerland)

Opalinus Clay at Benken shows only limited vertical heterogeneity with respect to mineral content or porosity and so can be considered as a single unit (see Section 2.3 and Figure 2.3-8). The other units that make part of the low-permeability sequence between the Malm and the Keuper aquifers are lithologically more heterogeneous (limestone, marl, siltstone, shale ± sandstone). However, transport parameters specific to these units are not currently available. In the absence of detailed data (notably porosities and diffusion coefficients), the whole low-permeability sequence is considered as a homogeneous unit, and its properties are approximated by those of Opalinus Clay. At least the assumption of constant porosity has only a small effects on the model results, as shown in Figure 4.10-1. Furthermore, a spatially constant mean temperature of 33 °C was used to correct the diffusion coefficients (see Appendix A3.1), leading to in-situ $D_p$ of 7.7E-11 m²/s (water tracers), 2.7E-11 m²/s (Cl⁻), and 2.3E-10 m²/s (He). The assumption of spatially constant temperature has a small effect only, as demonstrated in Figure 4.10-2.

As discussed in Section 2.3, the palaeo-hydrogeologic evolution is complex, including two successive stages of burial and erosion. As the original marine signature of the pore waters in the low-permeability sequence was obliterated in the Mesozoic and early Tertiary, sea-water composition is not a suitable initial condition for transport modelling. Instead, the Cl⁻ concentrations and δ values from the centre of the low-permeability sequence are used in the base cases to approximate the situation before the activation of the embedding aquifers. According to Section 2.3, the activation likely occurred at max. 1.8 – 2 Ma in the overlying Malm and at max. 1.8 Ma in the underlying Keuper, following the creation of new discharge zones and the increase of permeability in the Keuper aquifer. The relatively low hydraulic conductivity and the high salinity of the current ground water in the Malm aquifer indicate that flushing has been limited. In contrast, the tracer profiles in the low-permeability sequence were strongly affected by the change in the Keuper boundary condition. Modelling was started with the stable water isotopes, which have the best signal-to-noise ratio, and then proceeded with the Cl⁻ and δ³⁷Cl and the He data.

5.3.1 Stable water isotopes

Base-case simulations

In the base case, initial compositions of δ¹⁸O = -4.6 ‰ and δ²H = -40 ‰ were used. These are the values in the centre of the low-permeability sequence and are thought to best represent the situation before flushing of the aquifers in the Quaternary started. In accordance with geological evidence, it is assumed that both aquifers were activated simultaneously. The isotopic composition of water in the aquifers is assumed to be identical to the present values since flushing. As shown in Figure 5.3-1, good matches of model calculations with the data are obtained for an evolution time of 0.7 Ma¹⁸. This time is shorter than the earliest possible date for the flushing of the aquifers (1.8 Ma), but is within the geologically plausible range.

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¹⁸ Gimmi et al. (2007) used a pore diffusion coefficient of 1E-10 m²/s, which was based on a higher in-situ temperature of about 40 °C. Accordingly, their estimated evolution time (0.55 Ma) is somewhat smaller.
Note that climatic effects on $\delta$ values in the aquifers were not considered in the base case, i.e. it was assumed that there was no lowering of $\delta$ values during cold periods. Based on its stable-isotope composition, the Keuper ground water infiltrated under warm-climate conditions similar to those of present time. However, the absence of $^{14}$C indicates that its age is pre-Holocene and so must correspond to older warm periods of the Quaternary. It appears that infiltration during cold periods was limited or completely inhibited by permafrost and so did not affect the ground- and pore waters. A similar conclusion can be drawn for Opalinus Clay at Mont Terri (see Section 5.4).

**Figure 5.3-1: Base-case simulations for $\delta^{18}$O and $\delta^2$H at Benken**

Only diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the aquifers. Note that the results obtained here using FLOTRAN were verified with the code used by Gimmi et al. (2007).

Model runs B O-01 and B H-01

**Influence of the Keuper boundary condition**

The assumption of an instantaneous change of the isotopic composition in the Keuper aquifer that was made in the base case is a simplification of a probably more complex evolution. In order to estimate the effects of a gradual decrease of $\delta$ values, simulations with AgDif (Gimmi et al. 1993) were run, a quasi-two dimensional model that accounts for advective-dispersive transport in a flow domain that is in contact with a diffusively accessible aquitard or matrix domain. The Keuper aquifer was considered as the flow domain, and the low-permeability sequence as the aquitard (symmetrically on both sides). An advection velocity of 0.37 m/a in the Keuper aquifer was estimated based on the hydraulic gradient and conductivity observed at present (about 0.006 m/m and 1E-7 m/s, respectively), and a flow porosity of 0.05. A dispersion coefficient in the aquifer of 7.7E-7 m$^2$/s, leading to a dispersion length of about 65 m, was used.

The distance between the Benken borehole and the infiltration area of the Keuper aquifer is about 10 – 20 km. In case of plug flow without interaction with the aquitard, a step change of the isotope values of the infiltrating water would arrive after about 27 ka (10 km), 41 ka (15 km), or 55 ka (20 km) under these conditions (Figure 5.3-2). Because of the relatively long travel distances, the hydrodynamic dispersion in the aquifer adds – even when using a larger dispersivity of 650 m – little to the smearing of the breakthrough curve. However, diffusive exchange between water flowing in the
aquifer and matrix pore water is expected to occur along the flow path. It will retard the breakthrough of the new isotopic signal at Benken, and it will increase the dispersion in the breakthrough curve. However, when using the measured Dp in Opalinus Clay for the aquitard, the retardation and the additional smearing are barely noticeable, and breakthrough occurs in a relatively short time (less than 50 ka at 10 km, 100 ka at 20 km). Even for 10, 100, or 1000 times larger Dp in the aquitard, which are not meaningful values but were chosen just for illustrative purposes, most of the concentration change would have passed in a short time compared to the typical diffusive exchange times for the Benken aquitard (Figure 5.3-2).

We learn from these simulations that it is likely that a change of the inflow concentration in the aquifer has propagated relatively quickly – compared to the diffusive exchange with the aquitard – and without excessive dispersion to the Benken area. Consequently, scenarios with a slow change of the boundary concentration in the Keuper over a longer time are less likely than a relatively rapid initial change followed by a longer phase of only smoothly changing values. In any case, a smooth change of the boundary condition would lead to longer evolution times, so the 0.7 Ma derived for the base case are a minimum value.

Figure 5.3-2: Simulations of tracer concentrations in the Keuper aquifer at Benken for different diffusion coefficients in the adjacent aquitard

A distance of 10 km between infiltration area and Benken is considered. Flushing of the aquifer at the infiltration point starts at time = 0

Influence of the Malm boundary condition

No pore-water tracer data were obtained from the lowest part of the Malm, i.e. from the uppermost part of the low-permeability sequence. Thus, it is expected that the existing data have only a relatively small information content with respect to the evolution of the Malm boundary condition. Gimmi et al. (2007) tested a number of different Malm boundary conditions for the stable water isotopes, including constant concentrations as observed today with the same or a shorter evolution time as for the Keuper boundary, concentrations decreasing with time, and a zero-gradient condition. They concluded that the available tracer data are insufficient to discriminate between these cases. Fortunately, the influence of the Malm boundary condition on the observed profiles is small because of the small gradient of the δ values in the upper part of the profile. Changes in the upper boundary
condition do not affect the shapes of the profiles in the central and lower parts of the low-permeability sequence because the effects of such changes have a limited penetration depth over the time scales considered. Based on these conclusions, no further modelling of alternative upper boundary conditions is presented.

Influence of initial conditions

Because there is no independent support for the choice of the initial δ values in the base case, higher values (i.e., closer to the original sea water) were also considered. As shown in Figure 5.3-3, the choice of the initial values greatly affects the diffusion times. Initial values of δ¹⁸O = -4 ‰ and δ²H = -30 ‰ yield diffusion times that are still widely compatible with palaeo-hydrogeological data, whereas higher values lead to very long times that are in conflict with palaeo-hydrogeology. Moreover, the fits to the data are always less good than in the base case. The shapes of the simulated curves differ from the measured data. In particular, the steep observed gradient of the δ values in the lowermost part of the profile is not well reproduced. It is concluded that before the embedding aquifers were activated, the originally marine pore waters were already diluted by meteoric water.

Figure 5.3-3: Simulations for δ¹⁸O and δ²H at Benken considering higher initial δ values than in the base case

Conclusions

In the base case, the δ values observed in the centre of the low-permeability sequence are used as initial condition. The consideration of instantaneous flushing of both aquifers to current δ values (step function) leads to modelled tracer distributions that are in good agreement with the data for evolution times of ca. 0.7 Ma for both δ¹⁸O and δ²H. The best-fit evolution time depends on the assumed initial condition. A slight shift of the initial δ¹⁸O and δ²H to higher values yields markedly longer evolution times, but at the same time to a progressively less good match with the data. From this perspective, the evolution time 0.7 Ma can be considered as a minimum. If the assumed initial δ¹⁸O and δ²H are >0.6 and >10 ‰ higher than in the base case, calculated evolution times exceed 2 Ma and so are in conflict...
with independent evidence on the activation times of the aquifers. Also, the match with the data is then clearly worse than for the base case. Another uncertainty in the estimation of the evolution time is the evolution of $\delta^{18}$O and $\delta^2$H in the lower aquifer over time. If the drop to current values was not instantaneous but followed a more complex path, somewhat longer evolution times are obtained.

5.3.2 Chloride

Base-case simulation

The Cl⁻ data at Benken show more scatter than the stable water isotope data. A part of this scatter is thought to originate from uncertainties related to anion-accessible porosity. Notably, it is possible that the fractions of the pore space accessible for Cl⁻ vary as a function of lithology and salinity. For the base-case simulations, a step change of the boundary conditions was assumed, i.e. an instantaneous drop of Cl⁻ contents from the initial concentration of 6 600 mg/L to present values at both boundaries. Figure 5.3-4 shows the corresponding results. An approximate match with the data is obtained for an evolution time of about 1.4 to 2 Ma. However, due to the large scatter of the data, the match is not considered as completely satisfactory.

![Figure 5.3-4: Base case simulations for Cl⁻ at Benken](image)

Only diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the aquifers. Note that the results obtained here using FLOTRAN were verified with the code used by Gimmi et al. (2007).

Model run B Cl-01

The evolution time estimated for Cl⁻ is longer than the 0.7 Ma for stable water isotopes. However, the discrepancy is not regarded as critical for the following reasons:

- As stated above, 0.7 Ma is the minimum evolution time for the $\delta^{18}$O and $\delta^2$H profiles, and only a slight change in the initial isotopic composition would lead to times comparable to those obtained for Cl⁻.
The calculation of the Cl⁻ profile is based on laboratory measurements of tracer diffusion coefficients for Cl⁻. In reality, the relevant parameter is the salt diffusion coefficient for Na⁺-Cl⁻. Using Van Loon et al.'s (2005) diffusion coefficients for Na⁺, the salt diffusion coefficient is 1.9 times higher than the one for Cl⁻ (this factor applies to Dp; see also Section 2.3.4). However, Na⁺ is retarded by cation exchange on clay minerals, and this may reduce the salt-diffusion coefficient to a currently unknown degree.

**Influence of initial conditions**

Similar to the stable water isotopes, some calculations for higher initial concentrations of Cl⁻ were made. Figure 5.3-5 shows the results using initial concentrations of 9,000 mg/L and of 19,350 mg/L (present-day sea water). As for the stable water isotopes, the match with the data is generally worse, even though the large scatter of the data makes a definitive judgement difficult. What becomes clear from these simulations is that for all initial concentrations above those of the base case, the estimated evolution times become much too large and are in conflict with palaeo-hydrogeological evidence.

![Simulations for Cl⁻ at Benken considering higher initial concentrations](image)

Figure 5.3-5: Simulations for Cl⁻ at Benken considering higher initial concentrations

- Initial Cl⁻ concentration is 9,000 mg/L. Model run B Cl⁻04
- Initial Cl⁻ concentration is 19,350 mg/L. Model run B Cl⁻05a
- Only diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the aquifers

**Effect of anion-accessible pore fraction**

For this report, a Cl⁻-accessible pore fraction of 0.5 of water-accessible porosity was assumed in order to scale the pore-water data. The value was chosen based on a comparison with two squeezing data and the experience gained at Mont Terri. Only few diffusion data for Benken samples are available so far and suggest that this fraction could be markedly smaller, in the order of 0.3, possibly linked to the lower porosity and higher degree of compaction at Benken. In order to investigate this effect, the pore-water data were uniformly re-scaled with a value of 0.3 instead of 0.5. With this re-scaling, maximum pore-water concentrations of about 11,000 mg/L would be obtained in the
Dogger. The simulation, starting from a re-scaled initial value of 11 000 mg/L, is shown in Figure 5.3-6. The fit is about as good as in the base case, and the evolution time of 1.4 Ma is slightly shorter. It is concluded that the limited knowledge of the anion-accessible pore fraction does not critically affect the model calculations.

**Figure 5.3-6:** Simulations for Cl at Benken using an anion-accessible pore fraction of 0.3

Only diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the aquifers. Model run B Cl-05b

### 5.3.3 Cl isotopes

**Base-case simulation**

A series of model calculations, using only slightly different parameters, has already been performed by Gimmi & Waber (2004). In the base case, an initial $\delta^{37}\text{Cl}$ of 0.31 ‰ is assumed throughout the low-permeability sequence, corresponding to the measured values in the centre of the sequence. This is an assumption that is difficult to defend by independent data. The values at the boundaries are thought to be constant at present values since the time of activation of the aquifers. The corresponding results are shown in Figure 5.3-7. Clearly, there are some major discrepancies between data and simulations, and the following conclusions are made, in accordance with those of Gimmi & Waber (2004):

- A rough, at most qualitative match with the data could be obtained for the base case simulations. There were, however, considerable discrepancies in the upper part of the Dogger and in the Lias.
- The match in certain parts of the profile could be improved by either using a larger ratio of the diffusion coefficients for $^{35}\text{Cl}$ and $^{37}\text{Cl}$, a higher concentration gradient towards the Malm, a slight upward advective flow, or using other boundary conditions for $\delta^{37}\text{Cl}$. There was, however, no single model run that led to an equally good agreement for all parts of the sequence.
profile. This indicates that either the initial state and/or the evolution at the boundaries was more complex than the assumptions made for the simulations.

- The observed peaks in $\delta^{37}\text{Cl}$ in the upper and lower part of the aquitard point to ongoing diffusion in these regions.
- The $\delta^{37}\text{Cl}$ values do not clearly contradict the interpretations of the stable water isotope or Cl$^-$ profiles, but they can also not be used to corroborate them. This is because additional parameters and boundary and initial conditions are required, which are difficult to infer independently.

Also note that the simulation of Figure 5.3-7, performed with FLOTRAN, yields identical results as the calculations performed with the code used by Gimmi & Waber (2004).

**Figure 5.3-7: Base case simulation for the $\delta^{37}\text{Cl}$ data of Benken**

Only diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the aquifers. Constant Cl$^-$ and $\delta^{37}\text{Cl}$ values at the boundaries corresponding to the present values are assumed, together with a uniform initial value in the low-permeability sequence. A ratio of the $^{35}\text{Cl}$ to $^{37}\text{Cl}$ diffusion coefficients of 1.002 is used (see Appendix A4.4). Model run B $\delta^{37}\text{Cl}$-01

**Influence of initial conditions**

It was noted by Gimmi & Waber (2004) that the $\delta^{37}\text{Cl}$ signatures tend to persist for longer times when compared to the Cl$^-$ signatures. Thus, it is more difficult to assign initial and boundary conditions for $\delta^{37}\text{Cl}$ as compared to Cl$^-$. Notably, it is more uncertain whether a spatially uniform initial condition is appropriate for the $\delta^{37}\text{Cl}$ simulations. To test the impact of initial conditions, a calculation was made using a linearly varying distribution of $\delta^{37}\text{Cl}$, starting at -0.3 ‰ in the Keuper and rising to +1.2 ‰ near the Malm aquifer. This simulation (as some others using different assumptions) shows an improved but still not satisfactory fit to the data (Figure 5.3-8). The results mainly illustrate the relatively strong sensitivity of the simulations to not well known initial and boundary conditions.
Only diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the aquifers. Initial $\delta^{37}\text{Cl}$ is $-0.3$ ‰ in the Keuper and rises linearly to $+1.2$ near in the Malm. A ratio of the $^{35}\text{Cl}$ to $^{37}\text{Cl}$ diffusion coefficients of 1.002 is used (see Appendix A4.4). Model run B $\delta^{37}\text{Cl}$-22

5.3.4 Helium

Base-case simulations

From the mean U and Th contents given in Section 2.3.5, a mean He production rate of $1.05\times10^{-11}$ cm$^3$ STP/g$_{\text{water}}$/a is calculated for the low-permeability sequence. When comparing this rate with the measured He concentrations of about $1.8\times10^{-4}$ cm$^3$ STP/g$_{\text{water}}$, it becomes clear that over times in the order of 1 Ma (i.e. similar to the evolution times of the stable water isotope profiles), the He concentrations would increase only by about 5%. Thus, since the time of the flushing of the Keuper aquifer with fresh water, He production is of minor importance.

What can be more important is diffusion from or towards the aquifers, provided concentration gradients exist. The He profile within the low-permeability sequence is more or less flat, with virtually no concentration gradient towards the Keuper, but a somewhat higher concentration in the Malm. Considering the errors of the pore-water data and the fact that the Malm sample was contaminated (the Cl' concentration had to be corrected), the significance of the increase of the He concentration towards the Malm is questionable. Two base-case simulations for diffusion with an effective diffusion coefficient of $3.0\times10^{-11}$ m$^2$/s (for 33 °C) were made, one considering the measured value in the Malm as the upper boundary condition, and one using a lower value identical to the one in the Keuper. In both cases, initial conditions ($1.0\times10^{-4}$ cm$^3$ STP/g$_{\text{water}}$ and $1.5\times10^{-4}$ cm$^3$ STP/g$_{\text{water}}$, respectively) were chosen such that approximately correct values were obtained after diffusion times of 0.7 to 1 Ma – there are no independent constraints. The results, shown in Figure 5.3-9, indicate contrasting profile shapes for the two cases. The initially strong curvature in the case where the upper boundary corresponds to the measured He concentration in the Malm is in conflict with the essentially flat trend of the data in the low-permeability sequence for short diffusion times. However, if times of up to 1.8 Ma are considered,
the fit becomes more acceptable in view of the relatively large measurement errors. Considering a lower initial condition in the Malm yields a flatter profile, but overall it is not more convincing than the first case. Because the initial conditions could not be estimated independently, and also because there are no He pore-water data in the uppermost part of the low-permeability zone and the profile looks more or less flat, it cannot be used directly to infer large-scale transport parameters. It is concluded that the He profile can be roughly reproduced by simple diffusive models, but there is little independent information.

A question is why the He concentration in the Keuper aquifer is so much higher than that in air-equilibrated water (4.65E-8 cm³ STP/gwater at 10 °C and sea level). The likely explanation is an uptake of He on the way from the infiltration zones in the Wutach region towards the Benken area. Notably, the volcanic areas in the Hegau (Figure 2.3-2) that were active in the late Tertiary may have contributed to the high He concentrations. This hypothesis is also supported by the high ³He/⁴He ratios. A similar reasoning applies for the Malm water. As a consequence, no large He concentration gradients were established by the flushing of the Keuper aquifer, in contrast to the situation for stable water isotopes and for chloride.

**Figure 5.3-9: Base-case simulations for He at Benken**

![Diagram showing base-case simulations for He at Benken](image)

- Constant concentrations at the boundaries as measured, initial He concentration of 1.0E-4 cm³ STP/gwater. Model run B He-01
- Lower Malm and Keuper concentrations of 2.07E-4 cm³ (STP)/gwater, initial concentration of 1.5E-4 cm³ STP/gwater. Model run B He-01a

Diffusive transport and production considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the aquifers. He production rate of 1.05E-11 cm³ STP/gwater/°a. Note that identical results were obtained by using FLOTRAN and the code applied by Gimmi & Waber (2004) as modelling tools.

### 5.3.5 Considering vertical advection

**Water isotopes**

The present-day hydraulic gradient between the Keuper and Malm aquifers at Benken is in the order of -0.2 m/m and points to upward flow (ignoring the possible presence of an overpressured zone within the low-permeability sequence). With a hydraulic conductivity of 2E-14 m/s, flow porosity of...
0.12 (water isotopes) and 0.06 (anions), upward advection velocities of -3.3E-14 m/s and -6.7E-14 m/s can be calculated, respectively. Simulations of such low velocities show that the resulting profiles are indistinguishable from the cases that consider diffusion alone, even for evolution times up to 2 Ma. This is confirmed by the small calculated Peclet numbers that are <1 for both water isotopes and Cl⁻.

The effects of hypothetical higher advection velocities on the calculated profiles of water isotopes were explored in detail by Gimmi & Waber (2004), who made the following conclusions:

- Advection velocities <2E-12 m/s (corresponding to hydraulic gradients <12 m/m) yield fits to the data that are comparable to (but not better than) model calculations considering pure diffusion. Best fits are obtained for evolution times similar to those of the base case.
- Higher advection velocities distort the calculated profiles, and the fits to the data become progressively worse. Upward flow reduces and downward flow increases the evolution times for best fits.

These calculations are illustrated in Figure 5.3-10, which were obtained using the transport parameters described in Section 2.3 (slightly different from those used by Gimmi & Waber 2004). Each graph shows the calculated profile for various upward/downward advection velocities. In the case of upward advection, the misfit of the model to the data becomes considerable for advection velocities of -6.7E-12 m/s and higher. This relatively high value is largely due to the absence of tracer data in the uppermost 50 m of the low-permeability sequence (Malm limestone). It is specifically this part of the profile in which upward advection yields distinctly different model curves, and the fact that these cannot be discriminated against measured data leads to uncertainty.

In the case of downward advection, even a lower velocity of 4.2E-13 m/s leads to marked deviations of the calculated profiles from the measured data. As already noted by Gimmi & Waber (2004), best-fit evolution times become shorter for upward advection and longer for downward advection.

**Chloride**

The influence of vertical advection on the Cl⁻ profile has been studied by Gimmi & Waber (2004). In principle, the effects on calculated profiles are expected to be stronger when compared to water isotopes:

- Flow porosity is ca. 2 times smaller than that for water (0.06; see above), leading to 2 times larger advection velocity.
- Dp of Cl⁻ in Opalinus Clay is ca. 3 times smaller than Dp of water isotopes, which leads to a higher relative importance of advection (Table 2.3-1).

The combined effects of these two points leads to Peclet numbers ca. 6 times higher than for water isotopes. Figure 5.3-11 shows calculated Cl⁻ profiles for upward advection velocities of -1.7E-13 m/s and -1.7E-12 m/s. The deviation from the base case is substantial for vₐ = -1.7E-12 m/s, and also more substantial than that for water isotopes at the same velocity (Figure 5.3-10). As advection starts to dominate in this scenario, the evolution time becomes shorter in comparison to the base case. Due to the scatter of the measured data, it is more difficult than for water isotopes to define a maximum velocity that would still be consistent with the measured profile.
Figure 5.3-10: **Effect of vertical advection on calculated profiles of water isotopes at Benken**

Advective-diffusive transport is considered. Top: Green curves – upward advection with advection velocities of -4.2E-13 m/s (model run B W13), -8.3E-13 m/s (model run B W14), -1.7E-12 m/s (model run B W15), -3.3E-12 m/s (model run B W16) and -6.7E-12 m/s (model run B W17). Bottom: Blue curves – downward advection with advection velocities of 4.2E-13 m/s (model run B W12), 8.3E-13 m/s (model run B W11) and 1.7E-12 m/s (model run B W10). Black curves indicate the base case (model runs B O-01 and B H-01) without advection. Positive sign refers to downward flow. The curves represent the best-fit evolution times as indicated in the graphs. Best fits were obtained for the oxygen and hydrogen data together, *i.e.* do not represent the individual best fits.
Figure 5.3-11: Effect of upward advection on calculated profiles of Cl\(^-\) at Benken

Model run B Cl-02 (blue, with upward advection of -1.7E-13 m/s) and B Cl-01 (red, base case without advection). Identical evolution times are shown for both cases because the effect of advection is small.

Adveotive-diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the aquifers.

5.3.6 Conclusions

At Benken, the stable water isotopes provide the most consistent data set. From the modelling of these data and the Cl\(^-\) data, the following conclusions are drawn:

- Assuming pure diffusion towards the underlying aquifer for an evolution time of 0.7 to 2 Ma leads to a good (stable water isotopes) or reasonable (Cl\(^-\)) match between model and data. This points to the importance of diffusion as the transport process.

- Best fits were obtained when assuming initial values that are clearly lower as compared to sea water. This means that some (diffusive) mixing between the originally deposited water and the fresh water of upper layers has already occurred when the Keuper aquifer was activated.

- Because no data are available for the low-permeability zone sequence close to the upper aquifer, no statement can be made about the time of activation of this boundary. However, this boundary is clearly of minor importance with regard to the development of the profiles.

- The Cl\(^-\) data show more scatter than the stable water isotopes, and the times tend to be somewhat longer. However, in view of the uncertainties of the Cl\(^-\) data and the Cl\(^-\) diffusion coefficient, we do not consider this difference as significant.

- When including advection, the match with the data generally gets worse, as soon as advection starts to become important. However, because of the missing data near the upper boundary, it is difficult to judge the goodness of fit of some of the scenarios with upward velocity.

- Only a qualitative agreement between the modelled and the measured \(^{37}\)Cl values, or He concentrations, could be obtained. Furthermore, in both cases, the match depends strongly on
the unknown boundary and initial conditions. Both, the $^{37}$Cl and the He data do not contradict the interpretations made based on the other data, but they could also not be used to corroborate those interpretations.

5.4 **Opalinus Clay at Mont Terri (Switzerland)**

As presented in Section 2.4, systematic tracer profiles were identified for anions, water isotopes and helium. The shapes of the profiles differ between the types of tracers. Anions show a clear asymmetry in that maximum concentrations are observed well below the centre of the low-permeability sequence, whereas the helium profile is near-symmetric. The relatively low amplitude of the profiles of water isotopes makes a clear definition of the shape of the profile difficult. One of the objectives of the modelling efforts is the attempt to explain all tracer profiles with an internally consistent set of parameters and assumptions.

5.4.1 **Chloride**

The shapes of the profiles of Cl$^-$, Br$^-$ and I$^-$ are almost identical (Figure 2.4-5, Figure 2.4-6). Because the data density and the ratio of analytical error to the amplitude of the profile are highest for Cl$^-$, modelling is restricted to this tracer. Consideration of the other tracers does not add additional insights.

One remarkable finding is the nearly linear increase of Cl$^-$ concentrations from the upper boundary down to the apex of the profile at ca. 160 m (Figure 2.4-5). The weak or absent curvature suggests a near-steady-state profile, which implies long time scales in case diffusion is considered as the dominant transport process. The other remarkable feature are the contrasting depth gradients of Cl$^-$ contents on both sides of the profile. The gradient in the lower limb (ca. 160 – 210 m) is much steeper than the one of the upper limb, suggesting that the lower aquifer was activated at a more recent time.

Considering these observations, the Cl$^-$ profile can be modelled using the parameters given in Section 2.4. As the initial condition, sea-water Cl$^-$ concentration (19 350 mg/L) is assumed. There are several reasons for this choice:

- Opalinus Clay was deposited under marine conditions, and the connate water was sea water.
- Cl$^-$/Br$^-$ ratios are very similar to those of present sea water (Pearson et al. 2003, Figure 6.4).
- In the neighbouring anticline at Mont Russelin (Section 2.5), the maximum observed Cl$^-$ concentration is close to that of sea water.

Given the fact that the calculation runs over millions of years and because the Mont Terri region has been uplifting since maximum burial at 10 Ma, time-dependent diffusion coefficients were used to account for changing in-situ temperature using the approach of Van Loon et al. (2005). The time-dependent correction factors are given in Table 5.4-1.

Model calculations were performed considering first the activation of the upper (Dogger) aquifer and, at a later stage, of the lower (Liassic) aquifer. The times at which these aquifers were opened were used as fit parameters in the calculations. As shown in Figure 5.4-1, a good fit that well reproduces the observed asymmetry of the Cl$^-$ contents is obtained when the upper aquifer is activated at 6.5 Ma and the lower aquifer at 0.5 Ma. These times are at the upper end of the geologically plausible spectrum but, in principle, not in contradiction with geological evidence.
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Temperature in Opalinus Clay was obtained from the known thermal and uplift history (Mazurek et al. 2006), also considering variability of surface temperatures with time (assumed to be 5 °C higher than today in the Miocene and 10 °C lower during the Pleistocene). Correction factors relate to diffusion coefficients obtained at laboratory conditions (20 °C), following the experimental data set of Van Loon et al. (2005), as presented in Appendix A3.1.

The diffusion times needed to obtain good fits depend, among others, on the initial Cl$^-$ concentration. Reasons justifying the assumption of Cl$^-$ contents of present sea water as the initial condition have been given above. In order to quantify the impact of alternative assumptions regarding the initial concentration, additional calculations were made. Assuming an initial Cl$^-$ content above that of sea water renders the diffusion times even longer and inconsistent with independent information on the geological evolution. Conversely, lower initial contents shorten the diffusion times. For an initial Cl$^-$ concentration of 15 000 mg/L, i.e. only slightly higher than the currently observed maximum value, the diffusion time is reduced to ca. 4.4 Ma for the upper aquifer and 0.4 Ma for the lower aquifer (Figure 5.4-2). The fit shown in Figure 5.4-2 is slightly worse when compared to the case considering a sea-water initial condition, namely in the region of the apex (around 160 m). In any case, in order to reproduce the near-linear Cl$^-$ distribution with depth as observed in the upper and central parts of the profile, diffusion over extended geological periods is required, otherwise the curvature of the modelled curves is too pronounced.

It is concluded that diffusion alone is capable of explaining the observed asymmetric Cl$^-$ profile with parameters within the range of the geologically possible spectrum. The uncertainty regarding the initial Cl$^-$ content is reflected in the uncertainty of the time needed to build up the observed profile.
Only diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the upper aquifer. The initial Cl$^-$ concentration corresponds to that of sea water. Model run MT A13

Only diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the upper aquifer. Model run MT A14
5.4.2 Water isotopes

First, a model calculation was performed considering the same palaeo-hydrogeological evolution as in the base case for Cl\textsubscript{i}, i.e. the activation of the aquifers at 6.5 and 0.5 Ma. Similarly, sea-water values (\(\delta^{18}\text{O} = \delta^2\text{H} = 0\ \text{‰}\)) were used as initial condition. The resulting model curves, as shown in Figure 5.4-3, do not fit the data and predict much too high values. Much longer diffusion times would be needed to fit the data.

In a second step, the initial \(\delta^{18}\text{O}\) and \(\delta^2\text{H}\) values were treated as fit parameters (still using the same palaeo-hydrogeological scenario as in the first case). Figure 5.4-4 illustrates that excellent fits to the data are obtained when initial values of \(\delta^{18}\text{O} = -4.5\ \text{‰}\) and \(\delta^2\text{H} = -20\ \text{‰}\) are used. Thus, an internally consistent set of model calculations fitting the data is only obtained when the initial water composition had sea-water salinity but markedly negative \(\delta\) values for water isotopes. It is noteworthy that a water sample from the neighbouring Mont Russelin anticline (Section 2.5) has a near-marine Cl\textsubscript{i} content of 18 400 g/L but markedly negative isotopic compositions of water isotopes of \(\delta^{18}\text{O} = -4.9\ \text{‰}\) and \(\delta^2\text{H} = -28\ \text{‰}\). This sample comes from a hydrogeologically protected position in the core of the anticline and is considered to be dominated by a geologically old signature, unaffected or only weakly affected by the interaction with active aquifers. The similarity between the composition of this sample and the calculated initial \(\delta\) values at Mont Terri is an argument that the latter may be geologically meaningful.

*Evidence from water isotopes compared to that from Cl*

At Mont Terri, both anion concentrations and water isotope ratios approach current meteoric values adjacent to the boundaries of the low-permeability sequence. Within the sequence, the maximum value for Cl\textsubscript{i} corresponds to ca. 72 % of the concentrations in sea water. For water isotopes, the \(\delta\) values correspond to only ca. 30 % sea-water component. This means that the pore waters in the low-permeability sequence cannot be explained as simple mixtures of sea water and current meteoric water. Pearson *et al.* (2003, ch. 6.3.2) stated that “the saline end member has been depleted in \(^{18}\text{O}\) and \(^2\text{H}\) relative to sea water at some stage in its history”. They suggested that the contrasting mixing ratios can be explained solely by the higher diffusion coefficient for water when compared to that for anions. However, as shown in Figure 5.4-3, the effect of the different diffusion coefficients is insufficient to explain the discrepancy. As an alternative hypothesis, Pearson *et al.* (2003) discussed ultrafiltration as a possible process to explain the observed pore-water compositions, even though this is speculative and cannot be quantified.

It is concluded that the initial pore water from which the currently observed tracer profiles developed is derived from sea water that was modified in the earlier evolution of the formation. The nature of the underlying processes is not currently understood.

*Boundary conditions over time*

The calculations above were performed using the current \(\delta\) values at the boundaries over the entire model period, i.e. ignoring the possible variability of the \(\delta\) values of precipitation over geologic time. If lower \(\delta\) values are considered for the Pleistocene (-2 and -16 %) for \(\delta^{18}\text{O}\) and \(\delta^2\text{H}\), average values in accordance with the discussion in Appendix A4.1), it is impossible to obtain good fits to the data (Figure 5.4-5). In principle, the fact that the tunnel seepages defining the present boundary values contain tritium suggests that there is a direct hydraulic connection to the infiltration area, and so the \(\delta\)
values of precipitation at any time should be used as boundary conditions at that time. However, the following points need to be considered:

- Surface temperatures at Mont Terri were probably well below 0 °C over large parts of the Pleistocene, which means that the infiltration area was subjected to permafrost. The region of Mont Terri was never covered by ice sheets. Permafrost may have greatly limited infiltration (except in the interglacials when precipitation had δ values not far from those of present time).

- The presence of tritium in the tunnel seepages could be explained as an artefact due to the activation of flow paths by tunnel construction. One example where this has been actually observed at Mont Terri is documented in Pearson et al. (2003, ch. 6). A seepage from Posidonia shale was sampled shortly after its excavation and had a Cl⁻ content of 8 470 mg/L, which fits well into the trend of the adjacent pore waters. The ³H level in this sample was below detection. Further samples from the same seepage were taken 6 months and 10 years later, with Cl⁻ contents below 2 000 mg/L and ³H contents of 3 – 4 TU. Gautschi et al. (1993) and Pearson et al. (2003) argue that the latter samples do not represent the conditions before tunnel construction and are affected by fresh water infiltrated along a flow path that was activated by the tunnelling activities.

In summary, the limited infiltration due to permafrost in the Pleistocene as well as the uncertainty regarding the interpretation of tritium and therefore the travel times for waters in the aquifers are taken as arguments for approximating the δ values at the boundaries by the current values over the entire period considered in the model calculations.

Figure 5.4-3: Model for water isotopes at Mont Terri considering an initial composition corresponding to that in sea water

Only diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the upper aquifer. The underlying hydrogeological evolution corresponds to that of the base case for Cl⁻. Model run MT W5
Figure 5.4-4: Base-case model for water isotopes at Mont Terri

Only diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the upper aquifer. The initial isotopic compositions were treated as fit parameters to obtain good correspondence between the model and the measurements. Model run MT W6

Figure 5.4-5: Model for water isotopes at Mont Terri considering variable boundary conditions over time

Only diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the upper aquifer. Same parameters were used as in base case, with the exception of δ values at the boundaries: δ¹⁸O / δ²H considered to be 1.3/10 ‰ higher in the Miocene (6.5 – 2.4 Ma), 2/16 ‰ lower in the Pleistocene (2.4 – 0.01 Ma) when compared to present values. Model run MT W7
5.4.3 Helium

Comments to the work of Rübel et al. (2002)

Based on the known U and Th contents of Opalinus Clay at Mont Terri, Rübel et al. (2002) calculated the He accumulation rate in pore water \( (A = 1.1E-11 \text{ cm}^3 \text{ STP/g water/a}) \). From this, assuming zero initial He concentration and neglecting He loss via diffusion, they obtained a build-up time of 9.1 Ma to reach the maximum currently measured He contents in the centre of the low-permeability sequence (around 1E-4 cm³ STP/g water). Based on this value and the reported age of folding and faulting of the Jura Mountains of 10 Ma, they concluded that the currently observed He profile represents a steady-state situation in which in-situ production equals the loss via diffusion. The assumption of steady state finally led to the derivation of an in-situ diffusion coefficient \( D_a = D_p = 3.5E-11 \text{ m}^2/\text{s} \) by fitting an analytical solution to the data. There are a number of points to make:

- There is no independent support for the assumption that steady state has been established at Mont Terri after ca. 10 Ma. However, this assumption is a necessary basis for the model calculations. In any case, it is difficult to substantiate the time until steady state because the initial condition is unknown.

- The palaeo-hydrogeological scenario underlying the calculations assumes the simultaneous activation of both aquifers. It is distinctly different from the more complex scenario developed in this report, which is based on the palaeo-hydrogeological evolution of the Mont Terri anticline. Palaeo-hydrogeology suggests that the overlying Dogger limestone aquifer was exposed by erosion and thereby activated much earlier than the underlying Lias aquifer, which was activated only after the erosion of Opalinus Clay in the apex of the anticline. This view is corroborated by the strong asymmetry of the Cl⁻ profile, with a much higher concentration gradient towards the lower aquifer (ca. 30 g/100 m) when compared with the upper aquifer (ca. 7 g/100 m). In Section 5.4.1, activation times of 6.5 Ma (upper aquifer) and 0.5 Ma (lower aquifer) were obtained. Given the recent timing of the activation of the lower aquifer, it is unlikely that a steady-state He profile has been established.

- The calculated \( D_p \) of 3.5E-11 m²/s is smaller than the corresponding measured values for HTO and Cl⁻ at Mont Terri (Table 2.4-1), which is difficult to understand. As discussed in Appendix A3.2, the self-diffusion coefficient of He in free water is ca. 3 times larger than that of HTO, and similar results were also obtained for the Callovo-Oxfordian at Bure. It is concluded that Rübel et al.’s (2002) \( D_p \) value is likely too small because the underlying palaeo-hydrogeological scenario is probably too simplistic and because steady state was not attained.

Model calculations

Because the current He profile may not reflect a steady-state situation, modelling requires one additional input parameter, namely the He content in the formation before the activation of the aquifers. Because this parameter is essentially unknown, it is treated here as a fit parameter in a calculation that adopts the same hydrogeological evolution as that derived for Cl⁻, namely the activation of the aquifers at 6.5 and 0.5 Ma. A diffusion coefficient \( D_p = 2.5E-10 \text{ m}^2/\text{s} \) is used (see Section 2.4) and is corrected for the thermal evolution assuming the same correction factors as those for HTO (Table 5.4-1). As shown in Figure 5.4-6, good fits are obtained for an initial He content of 5E-4 cm³ STP/g water. Because there is no means to test the plausibility of this number, there is little predictive value in the calculation. In any case, it is evident that in this scenario, steady state has not been attained and that Opalinus Clay is still losing He to the embedding aquifers.
However, one piece of information that is independent of the choice of the initial concentration is the shape of the modelled profile, which is essentially symmetric, in contrast to the strongly asymmetric Cl⁻ profile and the slightly asymmetric profiles for water isotopes. The symmetry is explained by the higher diffusion coefficient for He, which leads to a more rapid upward migration of the apex of the model curves than for the other tracers.

**Figure 5.4-6: Base-case model for He at Mont Terri**

![Base-case model for He at Mont Terri](image)

Difusive transport and production are considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the upper aquifer. Model run MT N6

**5.4.4 Considering vertical advection**

*Can advection instead of diachronous activation of the aquifers explain the asymmetry of the Cl⁻ and water isotope profiles?*

In the base case (Section 5.4.1), the asymmetric profiles of Cl⁻ and water isotopes were explained by a time lag between the activation of the upper and lower aquifers, in consistency with the erosion history (Section 2.4). The alternative hypothesis proposed here assumes a simultaneous opening of both aquifers linked with downward\(^{19}\) advection. It is clear that this scenario is in conflict with the palaeo-hydrogeological evolution that suggests a significant time lag between the activation of the upper and lower aquifers, but it is considered as a "what if" scenario because it represents the simplest possible case. As shown in Figure 5.4-7, a good fit to the data is obtained for an evolution time of 2.5 Ma and a downward advection velocity of 8E-13 m/s, which corresponds to a hydraulic gradient of 1.9. Smaller and larger velocities yield clearly less good fits (Figure 5.4-8). The calculated evolution time is within the possible spectrum.

\(^{19}\) At Mont Terri, the strata are inclined (see profile in Figure 2.4-2). For the sake of simplicity, they are rotated back to the original stratigraphic position in all Figures showing tracer profiles. The terms "downward" and "upward" relate to directions normal to the stratification and so, in reality, are oblique relative to Earth coordinates.
In the next step, the scenario derived for Cl\textsuperscript{-} is applied to water isotopes. Figure 5.4-9 shows the results of the calculations assuming a simultaneous activation of both aquifers at 2.5 Ma and a downward advection velocity of 4.3E-13 m/s (which corresponds to the same Darcy velocity as in the case of Cl\textsuperscript{-}, given the fact that flow porosities for water and Cl\textsuperscript{-} are considered to be different; see Section 4.3.5). The calculated tracer distribution after 2.5 Ma shows fair agreement with the data, even though the fit is less good than that of the base case.

In the last step, the scenario for Cl\textsuperscript{-} is applied to He, in order to see whether it can equally well explain the symmetric He profile as the base case. In order to obtain a good fit, an initial concentration of 1.5E-3 cm\textsuperscript{3} STP/g\textsubscript{water} must be assumed, i.e. 3 times the value in the base case. Given the fact that the initial concentration is not known and was a fit parameter even in the base case, both values appear possible. The resulting profile is shown in Figure 5.4-10 and is very similar to the one of the base case (Figure 5.4-6), which means that both scenarios equally well explain the data. The profile is largely dominated by out-diffusion towards the boundaries. Advection affects the shape of the profile only to a very limited extent, which can be explained as follows:

- Dp for He is about 5 times larger than for Cl\textsuperscript{-}, resulting in a larger relative importance of diffusion (and a smaller Peclet number)
- At a given Darcy velocity, the accessible porosity for He is larger than that for Cl\textsuperscript{-} (factor of 1.84 in the present case), which leads to an accordingly smaller advection velocity.

The combined effects of these differences result in a Peclet number for He that is smaller by about a factor 10 compared to Cl\textsuperscript{-} under the same hydraulic conditions.

It is concluded that the alternative scenario for Cl\textsuperscript{-} and He with simultaneous activation of both aquifers at 2.5 Ma and a limited downward advection explains the data equally well as the base case without advection. For water isotopes, the fit to the data is less good than in the base case, but the misfit is not sufficient to invalidate the scenario. Even so, the alternative scenario is less well supported by independent data:

- Both aquifers were activated in response to erosion. It is less likely that this happened simultaneously, and a time lag due to progressive erosion is in better agreement with palaeo-hydrogeological understanding.
- There is no satisfactory support for assuming a downward directed hydraulic gradient in the past, and it does not exist today.

For these reasons, the base case remains the preferred scenario to explain the tracer profiles at Mont Terri.
**Figure 5.4-7:** Alternative evolution of the Cl⁻ profile at Mont Terri, assuming simultaneous activation of both aquifers

Advective-diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of both aquifers. A downward advection velocity of 8E-13 m/s is assumed. Model run MT A15

**Figure 5.4-8:** Alternative evolution of the Cl⁻ profile at Mont Terri, assuming simultaneous activation of both aquifers and different downward advection velocities

Advective-diffusive transport is considered. Model runs MT A17 (vₐ = 4E-13 m/s), MT A15 (vₐ = 8E-13 m/s) and MT A16 (vₐ = 1.6E-12 m/s)
Figure 5.4-9: **Alternative evolution of the water-isotopes profile at Mont Terri, assuming simultaneous activation of both aquifers**

Advection-diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of both aquifers. A downward advection velocity of 4.3E-13 m/s is assumed. Broken curve shows the best fit of the base case (taken from Figure 5.4-4). Model run MT W8

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Figure 5.4-10: **Alternative evolution of the He profile at Mont Terri, assuming simultaneous activation of both aquifers**

Advection-diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of both aquifers. A downward advection velocity of 4.36E-13 m/s is assumed. The initial He concentration is 1.5E-3 cm³ STP/gwater, i.e. 3 times the value in the base case. Model run MT N7
Advection added to the base-case scenario

In this section, the base-case scenario with diachronous opening of the over- and underlying aquifers is considered in conjunction with downward and upward advection.

Good model fits to the data, comparable to the fit of the base case, can be obtained for a wide range of downward advection velocities if the activation times for both aquifers are used as fit parameters (Figure 5.4-11). Downward advection results in more recent activation times for the upper aquifer but earlier times for the lower aquifer. The earlier activation times derived for the lower aquifer – for a small advection velocity of $4 \times 10^{-13}$ m/s, 0.7 Ma are needed for a good fit – are in conflict with palaeo-hydrogeologic evidence which indicates that erosion did not exhumate this aquifer before 0.5 Ma (Section 2.4). Therefore, velocities $>4 \times 10^{-13}$ m/s are considered as inconsistent with the data.

For upward advection, the situation is somewhat different, and good fits to the data cannot be achieved just by varying the activation times of the aquifers. Figure 5.4-12 shows that in the earlier part of the evolution, when only the upper aquifer is active, a steady-state profile is established after some time. This means that the diffusive Cl$^-$ loss into the upper aquifer is outweighed by the upward advective transport of Cl$^-$. For advection velocities in the order of $-4 \times 10^{-13}$ m/s, such an equilibrium state is reached after an evolution time of ca. 6 – 8 Ma. As illustrated in Figure 5.4-12, the curvature of the modelled Cl$^-$ profile is substantial and remains inconsistent with the near-linear trend of the data even if much longer evolution times would be considered. It is concluded that only very small advection velocities of ca. $-4 \times 10^{-13}$ m/s result in modelled profiles that agree with the data. The lowermost part of the profile, i.e. the evolution after the activation of the lower aquifer, can, in principle, be satisfactorily reproduced even for higher advection velocities.

In summary, the profile at Mont Terri is very sensitive to the effects of vertical advection, and even small velocities affect the calculated profiles. From the maximum advection velocities of $4 \times 10^{-13}$ m/s beyond which the data cannot be modelled in consistence with independent evidence, hydraulic gradients <1 and Peclet numbers of 1.5 – 2 can be calculated.

5.4.5 Conclusions

It has been shown that diffusion alone can explain the Cl$^-$, water isotope and He profiles when geologically plausible sets of input data are used for modelling. Internally consistent input-data sets explain the asymmetric Cl$^-$ profile as well as the symmetric He profile. The different shapes of the profiles can be attributed to the differences in the diffusion coefficients of the various tracers.

It must be noted that the information obtained from the different tracers is not fully independent. For example, the hydrogeological evolution obtained from the evaluation of the Cl$^-$ profile was used as input for the evaluation of the other tracers, for which no independent hydrogeological constraints can be made. In summary, the truly independent conclusions are as follows:

- The activation times of the over- and underlying aquifers can be constrained based on the evaluation of the Cl$^-$ profile. Assumptions regarding the initial Cl$^-$ concentration only moderately affect the resulting hydrogeological scenario.
- The initial δ values for water isotopes obtained from the evaluation of the tracer profiles are well below those of sea water but consistent with those of a ground-water sample from the Mont Russelin anticline. This water sample comes from a hydrogeologically protected position and is thought to represent an “old” signature.
- The near-symmetric shape of the modelled He is a result that is independent of assumptions regarding the initial He concentration. It is consistent with the shape of the observed profile.
Figure 5.4-11: Effect of downward advection on the base-case scenario for Cl\(^–\) at Mont Terri

Downward advection velocity: 4E-13 m/s  
Activation time of upper aquifer: 4 Ma  
Activation time of lower aquifer: 0.7 Ma

Downward advection velocity: 6E-13 m/s  
Activation time of upper aquifer: 3.2 Ma  
Activation time of lower aquifer: 1 Ma

Adveective-diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the upper aquifer. Model run MT A18 (left) and MT A19 (right).

Figure 5.4-12: Effect of upward advection on the base-case scenario for Cl\(^–\) at Mont Terri

Adveective-diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the upper aquifer. Upward advection velocity is -4E-13 m/s. A steady-state profile is reached after ca. 6–8 Ma. The lower aquifer is active in the last 0.5 Ma (in the calculation above, this is between 9.5 and 10 Ma since activation of the upper aquifer). Model run MT A20.
5.5 Opalinus Clay at Mont Russelin (Switzerland)

Regular profiles were identified for Cl\textsuperscript{−}, water isotopes and helium. There are a number of differences when compared to the data obtained at Mont Terri:

- The Liassic aquifer underlying the low-permeability sequence is not exposed on the surface and therefore hydraulically not active. This is reflected by the fact that the tracer profiles show increasing Cl\textsuperscript{−} and He concentrations and increasing δ values for water isotopes with increasing distance to the overlying Dogger aquifer, without any drop in the Liassic. Unlike at Mont Terri, the Liassic is located in a protected position in the fold core and is covered by Opalinus Clay and the Dogger limestones in the whole anticline.

- The internal structure of the anticline is complex. On the one hand, this renders the definition of the system geometry more difficult. On the other hand, thrust faults in Opalinus Clay are more frequent when compared to Mont Terri. One prominent fault zone in the section 138.1 – 166.4 m orthogonal distance from the contact to the Dogger limestones shows a clear disturbance in the δ\textsuperscript{18}O and δ\textsuperscript{2}H values and in the He concentrations, whereas the Cl\textsuperscript{−} concentrations are less affected, if at all. The question remains whether this disturbance is an \textit{in-situ} feature or associated to recent processes around the tunnel.

- The maximum Cl\textsuperscript{−} concentrations and δ values for water isotopes are higher than those at Mont Terri, \textit{i.e.} they are closer to those of sea water. Similarly, maximum He concentrations are also higher.

5.5.1 Chloride

The Cl\textsuperscript{−} profile shows a regular increase of concentration with increasing distance from the Dogger. Some limited scatter is observed in the fault zone (138.1 – 166.4 m), but this can probably be explained by lateral heterogeneity (due to the acute angle between the tunnel and the contact plane to the Dogger, a long section along tunnel is compressed in a short zone of the orthogonal projection). The maximum Cl\textsuperscript{−} concentrations in this zone scatter around the sea-water value, and a water sample from the Liassic yielded a value of 18 400 mg/L. Therefore, a sea-water Cl\textsuperscript{−} concentration of 19 350 mg/L is considered as the initial condition for modelling in the base case\textsuperscript{20}. In analogy to the approach used at Mont Terri, a time-dependent diffusion coefficient was used to account for temperature effects (Table 5.4-1). The base-case calculation, shown in Figure 5.5-1, considers the activation of the overlying Dogger aquifer at some point but assumes that transport in all underlying units is dominated by diffusion. A good fit is obtained for a build-up time of 3 Ma, \textit{i.e.} for a shorter time than at Mont Terri (6.5 Ma). A shorter time is also expected intuitively, given the stronger curvature of the Cl\textsuperscript{−} profile when compared to the near-linear upper part of the profile at Mont Terri. The shorter time also appears sensible from a geological point of view, given the fact that the erosion of the anticline is more limited than at Mont Terri, probably resulting in a more recent timing for the activation of the Dogger aquifer. Using the maximum measured Cl\textsuperscript{−} concentration of 21 716 mg/L as initial condition also provides a reasonable fit to the data, and the diffusion time is only insignificantly longer.

\textsuperscript{20} It was noted in Section 2.5.7 that the Cl\textsuperscript{−}/Br\textsuperscript{−} ratios of pore waters, unlike that of the Liassic ground-water sample, are variable and generally higher than in present-day sea water. The adequacy of the assumption of sea-water composition as initial condition is yet to be confirmed.
Figure 5.5-1: **Base-case model for Cl\(^-\) at Mont Russelin**

Only diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the aquifer. Model run MR A2

Figure 5.5-2: **Model for Cl\(^-\) at Mont Russelin considering an alternative position of the upper boundary**

Only diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the aquifer. The upper boundary is assumed to be located at -65 m instead at -45 m as in Figure 5.5-1. Model run MR A4
The Cl⁻ concentration in borehole NT-12 at -40.5 m, only 4.5 m away from a tritium-containing seepage into the tunnel, is remarkably high and is not well explained by the model calculations. It can possibly be due to local heterogeneity. Alternatively, it can be speculated that the tunnel seepage at -45 m was only activated by the tunnelling activities and that the boundary of the low-permeability sequence is even farther away from the contact to Opalinus Clay. However, there is no independent supporting information. In Figure 5.5-2, the upper boundary is moved another 20 m into the Dogger limestone, which results in a better fit to the data and extends the diffusion time to 4 Ma. Given the limited amount of data and the speculative character of this calculation, it is not considered further.

5.5.2 Water isotopes

The same palaeo-hydrogeological evolution as that applied for Cl⁻ was also used for stable water isotopes, i.e. the aquifer overlying the low-permeability sequence is thought to have been activated and flushed by meteoric water at 3 Ma. The modelling strategy pursued was analogous to that already described in Section 5.4 for Mont Terri. First, a sea-water initial isotopic composition was considered ($\delta^{18}$O = $\delta^2$H = 0‰ V-SMOW), and the resulting model calculation is shown in Figure 5.5-3. It is evident that, as for Mont Terri, it is impossible to obtain good fits, and the initial isotopic compositions must have had negative values. In Figure 5.5-4, the base-case calculation, the initial isotopic composition was treated as a fit parameter, and the best-fit initial values are $\delta^{18}$O = -4.8‰ V-SMOW and $\delta^2$H = -30‰ V-SMOW. These values compare well with those obtained at Mont Terri (-4.5/-20‰) and with the isotopic composition of the water sample from Posidonia Shale sampled at 176.8 m orthogonal distance at Mont Russelin (-4.9/-28‰). As already concluded for Mont Terri, the pore waters at Mont Russelin cannot be explained as a simple mixture of sea and fresh water.

In the calculations described above, it was assumed that the current isotopic composition at the upper boundary is representative for the entire period considered. In Figure 5.5-5, the isotopic composition of water at the upper boundary was varied as a function of climate according to the discussion in Appendix A4.1. It is evident that the fit to the data is less good than in the base case, and namely in the upper part of the profile, the model predicts lower δ values than actually observed. As for Mont Terri, it is concluded that permafrost probably limited or even prevented infiltration of water during cold periods.

The faulted zone at 138.4 – 166.4 m orthogonal distance is characterised by markedly lower δ values, and the disturbance appears to reach beyond this zone, namely for $\delta^2$H. The process by which the isotopic composition of water was lowered but salinity remained constant is not known (ultrafiltration?). Figure 5.5-6 shows a scoping calculation considering circulation of water in the faulted zone, considering the following assumptions:

- The starting point is the current tracer profile according to the base case (Figure 5.5-4).
- The fault is simplified into a single plane in the centre of the faulted zone.
- The isotopic signature of the water circulating in the fault is thought to be identical to that of the current infiltration into the Dogger limestones, i.e. $\delta^{18}$O = -9.4‰ and $\delta^2$H = -63.4‰, and is kept constant over time.

Figure 5.5-6 shows that, under these assumptions, it would take time in the order of tens of thousands of years to build up the observed disturbance. From a geological point of view, it appears unlikely that water flow in the fault over the last 10 – 100 ka was sufficiently high to maintain the assumed low δ values without any buffering by the matrix pore water. The scoping calculation in Figure 5.5-6 remains an insight model based on unsupported assumptions and so should not be over-interpreted. Another hypothesis to explain the low δ values is a possible disturbance due to tunnel construction in zones of bad rock quality, even though the actual mechanism is not currently clear.
Figure 5.5-3: **Model for water isotopes at Mont Russelin considering an initial composition corresponding to that of sea water**

Only diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the aquifer. Model run MR W2

Figure 5.5-4: **Base-case model for water isotopes at Mont Russelin**

Only diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the aquifer. Model run MR W7
**Figure 5.5-5:** Model for water isotopes at Mont Russelin considering a variable upper boundary condition over time

Only diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the aquifer. Model run MR W8

**Figure 5.5-6:** Modelled effects of hypothetical flow in the faulted zone (138.4 – 166.4 m orthogonal distance) at Mont Russelin

Diffusive transport in the whole sequence and advection in the fault are considered. Numbers indicate evolution times in Ma since activation of the aquifer. The fault is simplified into a single plane at 152.4 m in which water composition is kept constant at current surficial water isotope composition, i.e. $\delta^{18}O = -9.4 \, \text{‰}$ and $\delta^2H = -63.4 \, \text{‰}$. Model run MR W9
5.5.3 Helium

As the data set for dissolved He is quite limited, only scoping calculations can be performed. Figure 5.5-7 shows a simulation in which the initial He concentration was adjusted in order to match the uppermost two data points for an evolution time of 3 Ma (as in the base-case for Cl⁻). The resulting $He_{init}$ of 2.8E-3 cm$^3$ STP/g$_{water}$ is higher than the corresponding value for Mont Terri (5E-4 cm$^3$ STP/g$_{water}$). This higher value reflects the much steeper concentration gradient of He in the upper part of the Mont Russelin profile (almost an order of magnitude larger than at Mont Terri). It is also evident that the model does not capture the curvature of the data at greater depth, even though this could also be explained by He loss in the vicinity of the fault zone. A much shorter evolution time (well below 1 Ma) would better describe the observed curvature, but there is no independent evidence for such a scenario. Overall, the data set is too limited to provide firm constraints on the evolution of the system, and it does not contribute any independent information.

![Figure 5.5-7: Scoping model for He at Mont Russelin](image)

Diffusive transport and production are considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the aquifer. Initial He concentration = 2.8E-3 cm$^3$ STP/g$_{water}$ before activation of the Dogger aquifer. Model run MR N4

5.5.4 Considering vertical advection

In spite of the absence of an active aquifer in the Liassic, vertical\textsuperscript{21} advection is considered in the sense of "what if" scenarios. As shown in Figure 5.5-8, downward advection always yields worse fits than the base case for Cl⁻ in which only diffusion is considered. For advection velocities $\geq$5.2 E-13 m/s, the modelled profiles become heavily distorted and are not compatible with the data. Best-fit evolution times are reduced by downward advection.

\textsuperscript{21} Similar to Mont Terri, the inclined strata are rotated back to the original horizontal position in all graphs, and the terms "vertical", "downward" and "upward" relate to directions normal to the stratification and so, in reality, are oblique relative to Earth coordinates.
In the case of upward advection, the fit of the model to the data is comparable to that of the base case for velocities up to \(-5.2\text{E-13} \text{ m/s}\). For velocities \(\geq 1.0\text{E-12} \text{ m/s}\), the fit to the data is unacceptable, and evolution times become so long that they contradict palaeo-hydrogeological constraints on the activation time of the aquifer (the Jura Mountains started folding at 10.5 Ma, which is considered as the absolute maximum for the activation time). The fit is not improved even when longer evolution times would be assumed because a steady-state profile is established in which loss of Cl\(^-\) by out-diffusion is compensated by the upward flux.

Figure 5.5-8: Effects of vertical advection on Cl\(^-\) profile at Mont Russelin

Advective-diffusive transport is considered. Positive sign refers to downward advection. Model runs MR A2 (\(v_a = 0 \text{ m/s, diffusion only}\)), MR A6 (\(v_a = 5.2\text{E-13} \text{ m/s}\)), MR A5 (\(v_a = 1.0\text{E-12} \text{ m/s}\)), MR A7 (\(v_a = -5.2\text{E-13} \text{ m/s}\)), MR A9 (\(v_a = 1.0\text{E-12} \text{ m/s}\))

5.5.5 Conclusions

- As for Mont Terri, the older history of pore-water evolution is not well understood. Samples with Cl\(^-\) contents corresponding to that of sea water have negative \(\delta\) values (average: \(\delta^{18}\text{O} = -6 \%\), \(\delta^2\text{H} = -40 \%\)). Thus, the pore waters cannot be explained as simple mixtures of sea and fresh water, and the process that led to lower \(\delta\) values while maintaining salinity is unclear.

- The degree to which the pore-water signature was affected by out-diffusion in consequence of the folding and erosion of the Jura Mountains is less strong compared to Mont Terri. At Mont Russelin, the maximum observed Cl\(^-\) and He contents and the \(\delta\) values of water isotopes are higher.

- The observed tracer profiles are regular and consistent with out-diffusion towards the upper aquifer as the main transport process. The time at which this aquifer became activated is more recent than at Mont Terri, which is consistent with the more limited erosion at Mont Russelin.
• In contrast to Mont Terri, the underlying Liassic aquifer has never been activated because it is not currently exposed on the surface by erosion.

• A major faulted zone was penetrated by the tunnel and has a distinct signature in water isotopes and He but not in Cl\(^-\). This is the first evidence of a geochemical disturbance related to deep faults in Opalinus Clay (even though close to the underlying Jurensis Marl and Posidonia Shale). The process that led to the disturbance is not understood and so cannot be quantified. Given the fact that samples for the tracer studies originate from short boreholes and were taken ca. 4 m away from the tunnel surface, effects related to tunnel construction cannot be excluded.

5.6 Toarcian-Domerian at Tournemire (France)

Even though the Toarcian-Domerian at Tournemire is a marine formation, its low Cl\(^-\) content of <1 g/L indicates that most of the salinity originally present was lost. The palaeo-hydrogeological evolution of the aquifers is complex and not well known (Section 2.6). It includes long-lasting continental periods, and the last marine incursion occurred around the Cretaceous/Tertiary boundary or earlier. The evolution of tracer contents in the aquifers since then is not well constrained, and so modelling of the tracer profiles remains on a somewhat hypothetical basis.

The sea-water components of pore water in the centre of the low-permeability sequence (where Cl\(^-\) contents and \(\delta\) values are highest) are only around 3 % for Cl\(^-\) but 30 – 35 % for water isotopes. This means that simple out-diffusion of sea water into fresh-water aquifers alone cannot explain the data. At some stage, a preferential loss of Cl\(^-\) must have occurred, or a more complex palaeo-hydrogeological evolution must be considered. Also, the shapes of the Cl\(^-\) and of the \(\delta^{18}\)O and \(\delta^2\)H profiles are different. The latter show a smooth, curved profile, whereas the Cl\(^-\) profile has a near-linear upper part and a sharp peak in the middle Toarcian before declining towards the lower aquifer.

5.6.1 Chloride

The Cl\(^-\) profile shows an almost linear upper segment with an apex at about two thirds of the thickness of the low-permeability sequence. Cl\(^-\) contents in the lower part of the sequence are not well known, but the concentration gradient is certainly steeper, indicative of a less extended period of time over which the lower aquifer has been active.

Figure 5.6-1 shows a scoping calculation in which a simple out-diffusion scenario of an initially marine pore water is considered. The Figure shows that it takes ca. 35 – 40 Ma to obtain the currently observed maximum Cl\(^-\) content in the sequence. However, the shape of the model curves does not fit the data well. It is concluded that 1) a very long period of time is required to account for the observed salinity level when considering diffusion alone, and 2) a more complex palaeo-hydrogeological evolution must have occurred than single-stage out-diffusion. The long diffusion time is a consequence of the very low De (see Chapter 3 for comparison with other formations) in combination with the substantial thickness of the low-permeability sequence and the low current salinity. What remains unclear is the exact timing of the main stage of out-diffusion – the region has been predominantly continental since 150 Ma.

Figure 5.6-2 shows the results of another scoping calculation in which out-diffusion is considered only towards the upper aquifer. Even over 150 Ma, i.e. the time since which the formation has been exposed to predominantly continental conditions, out-diffusion into the upper aquifer alone cannot
explain the observed low Cl$^-$ contents. The near-linear upper segment of the Cl$^-$ concentration profile must be the result of the interaction with both the upper and lower aquifers.

In order to reproduce the near-linear trend of Cl$^-$ in the upper two thirds of the profile, a calculation was made assuming a time-invariant upper boundary with present-day Cl$^-$ concentration and a lower boundary concentration of 800 mg/L. The latter value was obtained by extrapolating the observed linear trend of Cl$^-$ concentrations in the low-permeability sequence down to the lower aquifer. There is no independent palaeo-hydrogeological support for this value. As shown in Figure 5.6-3, it takes about 60 Ma until the near-linear trend as shown by the data is established. Then, the Cl$^-$ concentration in the lower aquifer is reduced to the currently observed value. Figure 5.6-3 shows that this base-case scenario reasonably well explains the data when water with current Cl$^-$ content is assumed to have been present in the lower aquifer for 2 – 3 Ma, i.e. roughly throughout the Pleistocene and Holocene. It is concluded that it is possible to fairly well reproduce the observed Cl$^-$ profile considering diffusion alone, but the scenario needed for a good fit to the data is not sufficiently well supported by independent palaeo-hydrogeological evidence and so remains hypothetical.

Another approach to model the Cl$^-$ profile would be to start with an initial concentration below that of sea water and so consider only the younger part of the evolution. This approach was chosen, for example, for the low-permeability sequence at Benken (Section 5.3). However, this is difficult at Tournemire for the following reasons:

- In Benken, a well-developed plateau of Cl$^-$ concentrations is observed. This supports the scenario that, at some stage, Cl$^-$ concentrations in the sequence were near-constant and can be represented by the highest currently observed value. At Tournemire, such a plateau is not present, and so there is no basis for assuming that the highest observed value was at some time representative of the whole formation.

Figure 5.6-1: Scoping calculation: simple out-diffusion model for Cl$^-$ at Tournemire

Only diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the aquifers. Initial condition: Cl$^-$ = 19 350 mg/L (sea water). Model run TOU A1
Figure 5.6-2: Scoping calculation: Out-diffusion model for Cl\(^-\) towards the upper aquifer at Tournemire

Only diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the upper aquifer. Initial condition: Cl\(^-\) = 19 350 mg/L (sea water). Model run TOU A2

Figure 5.6-3: Base-case model for Cl\(^-\) at Tournemire

Only diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the upper aquifer. Out-diffusion model for Cl\(^-\) towards upper and lower aquifers at Tournemire (the lower aquifer with 800 mg/L Cl\(^-\)) until near steady state after ca. 60 Ma, then a change of Cl\(^-\) in the lower aquifer to present-day value. Model run TOU A4
When a scenario considering the highest observed Cl\(^-\) concentration as the initial value is considered, the resulting modelled profile will have a curved shape (similar to that in Figure 5.6-1) and will not capture the shape of the observed profile, including the near-linear upper limb. This means that such a scenario is not realistic.

5.6.2 Stable water isotopes

The profile of $\delta^2$H is regular with maximum values in the centre of the low-permeability sequence (Figure 5.6-4). The scatter in the uppermost part is considered to be due to analytical artefacts or the possible influence of faults and so may not be meaningful. In the case of $\delta^{18}$O, a similar profile is observed, even though less clearly. The more substantial scatter in $\delta^{18}$O is attributed to analytical problems related to vacuum distillation, as discussed in Section 2.6.

Due to the proximity to the Mediterranean, the Tournemire area was never glaciated and affected by permafrost only episodically (Antoine et al. 1999). Thus, infiltration could take place even during large parts of cold periods. For defining the evolution of the boundaries, it is assumed that flushing of the aquifers was rapid and that the isotopic composition of water closely reflected that of precipitation at all times. According to the discussion in Appendix A4.1 on the relationship between the isotopic composition of precipitation and temperature, $\delta^{18}$O/$\delta^2$H values at the boundaries are assumed to be 2/16‰ lower than today in the late Pliocene an Pleistocene (2.4 – 0.01 Ma), whereas values of 1.3/10‰ higher than today are used for the generally warmer periods pre-dating the glacial period.

In the calculation illustrated in Figure 5.6-4, the highest currently observed $\delta$ values (ignoring the outliers in the uppermost part of the sequence) are considered as the initial condition representative of the whole low-permeability sequence at the end of the Miocene. Diffusive exchange with the aquifers is thought to have occurred since 2.4 Ma, i.e. since the onset of cold climates. The model predictions are in good agreement with the data and also reasonably well reproduce the shapes of the profiles. A slightly shorter diffusion time of ca. 1.5 Ma would yield even better fits, which can be taken as an indication that the isotopic composition of water at the onset of the ice ages was higher than the highest currently observed values.

In a second step, the full evolution starting from sea-water composition was explored. As shown in Figure 5.6-5, an excellent fit is obtained when an activation of the aquifers is assumed to have started at 9 Ma. This is in good agreement with palaeo-hydrogeological evidence, according to which the aquifers were activated at max. 10 Ma (Section 2.6).

It is noteworthy that the full consideration of variable isotopic conditions at the boundaries in response to climate variations yields model results that very closely reproduce the data, including the Holocene shift towards higher $\delta$ values. In fact, the model fits would be substantially worse if the climatic effects were neglected.

Also, it needs to be noted that in the case of Tournemire, the choice of the initial condition affects the diffusion time but has only a limited effect on the shape of the resulting best-fit curve. Because the data show a substantial scatter, we cannot discriminate between models considering lower initial $\delta$ values combined with a shorter evolution time and higher (e.g. marine) $\delta$ values combined with a longer evolution time.
Figure 5.6-4: Scoping calculation: simple out-diffusion model for water isotopes at Tournemire

Only diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the aquifers. Initial condition = highest measured values. Model run TOU W2

Figure 5.6-5: Diffusion of water isotopes at Tournemire over the last 9 Ma

Only diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the aquifers. Initial condition = marine values ($\delta^{18}$O = $\delta^2$H = 0). Model run TOU W4
5.6.3 Integration of evidence based on Cl⁻ and water isotopes

In order to reconcile the seemingly contrasting conclusions based on the Cl⁻ and the water-isotope profiles, it can be envisaged that the aquifers were active to some degree over very long time scales and so diffusive exchange of all tracers occurred over at least several tens of Ma. This is a conceivable scenario, given the fact that the area has been predominantly continental since 150 Ma – probably more conceivable than the preservation of marine conditions until the late Tertiary. When values for δ¹⁸O and δ²H of -5 and -32 ‰ throughout the low-permeability sequence are assumed at the end of the Miocene, the climate-related changes of the boundaries during the Pleistocene and Holocene yield modelled profiles that fit the observed tracer distributions well. This scenario is summarised in Table 5.6-1 and illustrated in Figure 5.6-6.

Table 5.6-1: Evolution of boundary conditions for Cl⁻ and water isotopes in the aquifers embedding the low-permeability sequence at Tournemire

<table>
<thead>
<tr>
<th>Time period [Ma]</th>
<th>Chloride [mg/L]</th>
<th>δ¹⁸O [%o V-SMOW]</th>
<th>δ²H [%o V-SMOW]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Upper boundary</td>
<td>Lower boundary</td>
<td>Upper boundary</td>
</tr>
<tr>
<td>≥60 – 2.4</td>
<td>6</td>
<td>800</td>
<td>-5</td>
</tr>
<tr>
<td>2.4 – 0.01</td>
<td>6</td>
<td>73</td>
<td>-9.7</td>
</tr>
<tr>
<td>0.01 – 0</td>
<td>6</td>
<td>73</td>
<td>-7.7</td>
</tr>
</tbody>
</table>

The Table represents an internally consistent scenario for the evolution of all tracers.

Figure 5.6-6: Diffusion of water isotopes at Tournemire over the last 65 Ma

Only diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the aquifers. Scenario compatible with that used for Cl⁻ in model run A4 (Figure 5.6-3). Model run TOU W5
It is concluded that

- the currently observed large-scale curvature in the $\delta^{18}O$ and $\delta^2H$ profiles most probably reflects the Pleistocene evolution
- the $\delta^{18}O$ and $\delta^2H$ profiles contain very limited information on the pre-Pleistocene history
- the Cl$^-$ profile can only be explained by considering a more complex and longer evolution
- an internally consistent scenario for all tracers can be derived, involving flushing with fresh, isotopically light water during the Pleistocene.

5.6.4 Considering vertical advection

Given the substantial scatter in the stable-isotope data, the effects of vertical advection are studied for Cl$^-$ only. As even the base case for Cl$^-$ is hypothetical due to the limited knowledge of the palaeo-hydrogeological evolution, it is not sensible to explore the effects of advection on this scenario. In the light of these uncertainties, only one simple scenario is considered, namely the possibility to explain the asymmetry of the Cl profile by downward advection. In this scenario, both aquifers are assumed to have been activated simultaneously, and the variables are 1) the initial Cl$^-$ concentration and 2) the value for downward advection velocity. Figure 5.6-7 illustrates the results. Assuming an initial Cl$^-$ concentration of 539 mg/L throughout the low-permeability sequence (highest measured value) yields model curves that are similar to the base case for mean advection velocities of $3.77 \times 10^{-13} - 7.55 \times 10^{-13}$ m/s and an evolution time of $3 - 4$ Ma. Increasing the initial concentration to $1000$ mg/L extends the evolution time to $7 - 9$ Ma and reduces the advection velocity to $1.89 \times 10^{-13} - 3.77 \times 10^{-13}$ m/s but essentially results in the same profiles as in the base case. These calculations show that, in the case of Tournemire, the data can be equally well explained by diffusion only considering a two-stage hydrogeological evolution (base case) or by diffusion + advection and considering a single-stage evolution of the boundaries. Of course, a large number of additional scenarios (e.g. assuming advection to occur only during certain periods of time) also exist. As long as the palaeo-hydrogeological evolution cannot be constrained by independent arguments, the ambiguity remains.

Based on the current natural hydraulic gradient of ca. 0.5 across the low-permeability sequence (directed downwards; see Section 2.6), an advection velocity of about $2 \times 10^{-11}$ m/s can be calculated, which is about 2 orders of magnitude larger than the velocities needed to explain the asymmetry of the Cl$^-$ profile in the scenario of the preceding paragraph. Using this velocity leads to a model profile as shown by the broken line in Figure 5.6-7. This profile is completely dominated by advection (Peclet number around 200) and inconsistent with the observed Cl$^-$ distribution within the low-permeability sequence. The profile evolves within 0.5 Ma since the onset of flushing, when the advective front reaches the base of the low-permeability sequence, and represents a steady-state situation at all later times. Therefore, the choice of the initial Cl$^-$ concentration does not affect the shape of the curve at times $>0.3$ Ma. The following explanations can be put forward to rationalise the discrepancy:

- The relatively high hydraulic conductivity of about $1 \times 10^{-12}$ m/s as measured in borehole tests characterises fractures within a small rock volume adjacent to the test intervals. The value on the scale of the formation could be much smaller due to limited hydraulic connectivity of the fracture network.
- Darcy’s law may not be applicable in low-permeability argillaceous formations, at least below a certain threshold gradient (around 1 m/m in Opalinus Clay).
- The current hydraulic gradient could be a recent phenomenon, and values in the past may have been smaller.
Given the fact that the surface relief changed only slightly over the last few Ma, drastic changes in the hydraulic heads in the aquifers are unlikely over these periods of time. It follows that downward flow has not occurred in spite of the presence of a hydraulic gradient. The upscaling of hydraulic conductivity measurements as well as the applicability of Darcy's law in very low-permeability formations remain a matter of debate.

Figure 5.6-7: Scenarios for Cl\(^-\) considering downward advection at Tournemire

Advectional-diffusive transport is considered. Curves represent the best fits for different initial Cl\(^-\) concentrations and advection velocities. Model runs TOU A5 (v\(_a\) = 3.77E-13 m/s, Cl\(_{init}\) = 539 mg/L), TOU A6 (v\(_a\) = 7.55E-13 m/s, Cl\(_{init}\) = 539 mg/L), TOU A7 (v\(_a\) = 3.77E-13 m/s, Cl\(_{init}\) = 1000 mg/L), TOU A8 (v\(_a\) = 1.89E-13 m/s, Cl\(_{init}\) = 1000 mg/L), TOU A9 (v\(_a\) = 2E-11 m/s)

5.6.5 Discussion and conclusions

- The Cl\(^-\) profile has a different shape than that of stable water isotopes, and it shows a much lower sea-water component. Moreover, in contrast to water isotopes, there is some degree of lateral heterogeneity of Cl\(^-\) concentrations at the same stratigraphic level (see Section 2.6).
- The shape of the Cl\(^-\) profile is best reproduced by a two-stage evolution. The straight upper part of the profile could be explained by out-diffusion towards an overlying fresh-water aquifer and an underlying aquifer with Cl\(^-\) = ca. 800 mg/L. In order to obtain the observed near-linear distribution, tens of Ma equilibration time would be required. Following this stage, a period of 2 – 3 Ma (i.e. more or less the Pleistocene and Holocene) during which exchange with two low-salinity aquifers (current Cl\(^-\) contents) occurred would explain the decrease of Cl\(^-\) concentrations in the lower part of the profile.
- The simplest way to model the profiles of \(\delta^{18}O\) and \(\delta^2H\) in the low-permeability sequence is to consider the activation of the embedding aquifers at ca. 9 Ma, which is consistent with independent palaeo-hydrogeological evidence. On the other hand, the underlying initial condition (sea-water values) may not be realistic due to the much longer exposure of the site to continental conditions.
• The scenario above for stable water isotopes is not consistent with that derived for Cl−. Alternative calculations show that model fits to the δ18O and δ2H profiles are always good as long as the δ values are assumed to be spatially more or less homogeneous and slightly higher than the highest currently observed values at the onset of the Pleistocene. This also means that the δ18O and δ2H profiles contain little information on the pre-Pleistocene evolution.

• Good fits to the δ18O and δ2H profiles are only obtained if the isotopic composition in the aquifers is varied as a function of surface temperature. In particular, consideration of δ values that are lower in the Pleistocene is needed to explain the data. This finding contrasts that obtained for Mont Terri (Section 5.4), where only a weak climatic effect (if any) needs to be considered for good model fits. In contrast to those sites, Tournemire was affected by permafrost during the Pleistocene only to a limited degree, so infiltration occurred even during cold periods, which most likely was not the case at Mont Terri and in Essen.

• The observed lateral heterogeneity of Cl− contents is best explained by assuming a chemically heterogeneous lower aquifer in the Pre-Pleistocene. For boreholes TN1/TN3, on which the modelling was focussed, a Cl− concentration of 800 mg/L at times pre-dating the Pleistocene was derived. Higher concentrations would better fit the data of other boreholes, such as VF4 (Figure 2.6-3). Such heterogeneity, probably related to lateral heterogeneity of hydraulic conductivity, is typical of karstic limestone aquifers. The absence of lateral heterogeneity in the δ18O and δ2H profiles is likely due to the higher diffusion coefficients for water and the fact that there was enough time to develop flat equilibrium profiles in the low-permeability sequence before the Pleistocene (Figure 5.6-6).

• Model runs including downward advection and a simple, one-stage evolution of the boundaries can also explain the asymmetry of the Cl− profile and fit the data as well as the base case. In principle, a large number of scenarios combining advection and diffusion could lead to model fits that agree with the data, but the basis to judge the plausibility of the underlying assumptions remains weak.

• All scenarios that were quantified are hypothetical, and the basis to test their plausibility against independent palaeo-hydrogeological evidence is weak. Therefore, no unique statements can be made on the (ir)relevance of advection and on the applicability of lab-derived diffusion coefficients on the scale of the formation.

• The low-permeability sequence at Tournemire is highly indurated and therefore characterised by comparatively low diffusion coefficients (see also Section 3.2.1). At the same time, the thickness of the sequence (257.4 m) is substantial, so evolution times for diffusion profiles are long. This means that even very small vertical advection velocities would have an effect on the shapes of the tracer profiles (see Section 4.2.1, Peclet number). The fact that tracer profiles are curved and show maxima in the central parts of the sequence indicates that the role of advection is subordinate, if not negligible. The advection velocity calculated from the current hydraulic gradient across the sequence using Darcy's law yields advection-dominated tracer profiles that are inconsistent with the observations. Either the measured hydraulic conductivities cannot be used on the scale of the formation, and/or Darcy's law does not apply in this highly indurated low-permeability sequence.
5.7 Boom Clay at Mol (Belgium)

5.7.1 Anions

Tracer data are available for Cl\(^-\), Br\(^-\) and I\(^-\) but not for water isotopes or noble gases (Section 2.7). All anions yield somewhat scattered profiles across Boom Clay, even though the concentrations in the central parts are typically higher than at the contacts to the aquifers. In comparison to all other sites and to sea water, the concentrations of Cl\(^-\) and Br\(^-\) are very low, indicating a near-quantitative out-diffusion since emergence of the area from the sea. I\(^-\) content is higher than in sea water, which is a consequence of \textit{in-situ} enrichment from the decomposition of organic matter (De Cannière, pers. comm.). Thus, the initial condition to quantify the I\(^-\) distribution in Boom Clay cannot be reasonably well constrained, and so the I\(^-\) profile is not modelled.

According to Section 2.7, the area of Mol emerged from the sea at around 2 Ma, and so it is at this stage when flushing of the embedding aquifers by meteoric water is thought to have started. Let us note that the average present-day Cl\(^-\)/Br\(^-\) ratio in Boom Clay is 37, which is a factor 8 lower than in sea water. Essentially, this ratio is determined by the corresponding values in the embedding aquifers, which are 37 (Neogene) and 39 (Lower Rupelian), respectively (Table 2.7-2).

In a first calculation, the upper aquifer (Neogene) is assumed to contain fresh water since the time of emergence, while a linear decrease of salinity over the past 2 Ma is assumed for the lower aquifer (Lower Rupelian). The initial condition is sea-water salinity. The results are shown in Figure 5.7-1. It becomes evident that the predicted salinity in Boom Clay is much too high, \textit{i.e.} the assumption of a linear decrease of salinity in the lower aquifer appears not to be adequate.

In a second calculation, instantaneous flushing of both aquifers is assumed, \textit{i.e.} current anion contents over the last 2 Ma are considered. The resulting out-diffusion profiles for Cl\(^-\) and Br\(^-\) are shown in Figure 5.7-2 and Figure 5.7-3. The current Br\(^-\) profile (Figure 5.7-3) can be very well explained by this simple out-diffusion scenario over 2 Ma. For Cl\(^-\) (Figure 5.7-2), about 2.5 – 3 Ma out-diffusion time is needed to reach current Cl\(^-\) contents, which is still broadly consistent with palaeo-hydrogeological evidence in consideration of the uncertainties related to transport parameters and the precise activation times of the aquifers.

5.7.2 Conclusions

It is concluded that simple out-diffusion starting at the time when the area of Mol emerged from the sea explains the data reasonably well. Both aquifers must have been flushed at the time of emergence, and a gradual decrease of salinity yields model results that are in contradiction with the observed anion profiles. Given the high diffusion coefficient and the limited thickness of Boom Clay, quantitative out-diffusion occurs over geologically short periods of time. Because the current tracer profiles are almost flat, the potential role of advection cannot be evaluated quantitatively.
Only diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the aquifers. Initial condition: Cl⁻ = 19 350 mg/L (sea-water value). Instantaneous flushing of the upper aquifer, linear decrease of salinity in the lower aquifer. Model run MOL A12
5.8 Boom Clay at Essen (Belgium)

As presented in Section 2.8, tracer profiles of anions and helium show near-linear trends of increasing concentrations with depth, and they fit well together with the values measured in the bounding aquifers. In the simplest case, these profiles could be conceived as due to steady-state diffusion. The profiles for water isotopes are also linear but show a complication in the vicinity of the upper (Neogene) aquifer.

5.8.1 Anions

The profiles for Cl\(^-\) and Br\(^-\) across Boom Clay are almost linear and show a trend of increasing concentrations. They essentially connect the very low concentrations in the Neogene aquifer (fresh water) and the Lower Rupelian aquifer (ca. 20% sea-water component). The profile for I\(^-\) is similar, even though somewhat less regular, possibly due to analytical problems of I\(^-\) analysis. Due to the analogy of these profiles, only Cl\(^-\) will be modelled, because no additional information would be obtained from the other anions.

Until emergence from the sea at 1.7 Ma, ground water in both aquifers as well as the pore water in Boom Clay are assumed to have contained marine anion concentrations. Because the Neogene aquifer is not covered by a low-permeability unit, it is likely that it was flushed by meteoric water rapidly after emergence and maintained low ion concentrations since then. In the Lower Rupelian aquifer, the evolution of salinity since emergence is more complex and more uncertain. Due to the large distance of more than 40 km to the infiltration area of this aquifer (Figure 2.7-2), the dilution of sea water is not complete even today. Two bounding scenarios can be envisaged for the evolution of salinity in the Lower Rupelian aquifer:
1. Linear decrease of salinity over time;
2. Instantaneous drop of salinity to the current value at the time of emergence of the site (1.7 Ma).

A model calculation according to scenario 1 is shown in Figure 5.8-1, i.e. a linear decrease of Cl\textsuperscript{–} concentration from 19 350 mg/L (sea water) to 3 400 mg/L (present value in the uppermost part of the aquifer) is assumed. Even though the out-diffusion process is fast when compared to other case studies (due to the large effective diffusion coefficient in Boom Clay and its limited thickness), it is not fast enough to result in a linear, steady-state concentration profile as actually observed.

In the next model calculation, it was assumed that the Cl\textsuperscript{–} concentration in the Lower Rupelian aquifer corresponded to the present-day value since the time of emergence (scenario 2). The modelled evolution of the Cl\textsuperscript{–} profile as shown in Figure 5.8-2 shows a close correspondence to the data. After a diffusion time of ca. 1.2 – 1.4 Ma after emergence, the profile changes only slowly over time because it approaches steady state. Some data points in the lower part of the profile show some deviation from the modelled curves, which can be explained as follows:

- The data are affected by analytical errors (e.g. dilution of the pore water by drilling fluid – possible because of the higher sand content at the base of Boom Clay);
- The Lower Rupelian aquifer had lower Cl\textsuperscript{–} concentrations over a period in the past;
- The chosen diffusion coefficients are not representative in the lowermost part of the profile.

In spite of the slight misfit and related uncertainties in the lower part of the profile, it can be concluded that the observed near-linear profile of Cl\textsuperscript{–} over Boom Clay can be well explained by diffusion alone if the diffusion time exceeds 1.4 Ma at present-day Cl\textsuperscript{–} concentration in the Lower Rupelian aquifer. This means that a large part of the dilution process of this aquifer must have occurred in the early stages of the continental evolution, i.e. at ca. 1.7 – 1.4 Ma. While there are alternative model setups that would equally well fit the observations, the model shown in Figure 5.8-2 is considered as the base case because it explains the data with one single transport process and a simple but geologically sensible evolution of the embedding aquifers.

5.8.2 Stable water isotopes

The profiles of stable water isotopes through Boom Clay can be separated into two segments (Figure 5.8-3):

- Except for the uppermost ca. 20 m, the profiles for both δ\textsuperscript{18}O and δ\textsuperscript{2}H are near-linear and show increasing values with depth. This finding is analogous to the linearly increasing anion concentrations and could be interpreted as due to steady-state diffusion. However, the current isotopic composition of the Neogene aquifer does not fit the linear trend – the latter would require δ\textsuperscript{18}O = -6.5 ‰ and δ\textsuperscript{2}H = -49 ‰ at the top of Boom Clay, which is 0.5/6 ‰ lower than actually measured in the aquifer.
- In the uppermost 20 m, the linear trend of the δ values is disturbed. The profile shows a pronounced shift towards the higher δ values that are observed in the Neogene aquifer.

A plausible working hypothesis to explain the data assumes 1) the establishment of a steady-state profile across Boom Clay, with an upper boundary condition that has lower δ values than observed today, and 2) a more recent shift of the isotopic signature in the Neogene aquifer towards higher δ values, affecting only the uppermost part of Boom Clay. The steady-state profile would record a glacial signature, while the more recent shift in the Neogene aquifer would reflect Holocene warming.
Figure 5.8-1: **Model for Cl⁻ at Essen considering a linear decrease of Cl⁻ in the Lower Rupelian aquifer since emergence at 1.7 Ma**

Only diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the aquifers. The Cl⁻ concentration in the Lower Rupelian aquifer is assumed to decrease linearly since emergence of the site at 1.7 Ma. Blue bar represents concentration in ground water sampled from the test interval 285 – 383 m, corresponding to the full thickness of the Lower Rupelian aquifer. Model run ESS A12

Figure 5.8-2: **Base-case model for Cl⁻ at Essen**

Only diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the aquifers. The Cl⁻ concentration in the Lower Rupelian aquifer is assumed to be constant and at the current value since emergence of the site at 1.7 Ma. Blue bar represents concentration in ground water sampled from the test interval 285 – 383 m, corresponding to the full thickness of the Lower Rupelian aquifer. Model run ESS A13
Neogene aquifer

A linear regression of the linear segment of the tracer profiles (i.e. excluding the uppermost part) yields extrapolated values of $\delta^{18}O = -6.5 \, \text{‰}$ and $\delta^2H = -48.5 \, \text{‰}$ at the contact between Boom Clay and the Neogene aquifer, and these values are taken as the average isotopic composition of the aquifer in the Pleistocene. For the Holocene (10 – 0 ka), the present values are used (see Table 2.8-2). The difference between the Holocene and the Pleistocene values is $\Delta \delta^{18}O = -0.5 \, \text{‰}$ and $\Delta \delta^2H = -6 \, \text{‰}$.

An independent estimation of the average isotopic composition of water in the Neogene aquifer during the Pleistocene is not trivial due to

1) the substantial variability of surface temperature (determining the isotopic signature of infiltrating water, see Appendix A4.1) and infiltration rate (Figure A4.1-2),

2) the effects of isotopic fractionation between ice in permafrost near to the surface and the underlying liquid water, and

3) uncertainties regarding the hydrogeological situation in the aquifer during periods of permafrost (completely stagnant system?).

Some constraints can be obtained from the climate evolution as modelled by Marivoet et al. (2000) for the last glacial cycle in Belgium (Figure A4.1-2). Based on the modelled surface temperature, $\delta$ values of precipitation as a function of time can be obtained (using the relation of Philippot et al. 2000). According to the climate model, infiltration occurred only during warmer periods of the glacial cycle, i.e. at times without permafrost. Based on these data, the average $\delta$ values of water infiltrating into the Neogene aquifer can be estimated and are presented in Table A4.1-1. When infiltration over the last glacial cycle is weighted for the amount of precipitation, the average difference to the current values is $\Delta \delta^{18}O = -0.9 \, \text{‰}$ and $\Delta \delta^2H = -6.7 \, \text{‰}$. These values, even though derived from a quite different line of evidence, are remarkably similar to those obtained from the linear extrapolation of data from the tracer profile in Boom Clay. In both cases, the isotopic composition of water in the aquifer has only slightly more negative values than at present, which reflects the fact that precipitation within a glacial cycle occurs mainly in warmer periods, and, in addition, infiltration is limited by permafrost during cold periods.

Lower Rupelian aquifer

As for anions, there is considerable uncertainty on how the dilution process of the sea water originally present in the formation towards the current ground water worked since emergence at 1.7 Ma, and the same bounding scenarios are modelled as for $\text{Cl}^-$. 

Model results

Figure 5.8-3 shows the model calculation for lower boundary condition (Lower Rupelian aquifer) in which the $\delta$ values decrease linearly from 0 at 1.7 Ma to the current values. It is evident that this assumption does not result in a near-steady-state profile, and $\delta$ values are too high in the centre of Boom Clay. This result is fully compatible with the one obtained for $\text{Cl}^-$. In contrast, the model calculation considering a constant lower boundary represented by the current values provides excellent fits and, as for $\text{Cl}^-$, is considered as the base case (shown in Figure 5.8-4). A diffusion time of only 5 ka after the establishment of the current, Holocene isotopic composition in the Neogene aquifer well reproduces the data, even better than considering the full Holocene period (10 ka). Possibly, it took a few thousands years until the Holocene isotopic signal reached the bottom of the Neogene aquifer.
Figure 5.8-3: Model calculation for water isotopes at Essen considering a linear decrease of δ values in the Lower Rupelian aquifer since emergence at 1.7 Ma

![Diagram showing model calculation for water isotopes at Essen considering a linear decrease of δ values in the Lower Rupelian aquifer since emergence at 1.7 Ma.](image)

Only diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the aquifers. Lower Rupelian aquifer: Linear decrease of δ values from marine to present-day values. Neogene aquifer: δ¹⁸O / δ²H values in the Pleistocene are assumed to be 0.5 / 6 ‰ lower than today. Model run ESS W12

Figure 5.8-4: Base-case model for water isotopes at Essen

![Diagram showing base-case model for water isotopes at Essen with δ values.](image)

Only diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the aquifers. Lower Rupelian aquifer: δ¹⁸O and δ²H values are assumed to be constant at present values since emergence of the site at 1.7 Ma. Neogene aquifer: δ¹⁸O / δ²H values in the Pleistocene are assumed to be 0.5 / 6 ‰ lower than today. Model run ESS W14
5.8.3 Helium

Similarly to the profiles of anions and water isotopes, the profile of He contents over Boom Clay shows a near-linear increase with depth, connecting the values in the embedding aquifers. Figure 5.8-5 shows the results of a calculation in which the initial He content in Boom Clay is assumed to be zero. Given the large diffusion coefficient for He, the He concentrations adjust rapidly to the boundary conditions, and the profile reaches steady state after ca. 0.3 Ma. This means that the choice of the initial condition at emergence at 1.7 Ma is not a critical parameter, as the current profile contains information only on the last 0.3 Ma. If the He contents in the aquifers remained constant over this period, the measured data, which are matched well by the model calculation, can be interpreted as a steady-state diffusion profile.

Also note that in-situ production contributes very little to the He budget in Boom Clay, which is seen in the small curvature of the steady-state profile. The reasons for the insignificance of in-situ production is the high porosity of 0.43 (and therefore small rock/pore-water ratio), the large diffusion coefficient and the limited thickness of the Boom Clay.

Figure 5.8-5: Base-case model calculation for He at Essen

Difffusive transport and production are considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the aquifers. The initial He concentration in Boom Clay is assumed to be zero. Blue bar represents concentration in ground water sampled from the test interval 285 – 383 m (full thickness of the Lower Rupelian aquifer). Model run ESS N1

5.8.4 Considering vertical advection

Downward advection reduces the evolution times of the best-fit Cl⁻ profile, as shown in Figure 5.8 6. The model fit is about equal to that of the base case (no advection) for advection velocities up to 2E-12 m/s. In these cases, the best-fit model curves are near-linear because advection removes the curvature of the diffusion curves (as shown in Figure 5.8-2) that is present at evolution times <1.7 Ma. At velocities >4E-12 m/s, advection no longer simply pushes the diffusion curve downwards but yields sigmoidal shapes that do not well reproduce the linear trends of the data. Thus, this value is taken as the maximum advection velocity that can be broadly reconciled with the data.
Figure 5.8-6: Best-fit models for Cl⁻ at Essen considering diffusion and downward advection

Advective-diffusive transport is considered. Blue bar represents concentration in ground water sampled from the test interval 285 – 383 m, corresponding to the full thickness of the Lower Rupelian aquifer. Model runs ESS A13 (v_a = 0), ESS A16 (v_a = 1E-12 m/s), ESS A15 (v_a = 2E-12 m/s), ESS A14 (v_a = 4E-12 m/s) and ESS A19 (v_a = 8E-12 m/s).

Figure 5.8-7: Model for Cl⁻ at Essen considering diffusion and upward advection

Advective-diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the aquifers. An advection velocity v_a = -5E-13 m/s is considered. Blue bar represents concentration in ground water sampled from the test interval 285 – 383 m, corresponding to the full thickness of the Lower Rupelian aquifer. Model run ESS A18.
Upward advection enhances the curvature of the modelled Cl\textsuperscript{−} profile and so results in longer evolution times. Figure 5.8-7 shows that even a small advection velocity of -5E-13 m/s yields a model fit that is less good than the case that considers diffusion only. Even when considering evolution times >1.7 Ma (which is in conflict with palaeo-hydrogeology), the fit remains less good because a steady-state profile is established with a curvature that is not reflected by the data.

The effects of advection on modelled profiles as shown here for Cl\textsuperscript{−} are analogous for water isotopes and He, and so the same conclusions are reached based on all tracers.

5.8.5 Conclusions

- Diffusion alone, under the assumption of plausible boundary conditions, explains the observed tracer profiles.
- All tracers show near-linear trends connecting the concentrations and δ values in the embedding aquifers. These tracer distributions are consistent with steady-state diffusion that occurred since emergence of the region at 1.7 Ma.
- The only disturbance of the linear trends is the shift towards higher δ values for stable water isotopes in the uppermost 20 m of the Boom Clay. This shift can be explained by the changed boundary condition in the Neogene aquifer in response to Holocene warming. A diffusion time of 5 -10 ka reproduces the data well.
- The assumption of a progressive, linear mixing process of sea water and fresh water in the Lower Rupelian aquifer, operating since the time of emergence of the site until present, yields tracer profiles that are inconsistent with the observations.
- Upward advection with a velocity exceeding -5E-13 m/s yields curved profiles that are inconsistent with the data. A limited downward advection fits the data when shorter evolution times than 1.7 Ma are assumed. However, the shape of the best-fit profile becomes sigmoidal for velocities in excess of 4E-12 m/s, which contradicts the data. For all tracers, pure diffusion yields better fits to the data than combined diffusion and advection.

5.9 London Clay at Bradwell (UK)

Modelling of tracer transport at Bradwell is limited to London Clay, which is embedded between the surficial aquifer and the thin but active sandy aquifer of the Harwich Formation (Table 2.9-1). The underlying Lower London Tertiaries, with their low-permeability upper part, are not considered explicitly.

5.9.1 Chloride

The concentration gradients of Cl\textsuperscript{−} are steep in the uppermost part of London Clay in both boreholes (Figure 2.9-2). In borehole B101, values increase from 53 mg/L in the surficial aquifer to 432 mg/L at 14 m depth. In borehole B102, the opposite trend is seen, and Cl\textsuperscript{−} concentrations decrease from near-marine values to 2 190 mg/L at 21 m depth. These trends suggest that the upper boundary condition must have changed at a geologically recent time, towards meteoric conditions in B101 and towards marine conditions in B102.

The strong increase of salinity in the upper part of London Clay in borehole B102 is most likely the consequence of a marine transgression. In the base-case calculation shown in Figure 5.9-1, the initial Cl\textsuperscript{−} concentration is assumed to be low and constant throughout the sequence before a marine
transgression changed the upper boundary to the sea-water value of 19,350 mg/L. The model calculation considers diffusion as the only transport process and yields excellent fits to the data for diffusion times of 4–5 ka. According to independent evidence, a marine transgression occurred in the early Holocene at 9 ka, so the calculated values are a factor of 2 off. This can be explained either by uncertainties in the diffusion coefficients and/or in the palaeo-hydrogeological evolution, the details of which are not well known. Nevertheless, it is concluded that the shape of the profile can be well explained by diffusion alone, and that diffusion times are comparable, within the range of uncertainty, with independent evidence.

Overall, the data set for borehole B101 shows a regular increase of Cl⁻ concentration with depth (Figure 2.9-2). Scoping calculations indicate that it takes about 200–300 ka to establish a steady-state diffusion profile that roughly corresponds to the data (shown in Figure 5.9-2, curve for time = 0). Such long times are plausible, given the fact that the site was continental during the Pleistocene. The calculated steady-state profile quantifies the situation within the low-permeability sequence and assumes a value of 504 mg/L for the lower boundary condition, corresponding to the value of the uppermost sample of the lower part of the Lower London Tertiaries.

This profile is then used as the initial condition for the modelling of the steep Cl⁻ gradient observed at shallow level and the conspicuous relative maximum at 14 m (Figure 5.9-2). The tracer distribution suggests a geologically recent period of marine influence at the upper boundary. Unfortunately, there are no independent constraints on the timing of this episode, nor on the detailed evolution of the Cl⁻ concentration over time. Treating these parameters as unknowns (i.e. as free parameters), good model fits are obtained for Cl⁻ concentrations of 1,800 mg/L during the period 6.5–3 ka, as illustrated in Figure 5.9-2. In the absence of independent palaeo-hydrogeological information, this model calculation remains hypothetical but at least shows that, in principle, the complex Cl⁻ distribution can be explained as due to diffusion alone, i.e. there is no evident need to consider other processes, such as advection.

Figure 5.9-1: Base-case calculation for Cl⁻ in borehole B102 at Bradwell

Only diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the upper aquifer. Sea-water Cl⁻ concentration (19,350 mg/L) is assumed at the upper boundary. Model run BR102 A1
Only diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the upper aquifer. The curve at time = 0 corresponds to the steady-state diffusion profile between the two aquifers, assuming Cl = 504 mg/L in the lower aquifer. In the upper aquifer, the assumption of a higher Cl content of 1 800 mg/L in the upper aquifer in the period 6.5 – 3 ka before present leads to good fits to the data. Model run BR101 A1

5.9.2 Water isotopes

In the upper half of London Clay, a trend of strongly increasing δ values is observed in borehole B102, consistent with a marine influence at the upper boundary, as observed for Cl. In contrast to Cl, a trend of increasing values is also observed towards the lower aquifer in the Harwich Formation. The difference in the δ values between the minimum in the centre of London Clay and the lower aquifer is -1.2 ‰ for δ18O and -6 ‰ for δ2H. It is best interpreted as a glacial signature that is recorded in the central part of London Clay, whereas the lower aquifer represents recent precipitation. The base-case calculation shown in Figure 5.9-3 assumes the minimum δ values in London Clay as the initial condition, the present values in the Harwich Formation as the lower boundary, and marine values for the upper boundary at the surface. Reasonable fits are obtained for diffusive transport over ca. 4 ka, which is remarkably similar to the calculated evolution time for Cl. Even better fits would be obtained if slightly negative δ values were used at the upper boundary (δ18O about -3 ‰, δ2H about -20 ‰), i.e. a mixture of marine and fresh water. This finding contrasts that obtained for Cl, where a good fit is obtained for a marine upper boundary. The details of the Holocene evolution of the site are not well known and cannot be resolved by the model calculations. In particular, the question remains what happened in the older Holocene (10 – 4 ka) – the base-case calculations assume the full preservation of the glacial signature in London Clay, which may not be realistic. Alternatively, using diffusion coefficients 2.5 times smaller that those derived from laboratory experiments would lead to evolution times of ca. 10 ka for all tracers, which would correspond to the whole Holocene.
Only diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the aquifers. Model run BR101 W1

Stable-isotope data are more scattered for borehole B101, and they show less vertical variability. The most conspicuous feature is the trend towards higher δ values in the uppermost 20 m of London Clay (Figure 2.9-3). This trend could be due to the episode of marine influence as derived for Cl⁻ (Figure 5.9-2) and/or due to Holocene warming. Given the limited knowledge of the initial condition and of the processes governing the evolution of boundary conditions over time, it is concluded that the data set is insufficient for modelling purposes.

5.9.3 Considering vertical advection

Small hydraulic gradients in the order of 0.1 m/m were identified in borehole B102. They are directed downwards in the London Clay and upwards in the Lower London Tertiaries, suggesting that the Harwich Formation, which separates these units, could be a hydraulic sink. However, considering vertical advection that corresponds to this gradient does not affect the tracer profile, and the Peclet number is <1.

The infiltration areas of the Harwich Formation and of the Chalk aquifer are situated at an elevation of ca. 75 m farther inland. Assuming that both units are confined aquifers could result in an overpressure of 75 m at Bradwell. Even though such an overpressure was not observed, it is not unrealistic because ground-water abstraction over the past decades affected the natural flow system. Resulting hydraulic gradients in the low-permeability sequence are about -1 m/m (B101) and -1.7 (B102), corresponding to upward Darcy velocities of about -6E-12 m/s (B101) and -1E-11 m/s (B102). The calculated tracer profile for Cl⁻ in borehole B102 is shown in Figure 5.9-4 (advection velocity = -4.5E-11 m/s, considering a porosity of 0.24). The profile features a slightly more pronounced curvature at shallow levels, which results in a somewhat worse fit to the data when compared to the base case. The calculated evolution time of at least 10 ka is markedly longer compared to the base case. Assuming even higher upward advection velocities yields evolution times
much longer than 10 ka. These times are in conflict with the timing of the marine transgression (early Holocene, 9 ka), so such cases are not realistic.

For stable water isotopes, the overpressure of 75 m in the Harwich Formation leads to an upward advection velocity of -2.2E-11 m/s (because porosity is twice that for Cl). The resulting tracer profiles are illustrated in Figure 5.9-5. While the evolution time is only weakly affected, the fit to the data is worse than in the base case, namely in the lower half of the profile.

In summary, upward advection velocities larger than -2.2E-11 m/s (water isotopes) to -4.5E-11 m/s (Cl) are considered as the maximum values that can still largely be reconciled with the observed tracer distributions and with the palaeo-hydrogeological evolution.

From the viewpoint of the hydrogeological setting, it is difficult to envisage downward advection triggered by a hypothetical underpressure in the Harwich Formation. Nevertheless, this situation is explored for Cl in Figure 5.9-6. An advection velocity of 2.3E-11 m/s yields a fair agreement with the data, even though the fit is less good when compared to the base-case model. Doubling the advection velocity to 4.5E-11 m/s yields an even worse fit and a shorter evolution time. A velocity of 2.3E-11 m/s is considered as the maximum that is still in general correspondence with the data. For stable water isotopes, downward advection velocities of 2.3E-11 – 4.5E-11 m/s yield fits comparable to those of the base case, but the evolution times become progressively shorter (3 and 2 ka, respectively). Thus, water isotopes do not provide clear constraints on maximum downward velocity.

Figure 5.9-4: Effect of upward advection on the Cl profile of borehole B102 at Bradwell

Advective-diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the upper aquifer. Upward advection velocity is -4.5E-11 m/s, corresponding to an overpressure of 75 m in the Harwich Formation. The calculated profile changes only weakly at evolution times >10 ka and evolves towards steady state.

Model run BR102 A2
Figure 5.9-5: Effect of upward advection on the $\delta^{18}$O and $\delta^2$H profiles of borehole B102 at Bradwell

Advective-diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the aquifers. Upward advection velocity is $-2.2E-11$ m/s, corresponding to an overpressure of 75 m in the Harwich Formation. Model run BR102 W2

Figure 5.9-6: Effect of downward advection on the Cl$^-$ profile of borehole B102 at Bradwell

Advective-diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the upper aquifer. Left: advection velocity = $2.3E-11$ m/s (model run BR102 A4); right: $4.5E-11$ m/s (model run (BR102 A3)
5.9.4 Conclusions

The two tracer profiles obtained from boreholes at different distances to the present shoreline are contrasting. High chemical gradients in pore water developed mainly in borehole B102 due to the strong marine effects in the Holocene. Gradients are much smaller in borehole B101, where pore water was essentially affected by continental conditions. Therefore, borehole B102 is better suited for quantitative evaluation of the development of pore-water chemistry.

Due to the high porosity, hydraulic conductivity and diffusion coefficients in London Clay and because of the limited thickness of the low-permeability sequence, both diffusion and advection affect tracer concentrations over time scales of only thousands of years. The tracer profiles observed today evolved during the Holocene, and older signals are largely obliterated. All profiles can be satisfactorily be explained by diffusion alone. Base-case evolution times of 4 – 5 ka for borehole B102 are shorter than the marine transgression that occurred at 9 ka. This discrepancy is best explained by parameter uncertainties (e.g. diffusion coefficients, timing of the transgression).

Upward advection exceeding -2.2E-11 to -4.5E-11 m/s yields model results that are no longer in good agreement with the data. Moreover, compared to the base case, evolution times become longer for Cl but remain almost constant for water isotopes, i.e. an inconsistency arises that is not present in the base case. Downward advection shortens the evolution times and results in worse fits than the base case for the same maximum values as for upward advection.
6. SUMMARY OF SITE-SPECIFIC MODELLING AND CONCLUSIONS

Role of this Chapter

Chapter 2 provides, for each site considered, a detailed documentation of
(i) available Cl<sup>-</sup>, δ<sup>18</sup>O and δ<sup>2</sup>H, He and δ<sup>37</sup>Cl natural tracer profiles,
(ii) relevant formation properties for the low-permeability and bounding aquifer sequences, and
(iii) the palaeo-hydrogeological evolution of the site.

Chapter 3 provides comparative summaries for the main features of the natural tracer profiles in Table 3.1-1, and for the geometrical and physical parameters for the low-permeability sequences in Table 3.2-1. Furthermore, the transport parameters are discussed and compared with data sets from the literature.

Chapter 4 documents the strategy pursued for modelling the observed tracer profiles and the model results are presented, site by site, in Chapter 5. The modelling set out to use the parameters in Table 3.2-1 to reproduce as closely as possible the features in Table 3.1-1 and the overall shape of each profile.

This Chapter summarises the essential system characteristics, the modelling and results for each site and draws conclusions about how well the transport processes for solutes and water through these clay rocks are understood on the basis of the matches between models and observed data. Uncertainties in this arise mostly from palaeo-hydrogeology, with respect to both changes of hydrochemistry and timing of changes in ground-water systems, and also from the parameterisation of the diffusion model. In this sense this Chapter provides a short summary of Chapter 2 and Chapter 5, intended to give the reader an overview without having to go through all the details of those Chapters. It remains on a site-specific level without the ambition to compare and synthesise. A high-level discussion, together with general conclusions of the study as a whole, follows in Chapter 7 below.

Main characteristics of the modelling

In the model simulations for each site, the base cases for Cl<sup>-</sup> and δ<sup>18</sup>O/δ<sup>2</sup>H are mostly the simplest diffusive models which make straightforward assumptions for defining the initial and boundary conditions, i.e. initial Cl<sup>-</sup> or δ<sup>18</sup>O value equal to the peak value seen in the present profile (or in some cases sea-water value for Cl<sup>-</sup>) and boundary compositions equal to the present day values in adjacent higher-permeability layers. The diffusion models have been run forwards, simulating the evolution of tracer profiles starting from the assumed initial distribution of tracer for a range of times so that the modelled tracer concentration curves bracket the observed tracer profile. The model time producing the best fit has then been compared with an estimate of the timing of activation of the bounding aquifers based on palaeo-hydrogeology.

In most cases, the boundary conditions and initial conditions have then been varied to test the sensitivity of the model fit to uncertainties in the assumed values. Palaeo-hydrogeological constraints on the magnitudes of uncertainties in values for boundary and initial conditions and in timing of
aquifer activation indicate, in many cases, the most plausible combinations of these parameters for a diffusion-only model of the evolution of the tracer profiles.

For some of the sites, additional sensitivity modelling has been carried out to assess the significance of uncertainties in other parameters such as diffusion coefficients or diffusion-accessible porosities, or in the temporal evolution of composition in a bounding aquifer. It is worth noting that the modelling has shown that temperature-dependence of diffusion coefficients and, if long evolution times are considered or an uplift occurred, the variation of geothermal temperature have a significant effect on modelled diffusion profiles and therefore need to be taken into account. Finally, alternative models have been run in which vertical advection is superimposed on diffusion, indicating the maximum flux beyond which the modelled tracer profile becomes too distorted by ‘piston displacement’ advection to be a plausible match with observed tracer data.

For modelling the He profiles, a less structured approach has been necessary because the initial He concentration through the profile at the time of aquifer activation cannot be estimated with any confidence. Therefore, the initial He content has been treated as a fit parameter in modelling the development of observed He values over the time scale suggested by the evaluation of other tracers and by palaeo-hydrogeology. The ability to replicate the shape of the observed He profile by modelling in this way is an additional test of diffusion which is to some extent independent of the other natural tracers because of the higher diffusion coefficient of He.

$\delta^{37}$Cl has been modelled for only three sites for which there are sufficient data to provide a worthwhile comparison. However, the overall geochemical systematics of stable Cl isotopes in sedimentary basins are not well enough understood to have any degree of confidence in estimating initial conditions and subsequent evolution. For $\delta^{37}$Cl, therefore, the modelling has just been a study of how this isotope ratio would evolve by theoretical diffusive fractionation. The results suggest that, given better theoretical understanding and improved analytical precision that is appropriately lower than the rather small range of natural variability, stable Cl isotopes could be an additional useful tracer in the future.

6.1 Callovo-Oxfordian at Site Meuse/Haute Marne (Bure, France)

The low-permeability sequence at the Bure URL site is 256 m thick and comprises 130 m of the Callovo-Oxfordian shale plus the bottom 63 m of the overlying Oxfordian and the top 63 m of the underlying Dogger limestone formations (Table 2.1-1, Table 3.2-1). The hydrogeological boundaries at the top and base of the shale sequence are inferred to correspond to distinct flowing horizons in Oxfordian and Dogger formations respectively. Ground waters in these flowing horizons are chemically distinct, indicating that these formations are not connected hydraulically by pathways that by-pass the matrix of the low-permeability rocks. Meteoric ground-water movement through these limestones has probably been active since the system emerged from marine cover at ca. 65 Ma, with the present salinity in the Dogger probably being derived from underlying Triassic. Depositional sea water has long since been flushed from the low-permeability sequence. At the interface between the Callovo-Oxfordian and the Dogger, there is a thin limestone called the Dalle Nacrée that is reported to have low permeability but that appears to have some influence on the shape of the natural tracer profiles.

There are a good number of data points for Cl$, \delta^{18}$O, $\delta^{2}$H and He in pore water through the upper three-quarters thickness of the sequence at the URL site, but the lower part, at the top of the Dogger, was not sampled and so the shape of the profile towards the Dogger flowing horizon is not known. The general pattern of the Cl$^{-}$ profiles is of increasing concentrations with depth to the centre of the
Callovo-Oxfordian (Figure 6.1-1). However, the data have quite a lot of scatter for some boreholes (possibly for methodological reasons) and possibly show some differences between closely adjacent boreholes in the URL site. At the upper boundary of the profile, the pore-water concentrations are consistent with the composition of water in the Oxfordian flowing horizon, whilst for the unsampled basal part of the profile it can be reasonably hypothesised that pore water concentrations fall on a smooth trend towards the composition of water in the Dogger flowing horizon. Stable isotope ratios show a similar pattern with maximum $\delta^{18}$O and $\delta^2$H values within the Callovo-Oxfordian, but the scatter is more substantial, which renders a quantitative interpretation somewhat difficult. Concentrations increase continually with depth through the clay rock sequence, and then continue to increase with depth below the flowing horizon in the Dogger limestone. $\delta^{37}$Cl values do not have a marked variation except to slightly lower values in the deeper part of the Callovo-Oxfordian.

The general shapes of the Cl$^-$ profiles, despite the scatter within individual profiles and the variability between them, are consistent with diffusion as the only transport process. However, there are no constraints on the initial Cl$^-$ concentration other than the possibility that sea water can be argued to be a maximum limit. Therefore modelling has assumed a range of initial conditions between sea water and the maximum currently observed in each borehole profile, e.g. about 2 150 mg/L for borehole EST211 (Table 3.1-1), and for each initial Cl$^-$ has evaluated the diffusion time for the modelled profile to match the data. Results indicate that the model is fairly insensitive to the range of uncertainty in initial conditions (Figure 6.1-1). The model times to achieve good fits of the model to observed profiles, ranging from 11 to 1.2 Ma for EST211, are all plausible in terms of palaeo-hydrogeology. They suggest that the starting point of this phase of ground-water movement and diffusive exchange of solutes and water through the system occurred much more recently than the time of initial emergence of the rock sequence from marine conditions. Independent evidence of these palaeo-hydrogeological changes is not yet available.
In addition to the data from the URL site at Bure, Cl\textsuperscript{−} data from pore- and ground waters were obtained from a number of regional boreholes up to 13 km away. There are major lateral differences in the composition of the Dogger aquifer, and the Cl\textsuperscript{−} profiles across the overlying low-permeability sequence also reflect this heterogeneity.

Water-isotope profiles are more difficult to interpret due to the considerable scatter of the data. The He profile must be considered to represent a transient situation (i.e. the He contents are still decreasing today) unless a lower diffusion coefficient than the independently derived value is chosen for the Oxfordian limestone. δ\textsuperscript{37}Cl adds little to the understanding of the system because the evolution is not well constrained (e.g. initial and boundary conditions) and because the scatter of the data is considerable in comparison to the larger-scale spatial variability of this tracer.

### 6.2 Couche Silteuse at Marcoule (Gard, France)

The thickness of the Couche Silteuse at Gard varies greatly due to local differences in subsidence of fault-bounded blocks of the sequence in this area, just to the west of the Rhône valley. In three boreholes that are <5 km apart, the thickness of the Couche Silteuse is 404, 246 and 163 m. Hydrogeological boundaries for the system are inferred to be sandstone aquifers in the overlying Cenomanian and underlying Vraconian formations. In the Miocene period, the regional hydrogeology was affected by the Messinian fall of >1 500 m in Mediterranean Sea level which led to incisions of valleys and flushing of aquifers. The system was probably flushed since the Eocene period, ~50 Ma, but a final marine transgression probably filled the aquifers with Mediterranean Sea water in the early Pliocene, following which the present solute distribution began to evolve at some time between 5.35 and 3 Ma.

Data were obtained for Cl\textsuperscript{−} and Br\textsuperscript{−} in all three boreholes and for δ\textsuperscript{37}Cl in the thickest sequence only. The three profiles for Cl\textsuperscript{−} are different in relation to their thickness (Figure 6.2-1). The profile from the thickest low-permeability sequence has a symmetrical shape with a maximum Cl\textsuperscript{−} concentration of ca. 26 000 mg/L in the centre of the sequence (Table 3.1-1). The next thickest section has a similar shape but has a maximum Cl\textsuperscript{−} of 17 400 mg/L. These two Cl\textsuperscript{−} profiles are characterised by relatively high gradients on the upper and lower limbs towards the aquifers (see Table 3.1-1). The thinnest borehole sequence through the Couche Silteuse has few samples and much lower maximum Cl\textsuperscript{−} of about 1 500 mg/L. Both the overlying Cenomanian and the underlying Vraconian aquifers have low salinity.

The initial salinity of pore waters in the Couche Silteuse when the present profile began to evolve is somewhat uncertain because various hypotheses are possible for the post-Messinian palaeohydrogeology of the aquifers at that site. The maximum present pore-water Cl\textsuperscript{−} concentration among the three profiles has been taken as the initial concentration for base-case modelling, i.e. 25 875 mg/L (Table 3.1-1). This value is slightly higher than the current value in the Mediterranean (about 20 500 – 21 500 mg/L) and a plausible initial condition for times when the connection to the Atlantic was even more restricted. Even more saline initial conditions, which would make evolution times longer, cannot be rigorously excluded.

There is very strong support for diffusive solute transport from modelling of the three profiles with different thicknesses. Modelling of Cl\textsuperscript{−} shows that the marked variations of salinity among the three profiles, from saline to brackish, are entirely consistent with diffusion with the same boundary conditions and for the same, or very similar, lengths of time since activation of the aquifers, i.e. >3 to 1.5 Ma (Figure 6.2-1). In other words, the observed Cl\textsuperscript{−} variations are explained simply by the differing thicknesses of the diffusive system. The range of apparent times for out-diffusion is
compatible with the scatter of data with which the model curves are matched and with model parameter uncertainties and variabilities. For example, the shorter apparent time of 1.5 Ma from modelling the profile of intermediate thickness (MAR402) can be attributed to the substantially greater depth at which the formations of interest occur and to the larger distance from potential in- and exfiltration areas of the aquifers.

Appropriate initial and boundary conditions for the model of $\delta^{37}$Cl in the Couche Silteuse cannot be defined. Modelling with diffusive isotope fractionation has not been able to achieve a reasonable match with $\delta^{37}$Cl data unless heterogeneous initial $\delta^{37}$Cl distribution is assumed. It is impossible to establish any independent support for that inference, which points to the inadequate understanding of the processes that would have affected this tracer through the geological evolution of this sedimentary system.

Figure 6.2-1: Scoping model for the out-diffusion of Cl\textsuperscript- at Marcoule considering an initial concentration of 25875 mg/L (max. observed value)

Only diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the aquifers. Model runs G203 A5, G402 A5, G501 A5

6.3 Opalinus Clay at Benken (Switzerland)

Benken is located at the northern edge of the Molasse Basin where it abuts the Tabular Jura; sedimentary bedding is horizontal and there are no major faults in the vicinity. The low-permeability sequence, 312 m thick, extends downwards from the base of the late Jurassic Malm, through the Middle Jurassic Dogger and into the early Jurassic Lias. The largest element of the sequence is the Opalinus Clay, 113 m thick, and is embedded by a variety of other rock types (limestone, marl, shale) (Table 3.2-1). The hydrogeological boundaries for the low-permeability sequence are provided by the Malm aquifer at the top and the Keuper aquifer at the bottom. The tectonic and palaeohydrogeological evolution of the basin is complex, and the waters in the aquifers as well as within the low-permeability sequence are thought to have varied between fresh and marine since the late Cretaceous. The Malm aquifer at Benken has been stagnant over geological periods of time and has a high Cl\textsuperscript- content of 4550 mg/L. Based on the erosion history, the Keuper aquifer was probably activated in the early Pleistocene period at 2.2 – 1.8 Ma.

A good number of tracer data from the low-permeability sequence were obtained for $\delta^{18}$O, $\delta^{2}$H, Cl\textsuperscript- and $\delta^{37}$Cl. More limited data sets are available for He and for $^{40}$Ar/$^{36}$Ar.

There is a reasonable distribution of samples to define the Cl\textsuperscript- profile except at the top because data from the Malm limestone are missing. The scatter of data makes the definition of the Cl\textsuperscript- profile
rather poor; it is not clear whether the scatter is real and reflects varying properties or whether it is an artefact of measurement. Nevertheless, the profile is clearly asymmetric. The maximum Cl concentration of about 7 300 mg/L occurs in the upper part of the profile, and a major decrease towards the lower aquifer (500 mg/L Cl) but only a slight drop towards the upper aquifer (4 550 mg/L Cl) is identified.

A similar number of $\delta^{18}O$ and $\delta^2H$ data defines a rather clearer distribution and sharper asymmetric profile (Figure 6.3-1), suggesting that data uncertainty may explain the scatter on the Cl profile. There is a good spread of stable isotope ratios between the bounding aquifers, -5.5 and -9.5‰ $\delta^{18}O$, and there is also a contrast between these values and the peak value in the low-permeability sequence, -4.5‰ $\delta^{18}O$ (Table 3.1-1). Therefore, the better base-case model in terms of assessing the goodness of fit with data is the model of $\delta^{18}O$ and $\delta^2H$ (Figure 6.3-1), in contrast to many of the other sites where Cl provides clearer constraints.

The base-case model for $\delta^{18}O$ and $\delta^2H$ has been constructed with an initial composition given by the current peak stable isotope ratios in the low-permeability sequence. Best fit between this model and stable isotope data indicates a time since activation of aquifers of about 0.7 Ma, which is slightly more recent than the timing based on palaeo-hydrogeological evidence and thus suggests that the assumed initial isotope ratios are possibly too low. Higher initial $\delta$ values increase the evolution times, but the corresponding models tend to provide progressively less good fits to the data. The slope on the lower limb of the profile is a particularly illustrative test of the goodness of fit and the model result is a convincing confirmation that water movement and isotopic exchange across the low permeability sequence has occurred only by diffusion.

The Cl profile was modelled with similar constraints, i.e. an initial concentration of 6 600 mg/L based on the maximum in the profile (though there is one outlier to a higher value). The timing of aquifer activation based on the best fit model curve is about 1.4 – 2 Ma. Considering the scatter on Cl data and other sources of uncertainties, this is not significantly different from the result from the stable isotope modelling. Although the selection of the initial Cl concentration and $\delta^{18}O$ and $\delta^2H$ values to correspond with the presently-observed maxima does not have any palaeo-hydrogeological rationale, its validity as an approximation tends to be supported by the way that the profiles have plateaux at these values. In the case of Cl, higher initial concentrations would lead to longer modelled evolution times, which would be in contradiction with the independently derived activation time of 1.8 – 2.2 Ma for the Keuper aquifer.

The relatively well-defined data profiles, namely for $\delta^{18}O$ and $\delta^2H$, have allowed the sensitivity of the diffusion model to various factors to be studied:

- One such factor is the spreading over time and distance of the change of composition of water in the Keuper aquifer when it was opened to meteoric input. This is pertinent at Benken because of its distance from the point of infiltration to the Keuper at outcrop (ca. 10 – 20 km). However, modelling of the propagation through the aquifer of a step change in the composition of infiltration indicates that any dispersion of the compositional signal would have been negligible in relation to the rate of diffusive exchange with the low permeability pore waters. This conclusion equally applies to many of the other sites studied in this report.

- Sensitivity testing of the model to different initial and boundary conditions shows that both the slopes of the lower parts of the profiles and also the palaeo-hydrogeological evidence for activation of the aquifers are not consistent with any substantial changes from the values chosen for the base-case models for stable water isotopes and Cl.
In view of the relatively extensive considerations of what are appropriate values for anion accessible porosities in the Opalinus Clay at this site and at Mont Terri, the overall sensitivity of the diffusion model to this factor has been examined. It is concluded that this is not a major issue, in relation to the other uncertainties.

$\delta^{37}\text{Cl}$ data indicate two possible maxima close to the upper and lower boundaries of the low-permeability sequence. A qualitative match with the data could be achieved with a diffusive transport and isotopic fractionation model, but this required the selection of an initial isotope ratio value for which there is no independent evidence or reasoning. As was concluded for the $\delta^{37}\text{Cl}$ profile in the Couche Silteuse, there are evidently factors controlling evolution of initial and/or boundary compositions that are not understood.

The small number of He data gives a more or less flat depth profile, with the exception that the measured concentration in the Malm aquifer is rather higher than the other values. The model is not well constrained by these data, and the shape of the upper part of the model profile strongly depends on the value chosen for the Malm boundary. Moreover, the model profile of course strongly depends on the choice of initial concentration, which is treated as a variable to achieve the best match. Overall, there are too many variables and too much uncertainty for these data to offer significant additional value to the diffusion model, and in this case the flatness and scatter of the He profile does not offer any significant weight to the case for diffusion-controlled transport.

In contrast to He, the $^{40}\text{Ar}/^{36}\text{Ar}$ profile shows a distinct curvature, with a maximum in the lower third of the low-permeability sequence. The pore-water values fit well with those in the aquifers. The elevated $^{40}\text{Ar}/^{36}\text{Ar}$ of up to about 340 indicates that \textit{in-situ} production is important. Because of the large number of unknowns (e.g. initial condition, release rate of $^{40}\text{Ar}$ from the rock to the pore water, diffusion coefficient), no quantification was attempted.

Figure 6.3-1: \textit{Base-case simulation for $\delta^{2}H$ at Benken}

Only diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the aquifers. Model run B H-01
6.4 Opalinus Clay at Mont Terri (Switzerland)

The Opalinus Clay formation which has been sampled in the tunnel at Mont Terri occurs in a faulted anticline of the Folded Jura, so the bedding is inclined, unlike the case at Benken. The low-permeability sequence extends from the basal Dogger limestone through the Opalinus Clay to the upper Lias shale with a total thickness of 219 m (Table 3.2-1). Because the strata are not horizontal and have been sampled from the tunnel, the thicknesses of beds have been estimated as distances normal to the bedding dip. The resulting uncertainty of effective distances for solute transport across the low permeability sequence is an additional factor in judging the match between model and data at this site. Folded Jura deformation during which the anticline was formed occurred at 10 – 3 Ma. Erosion exhumed progressively deeper strata and thereby activated the aquifers. The activation time of the Dogger aquifer overlying the low-permeability sequence can be constrained to 10 – 1.2 Ma, whereas the underlying Liassic aquifer was activated later, in the range 0.5 – 0.2 Ma.

There is good coverage across almost the whole sequence for Cl⁻, Br⁻, stable water isotope ratios and He data, and these data (except Br⁻ that does not provide any constraints over and above those obtained from Cl⁻) have been used for modelling. δ³⁷Cl was measured in just a few samples which gave positive values that are fairly similar to those in Benken pore waters, but there are insufficient data to justify modelling in this case.

The shape of the Cl⁻ profile in pore water is distinctly curved and has a large amplitude, with the highest Cl⁻ concentration of 13 850 mg/L at the boundary between the Opalinus Clay and the Lias claystone, giving a distinctive asymmetric shape to the profile with the maximum well below the centre of the low-permeability sequence (Figure 6.4-1). The gradients of Cl⁻ concentrations towards both upper and lower boundaries in the profile are higher than at Benken (Table 3.1-1), so, as in that case, the shape of the profile here is a convincing test of diffusion as the controlling process on solute transport. Measured Cl⁻ in the embedding aquifers are <100 mg/L. Cl⁻/Br⁻ is close to the sea-water ratio throughout the profile, independent of the absolute concentrations. This is a remarkable difference to the observations made at Benken and illustrates lateral differences in the palaeohydrogeological evolution.

The shapes of the δ¹⁸O and δ²H profiles differ from those for anions. They have more scatter and less pronounced curvatures with peak values closer to the centre of the sequence. Interestingly, in contrast to what has been found at Benken, this means that the stable isotopic data are a less valuable test of the model than are Cl⁻ data.

The maximum Cl⁻ and Br⁻ contents indicate a sea-water component of about 70 %, whereas the corresponding value for stable water isotopes is closer to 30 %. This means that the pore waters at Mont Terri cannot be considered as simple mixtures of meteoric and sea water. There appears to have been an additional process, over and above simple dilution during the long-term evolution of the pore waters to their initial compositions at the start of the recent phase of diffusive exchange following Jura folding, which has fractionated water isotopic composition from Cl⁻. This identifies a gap in understanding about long-term solute transport processes, though its significance to the shorter-term diffusive solute transport of interest here is probably low.

The asymmetric shape of the Cl⁻ profile suggests that the upper and lower bounding flowing ground-water systems were activated at different times, which is consistent with the palaeohydrogeological interpretation. The base-case model for Cl⁻ has been constructed with an initial concentration equal to sea water (unlike the choice for the base case model of the Benken profile) and with fresh-water boundaries (Figure 6.4-1). The timing of activation of these boundaries were each adjusted to achieve the best match between model and data, giving 6.5 Ma at the upper boundary and
0.5 Ma at the lower boundary, *i.e.* totally consistent with palaeo-hydrogeology. An alternative model with slightly lower initial Cl⁻ at 15 000 mg/L, *i.e.* just higher than the current peak concentration, gives corresponding evolution times of 4.4 and 0.4 Ma, which are still reasonable and illustrate the effect of uncertainty in initial composition.

**Figure 6.4-1: Base-case model for Cl⁻ at Mont Terri**

Only diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the upper aquifer. The initial Cl⁻ concentration corresponds to that of sea water. Model run MT A13

A base case model for the stable isotope profiles with corresponding initial and boundary conditions, *i.e.* 0 ‰ δ¹⁸O and δ²H for the initial composition, and using the ground-water activation times from the model for Cl⁻, results in model profiles that have much higher δ values than are observed. This is a direct outcome of the unidentified process that has fractionated Cl⁻ from water isotope ratios during their long-term evolution from depositional sea water. So in this case, in contrast to what has been done for Benken, the stable isotope profiles have been simulated by fixing the initial isotope compositions on the basis of the best fit for diffusive exchange with the boundary ground waters being activated at the times given by the Cl⁻ model. The resulting initial δ values are close to those for a ground-water sample from the adjacent anticline at Mont Russelin. This sample has marine Cl⁻ and Br⁻ contents but distinctly negative δ values for water isotopes, and so it is considered as an independent support for the choice of initial δ values at Mont Terri.

The He data set is larger than for Benken and gives a parabolic profile that is distinct from the Cl⁻ and stable isotope profiles in being symmetric with its peak near to the centre of the sequence. Qualitatively, this can be understood as an outcome of the higher diffusion coefficient for He in comparison with the other tracers. As was done for stable isotopes at this site and also for He at Benken, the He profile was modelled by estimating the initial concentration on the basis of a best fit for the model with activation times for the boundaries derived from the Cl⁻ model. Because of its symmetrical shape and the steeper gradients on the upper and lower limbs of the He profile (Table 3.2-1), this provides better qualitative support to the concept of diffusion than for He at
Benken, but the main issue here, as at most of the other sites, is the lack of knowledge of what initial He contents would have been prior to the ‘opening’ of the system. Therefore, the only truly independent piece of quantitative information is the fact that the symmetric shape of the He profile can be reproduced by the same scenario that also rationalises the asymmetric Cl⁻ profile. Modelling also demonstrates that the He profile is not at steady state (which would mean that out-diffusion is outweighed by in-situ production), and He concentrations are steadily decreasing.

6.5 Opalinus Clay at Mont Russelin (Switzerland)

Similarly to Mont Terri, Opalinus Clay at Mont Russelin is located in the core of an anticline of the Folded Jura and was also sampled in a tunnel transecting the anticline. However, the degree of brittle deformation is substantially higher at Mont Russelin, and major thrusts are identified within Opalinus Clay. A major fault zone is identified in the lower part of Opalinus Clay. The anticline was subjected to much less erosion when compared to Mont Terri, and so the Liassic aquifer that defines the lower limit of the low-permeability sequence at Mont Terri has no local outcrop at surface and therefore has never been activated at Mont Russelin. This means that the lower hydrogeological boundary for the low-permeability sequence is not defined. The upper boundary lies within the Dogger limestones, and as at Mont Terri, the lowermost part of these limestones (45 m thick) is part of the low-permeability sequence (Table 3.2-1). There is a reasonable coverage and distribution of samples from across the low permeability sequence with a cluster of sample points in the fault zone. Cl⁻, δ¹⁸O, δ²H and a smaller number of He data are available for these samples.

Cl⁻ concentrations in pore waters increase regularly with depth through the sequence, starting from the fresh water at the upper boundary (Dogger seepage) to a maximum of 21 700 mg/L in the Liassic (Table 3.1-1). In contrast to Mont Terri, there is no drop towards low concentrations in the Liassic. Thus, the shape of the profile reflects the different hydrogeological setting. The higher peak values of Cl⁻ in relation to that seen in the Mont Terri profile, and similarly for the stable isotope ratios and He contents, reflect less severe effects on pore water and solute distribution of Jura folding at Mont Russelin.

δ¹⁸O, δ²H and He increase with depth similarly to Cl⁻ except that both these tracers have evidence of potentially significant negative anomalies where the profiles pass through the fault zone (Figure 6.5-1). A comparable anomaly is not apparent in the Cl⁻ profile though there is a general scatter of values for the same cluster of samples. Whereas the Cl⁻ concentration in the Liassic is close to that of sea water, the corresponding maximum δ¹⁸O and δ²H values are still negative, which points to the same problem of inconsistent mixing ratios of sea and fresh water that was already seen at Mont Terri.

The base-case model for Cl⁻ has used a marine initial pore-water composition, as at Mont Terri. This is close to the average observed Cl⁻ concentration at the base of the profile. The modelled time for evolution to a best fit to the observed profile is 3 Ma, rather less than the 6.5 Ma for Mont Terri. Sensitivity of the model to the position of the upper boundary has been tested by moving it 20 m higher into the Dogger. This gives a 4 Ma evolution time, so the exact position of the upper boundary, even with this steep concentration gradient, is not so important. Given the slower erosion rate, a more recent activation time for the Dogger aquifer when compared to Mont Terri is plausible.

The initial condition for the modelling of δ¹⁸O and δ²H was constrained by the composition of a stagnant ground-water sample in the Liassic. Based on this, an evolution time of 3 Ma was obtained, consistent with that for Cl⁻. The currently available He data set is insufficient to contribute independent constraints on processes and system evolution.
It is uncertain whether the apparent anomalies in $\delta^{18}$O and $\delta^{2}$H and He in the fault zone are real or artefacts of some sort, e.g. related to processes since tunnel construction (samples were taken from 3 – 4 m deep boreholes drilled from the tunnel). The hypothesis of a natural hydrogeological activity was explored by modelling, which shows that the age of the disturbance would be only in the order of tens of thousands of years.

**Figure 6.5-1: Base-case model for $\delta^{18}$O at Mont Russelin**

Only diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the aquifer. Model run MR W7

### 6.6 Toarcian-Domerian at Tournemire (France)

Boreholes (several >100 m in length) were drilled upwards and downwards from a tunnel that penetrates flat-lying shales of Lias (Toarcian and Domerian) age, with total thickness of 257 m (Table 3.2-1). The shales are highly consolidated and have suffered brittle deformation and fracturing. The upper and lower hydrogeological boundaries are limestone layers of Aalenian and Carixian ages respectively, which contain fresh ground waters. The area has been continental since the early Cretaceous (i.e. for >100 Ma), with a possible but not proven marine incursion around the Cretaceous/Tertiary boundary (65 Ma). Meteoric water influx and karstification of the limestone layers are documented to have occurred since about 40 Ma. The extent to which meteoric waters affected the low-permeability sequence during the early continental evolution cannot be independently constrained, but it appears unlikely that the original marine signatures would be preserved. Incision of surrounding valleys has been initiated at 15 – 13 Ma, so that an estimate of the timing of the final activation of the boundary aquifers is between 15 and 6 Ma, i.e. typically around 10 Ma.

Only the upper part of the clay-rich sequence, comprising the Toarcian shales, has been sampled, whereas virtually no data are available from the lowermost 58 m, corresponding to the Domerian. There is a large set of Cl' data and an even larger set of stable water isotope analyses. However, both data sets have had to be used cautiously for comparisons with modelled profiles because in each case
they are compilations of data obtained by slightly different methods and they also come from samples that are laterally distributed at a local scale.

A subset of Cl⁻ data, all from one single profile and obtained by the same method, has been selected for comparison with modelling. Cl⁻ increases in a near-linear trend with depth to a maximum value of 539 mg/L in the Middle Toarcian, below the midpoint of the profile, and then decreases through the Middle and Lower Toarcian beds (Figure 6.6-1). The concentration gradient on the upper limb of the profile is well defined but is low because of the low mineralisation of the pore water throughout (Table 3.1-1).

A simple model considering simultaneous out-diffusion of Cl⁻ to both upper and lower boundaries and assuming a marine initial composition illustrates the long time of 35 – 40 Ma required to achieve the measured Cl⁻ concentrations in the low-permeability sequence. This long time is the consequence of the low current Cl⁻ contents and, more importantly, of the low effective diffusion coefficient (Table 3.2-1), which is affected by the strong degree of induration and therefore low porosity. However, this simple model fails to properly reproduce the shape of the Cl⁻ profile, and so a more complex evolution of the system has had to be inferred to achieve a match of model and data. In this model, both upper and lower aquifers are assumed to have been active for about 60 Ma, but with the lower aquifer being slightly more mineralised (800 mg/L Cl⁻) than the current pore waters up to the last 2 – 3 Ma at which time the composition of the lower aquifer is switched to the present low Cl⁻ value. The fit of model with data is good, especially for the linear upper limb of the profile (Figure 6.6-1). Unfortunately, there is no independent palaeo-hydrogeological basis for this scenario. Nevertheless, this model gives some confidence that, even for a system that evidently has an evolution history that cannot ever be fully deconvoluted over its very long time scale, a reasonable simplification based consistently on diffusive solute transport alone, can explain observed pore-water data.

Figure 6.6-1: Base-case model for Cl⁻ at Tournemire

Only diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the upper aquifer. Out-diffusion model for Cl⁻ towards upper and lower aquifers at Tournemire (the lower aquifer with 800 mg/L Cl⁻) until near steady state after ca. 60 Ma, then a change of Cl⁻ in the lower aquifer to present-day value. Model run TOU A4
The $\delta^{18}$O and $\delta^2$H profiles are based on low-temperature vacuum distillation and had to be corrected in order to represent in-situ values. The $\delta^2$H profile is curved, with a maximum in the centre of the low-permeability sequence, whereas the $\delta^{18}$O is difficult to interpret due to the substantial scatter attributed to analytical difficulties. The limbs of the $\delta^2$H profile trend towards values at both boundaries that are markedly below the current values measured in the aquifers. This mismatch is interpreted (and successfully modelled) as due to a recent increase in $\delta^2$H in the aquifers since the onset of the Holocene, in response to higher $\delta$ values in warm-climate precipitation. The limbs of the $\delta^2$H profile are therefore interpreted to record a cold-climate (Pleistocene) situation dictated by boundary values that were distinctly lower than today. Indeed, using the highest $\delta^2$H in the centre of the sequence as initial condition yields good model fits to the data for evolution times of about 2.4 Ma. Cold-climate effects on the boundaries are plausible at Tournemire because, due to its southern location close to the Mediterranean, permafrost was absent or discontinuous and so did not inhibit the infiltration of cold-climate ground waters. Notably, the 2.4 Ma obtained for $\delta^2$H is in good agreement with the 2 – 3 Ma obtained from the Cl- profile for the activation of the lower aquifer.

The Tournemire site is one where the tracer profiles with low Cl- contents and limited variation of stable water isotopic ratios each contain information representing different periods of the overall evolution. The pore-water profiles contain only brackish water, far away from sea water. The dilution of original sea water that has long since lost any detectable isotopic trace of the marine end member is recorded by the Cl- profile. The $\delta^2$H profile, on the other hand, represents a more recent period of changing boundary conditions.

6.7 Boom Clay at Mol (Belgium)

The Boom Clay at Mol is a flat-lying Tertiary (32 – 29 Ma) marine clay formation with a thickness of 103 m (Table 3.2-1). It is lithologically homogeneous except that the basal 12 m is sandier clay. It was never buried deeper than today (161 – 264 m) and so is less well consolidated and more porous than most other formations discussed here. The hydrogeological boundaries are the overlying Neogene (Berchem) aquifer and the underlying Lower Rupelian aquifer, which are both sandy and contain fresh ground waters. Meteoric infiltration to the aquifers started at around 2 Ma when the overlying sea retreated. The upper aquifer is almost unconfined and is recharged locally, whereas the lower aquifer recharges about 30 km away. At a regional scale, salinity in the latter aquifer increases towards the north away from recharge; however, Mol is evidently close enough to recharge so that salinity has already been flushed.

The large number of pore-water samples through the Boom Clay originate both from extraction by squeezing from cores from three boreholes drilled from the surface and from seepage into piezometers installed from the Underground Research Laboratory. Sufficient data are available for Cl- and Br- but not for stable water isotope ratios. Cl- and Br- concentrations in water samples obtained by these methods are consistent and are all very low, so the tracer profiles are essentially flat, with very low gradients towards the aquifers (Figure 6.7-1, Table 3.1-1). Cl- increases only from 15 – 25 to 20 – 40 mg/L with increasing depth through the clay, though the trend in the lowermost 20 metres is unclear. This is thought to be due to the quantitative out-diffusion of salinity since emergence of the area at 2 Ma. The shape of the Br- profile is similar to that of Cl-. The current Cl-/Br- ratio of ca. 37 is much lower than that in the original sea water (290). The drastic decrease of this ratio during out-diffusion is probably determined by the low ratios of 37 – 39 in both embedding aquifers, even though other effects, such as a weak retardation of Br-, may also play a role, in addition to the uncertainties of Br- analysis by ion chromatography (De Cannière, pers. comm.).
Calculations indicate that a straight-forward model considering simple out-diffusion of Br starting at 2 Ma, *i.e.* the time of marine regression from the area, well reproduces the observed flat profile. However, in the case of Cl, a time of about 3 Ma would be required to reach the currently observed low concentrations (Figure 6.7-1). The inconsistency with the palaeo-hydrogeological evidence is not critical and can possibly be explained by uncertainties in diffusion coefficients and their temperature dependence, but the marked difference between Cl and Br is remarkable and was not observed at any of the other sites. Thus, not everything is yet fully understood about the parameterisation of the solute transport model. In any case, the complete flushing of the lower aquifer to very low salinity must have occurred soon after emergence, whereas the assumption of gradually decreasing salinity results in predicted anion contents in Boom Clay that are much higher than those observed today. Further insights into the quantitative out-diffusion of sea-water salinity over a known period of time could be obtained from a $\delta^{37}$Cl profile because the scenario is reasonably well constrained and the initial condition ($\delta^{37}$Cl = 0) is known – in contrast to all other sites considered here. As discussed in Chapter 7 below, the "memory" of $\delta^{37}$Cl is longer than that of Cl, *i.e.* a signal would be expected even at times when the Cl profile has become flat and equilibrated with the boundaries.

![Model for Cl at Mol](image)

Only diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the aquifers. Initial condition: Cl = 19 350 mg/L (sea-water value). Instantaneous flushing of both aquifers. Model run MOL A11

6.8 *Boom Clay at Essen (Belgium)*

The low-permeability sequence consists of flat-lying Boom Clay, 127 m thick, sandwiched between the overlying (Neogene) and underlying (Lower Rupelian) aquifers. The setting is very similar to that of Mol, with the exception that emergence from the sea occurred only at about 1.7 Ma. The other difference to Mol is the fact that the Lower Rupelian aquifer is not fresh but contains a sea-water component of about 20 %. The increase of the sea-water component in the Lower Rupelian aquifer towards the northwest, *i.e.* with increasing distance from the infiltration area, is a well-known
feature. After emergence, the surface was affected by stages of permafrost, during which infiltration of meteoric water may have been reduced.

Samples were obtained from a single borehole, from which profiles of Cl\(^-\), Br\(^-\), I, \(\delta^{18}O\), \(\delta^2H\) and He cover the whole sequence, and from which data for the overlying (Neogene) and underlying (Lower Rupelian) aquifers have also been obtained. The common pattern of all tracer profiles is the linear increase of concentrations of Cl\(^-\), Br\(^-\) and He as well as of \(\delta^{18}O\) and \(\delta^2H\) values with depth. The tracer profiles in Boom Clay link the respective values at the boundaries, and so can qualitatively be considered to reflect a steady-state exchange between pore waters and the bounding aquifers. Even though the increase with depth of \(\delta^{18}O\) and \(\delta^2H\) values is only slight, it is systematic but shows an excursion towards higher values near to the top of the Boom Clay, at about 20 m below the boundary with the Neogene aquifer (Figure 6.8-1).

Figure 6.8-1: Base-case model for water isotopes at Essen

![Base-case model for water isotopes at Essen](https://example.com/base-case-model.png)

Only diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the aquifers. Lower Rupelian aquifer: \(\delta^{18}O\) and \(\delta^2H\) values are assumed to be constant at present values since emergence of the site at 1.7 Ma. Neogene aquifer: \(\delta^{18}O / \delta^2H\) values in the Pleistocene are assumed to be 0.5 / 6 ‰ lower than today. Model run ESS W14

Transport modelling (assuming constant boundary conditions corresponding to current values since activation of the aquifers) indicates that the minimum build-up times for linear diffusion profiles of these tracers vary between hundreds of thousands of years for He to 1.5 – 2 Ma for anions and water isotopes. These times are consistent with the time of emergence of the site (1.7 Ma). Closest model fits are obtained when assuming diffusion to be the only transport process. Advection in the vertical dimension must have been very limited, as it would introduce a curvature in model profiles, but this contradicts the linear observed tracer distributions.

Sensitivity modelling of different temporal conditions in the Neogene and Lower Rupelian aquifers has examined the case of a linear decrease of salinity and \(\delta\) values in the Lower Rupelian aquifer from the time of emergence up to now, instead of the immediate step change of Cl and \(\delta\) values at emergence that was assumed in the previous scenario. Modelling results show that this
alternative set of boundary conditions worsens the match with data for the evolution time of 1.7 Ma, and much longer evolution times would be required. This observation is analogous to that made for Boom Clay at Mol.

In the uppermost 20 m of Boom Clay, the shift towards higher δ values is attributed to a change in the upper boundary condition in the Holocene, whereas the linear part of the profile is considered to represent a cold-climate equilibrium. The suggested recent climatic effect has been included in the model, which applies δ values lower than the present ones for the upper boundary (Neogene aquifer) during the Pleistocene, followed by a step change to higher, warm-climate values (i.e. those currently measured) since the onset of the Holocene (Figure 6.8-1). This model fits the data trend in the upper 20 m of the pore water profile and thus supports the hypothesis that the shift of stable isotope compositions is due to Pleistocene climatic effects on infiltration to the Neogene aquifer.

The linear profile of He across the Boom Clay has been shown by modelling to be entirely the result of steady-state transport across the clay from a higher concentration in the Lower Rupelian aquifer to the near-zero concentration in the Neogene aquifer. In-situ production has no effect on the shape of the profile because of the rapidity of He diffusion. Also, steady state is established so quickly that, in the case of Essen, the resulting model profile is independent of the choice of the initial He concentration.

6.9 London Clay at Bradwell (UK)

Bradwell is on the coastline of southeast England, and the studied formations include the London Clay and the underlying Lower London Tertiaries. These formations have remained close to the surface throughout their evolution, and so their degree of consolidation is weak and comparable to that of Boom Clay (Table 3.2-1). Two boreholes were located at surface elevations of about 6 and 1.3 metres above sea level, about 600 m apart. The London Clay at this site is different from the other low-permeability sequences studied in this report in having its upper boundary at the surface. Therefore, the upper hydrogeological boundary here is effectively surface water and its composition varies according to transient local hydrological conditions. Since marine transgression in the Holocene between about 9 and 6 ka, the surface at the borehole location closer to the shore has been susceptible to sea-water inundation because there are 4.8 metres of permeable alluvium on top of the clay. In contrast, the location of the borehole situated farther inland has seen predominantly meteoric water conditions. These differences are reflected in very different compositions of pore waters at the top of the London Clay in each borehole profile, despite their proximity.

The position of the lower boundary of the low-permeability sequence is not entirely clear. For the purpose of modelling, a small aquifer at the base of the London Clay was taken as the boundary in the profile near to the coast line, whereas this aquifer is very thin and apparently hydraulically not relevant in the borehole farther inland, so the Lower London Tertiaries are also thought to be part of the same low-permeability sequence at that site. The resulting thicknesses for the sequences are 46 and 72 m, respectively.

There are data points for Cl⁻ and stable water isotope ratios in the pore waters through the whole sedimentary sequence and also for surface water and deeper aquifer ground waters. In the borehole near to the coast line, both Cl⁻ concentrations and δ¹⁸O and δ²H isotope values are only slightly below those of sea water near to the surface but decrease sharply within the uppermost 30 m of London Clay (Table 3.1-1, Figure 6.9-1). Whereas the Cl⁻ concentrations remain low with increasing depth (500 – 700 mg/L), the δ values increase again slightly towards the small aquifer below London Clay, so there is a minimum within the low-permeability sequence. In the borehole located farther inland, Cl⁻
contents are low in spite of an increasing trend with depth, and δ values are dominated by meteoric water throughout. Cl− concentrations in aquifer ground waters at the base of the Tertiaries are about 500 mg/L in both boreholes.

A scoping model shows that a steady-state, linear distribution of Cl− between fresh water at the surface and the aquifer at the base of the Lower London Tertiaries would have taken about 200–300 ka to develop by diffusion. This is the process that occurred throughout the sequence after Neogene uplift and flushed out all evidence of depositional marine pore water.

Separate models for the two profiles have been constructed for the more recent evolution, with differing temporal patterns of conditions at the upper boundary. At the near-coastal site, the sharp increase of Cl− at the top of the profile to close to sea-water composition has been simulated with a fresh initial pore water composition and a step change of Cl− from fresh water to sea water at the upper boundary. The model indicates that the best-fit diffusion time is 4–5 ka (Figure 6.9-1). This is reasonably consistent with the timing of Holocene marine transgression, considering palaeohydrogeological uncertainties. That consistency and the smooth shape of the shallow Cl− profile indicate strongly that diffusion accounts for solute transport in this clay. The corresponding simulation of the δ18O and δ2H profiles has been modelled with an initial pore water composition equal to the lowest isotope ratios, i.e. the minima values seen at about 30 m depth. In other words, it was assumed that prior to marine transgression the pore waters would have been dominated by Pleistocene meteoric water with cold-climate isotopic compositions. The upper boundary is assumed to have had a step change to marine isotopic composition, as for Cl−, and the lower boundary composition is assumed to have remained constant as at present. The model fit indicates the same time for in-diffusion of sea water as does the Cl− model, ca. 4 ka (Figure 6.9-1).

Figure 6.9-1: Base-case calculation for Cl− and δ18O in near-coastal borehole B102 at Bradwell

Only diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the upper aquifer. Sea-water Cl− concentration (19 350 mg/L) is assumed at the upper boundary. Model run BR102 A1

Only diffusive transport is considered. Numbers adjacent to model curves indicate evolution times in Ma since activation of the aquifers. Sea-water composition (δ18O = 0 ‰) is assumed at the upper boundary. Model run BR101 W1
The data from the near-coastal site have been used to study the sensitivity of the system to advective Cl$^-$ and water movement being superimposed on diffusion. The upwards advective movement has been estimated on the basis of the maximum hydraulic gradient that could originate from the elevation of recharge to the lower aquifer (ca. 75 m a.s.l.). The resulting advection-diffusion models have rather worse fits to the data than do the diffusion-only models. This suggests that the overall impact of advection with recent hydraulic conditions on solute transport and water movement through the London Clay here is minor relative to diffusion.

In the borehole located farther inland, a localised Cl$^-$ peak at ~15 m depth has been simulated by finding the best fit for a transient change of Cl$^-$ at the upper boundary, i.e. a stage in the past in which a small marine transgression may have occurred. Diffusion modelling finds that the best-fit conditions are a transient increase of Cl$^-$ to 1800 mg/L over the period 6.5 – 3 ka. This could plausibly correspond to a time-averaged effect of a Holocene marine transgression at this specific location. The corresponding stable water isotope profile was not modelled because there is too much uncertainty over relevant variations of conditions at the upper boundary. The isotopic profile probably contains the effects of both transient Holocene marine input and Pleistocene cold-climate meteoric water.
7. DISCUSSION AND CONCLUSIONS

7.1 General understanding of tracer profiles

7.1.1 Transport mechanisms and relevant parameters

- Natural tracers are powerful evidence of non-sorbing solute transport and water movement in clay-rich rocks. Moreover, the interpretation of natural tracers is in general scientifically robust and consistent with physical concepts. For the sites and clay-rich formations that have been studied, there is strong evidence that movement is controlled by diffusion. In the model cases where advective movement was also considered, the goodness of the model fits to the data could not be improved. Therefore, the advective transport rate is at best comparably slow with diffusion, if not slower or absent.

- The most compelling evidence for diffusion comes from the consistency of the shapes of tracer profiles with what is expected from palaeo-hydrogeological interpretation of boundary conditions. These qualitative interpretations and comparisons have been generally consolidated by quantitative modelling at a number of sites with contrasting properties and hydrogeological evolutions. For example, the differing shapes of Cl- tracer profiles in the Opalinus Clay at Benken, Mont Terri and Mont Russelin are entirely consistent with ideas about the contrasting ground-water histories both between sites and between the upper and lower boundaries at a particular site. Moreover, these qualitative ideas can be quantified with “best-fit” modelling that indicates sensible values for time scales. Equally compelling support for diffusion comes for the three profiles with varying thickness through the Couche Silteuse at Marcoule. Modelling of Cl shows that the marked variations of salinity among the three profiles, from saline to brackish, are entirely consistent with diffusion with the same boundary conditions and for the same, or very similar, lengths of time since activation of the aquifers. In other words, the observed Cl- variations are explained simply by the differing thicknesses L of the diffusive system.

- The example of Marcoule illustrates that the dependence of solute travel times on the geological and environmental parameters is fundamentally different for diffusive and advective systems. Consideration of these differences in terms of the Peclet number \( \left( \frac{v_{\text{advection}} \times L}{D_p} \right) \) indicates that, in formations with very low permeabilities and low hydraulic gradients, diffusion is the more efficient process for transporting and mixing solutes over small distances, whilst advection may become the more effective transport process for larger distances (if Darcy's law applies in compacted argillaceous formations). The mathematical relationships in the diffusion equation (Fick’s Law, in which \( t_{\text{diffusion}} \) is proportional to \( L^2 \)) mean that formation thickness L, pore connectivity (which affects the value of diffusion coefficient \( D_p \)) and porosity (which is incorporated in the effective diffusion coefficient \( D_e \)) are factors that govern transport rates across a clay rock. In addition, the effect of temperature on \( D_p \) or \( D_e \) must also be taken into account when modelling thick clay-rich sequences if temperature increases with depth might be significant.

- Model calculations quantifying diffusion in low-permeability sequences are based on four key elements: the description of the diffusion process by Fick’s laws and the sensitivity of diffusion coefficients to properties of the system, the time for which pore waters have
evolved, the initial tracer compositions from which they evolved, and the time-dependent boundary conditions which the pore water profiles have experienced.

- Uncertainties in the detailed spatial and temporal variations of initial and boundary conditions propagate into the modelled profiles. In some cases, there is sufficient palaeohydrogeological information available to place independent constraints on initial and boundary conditions for one or more of the tracers (almost invariably these will be Cl, δ¹⁸O and δ²H). In those cases, the qualitative interpretation of processes that control solute transport and water exchange at the scale of the formation thickness and over time scales up to millions of years, thus covering periods of major external environmental changes, is highly credible and scientifically robust.

### 7.1.2 Evolution times

- With the exception of Boom Clay at Essen, all studied tracer profiles are curved and so reflect transient conditions (except for He, where curved profiles can be obtained for transient or stationary conditions).
- Modelled evolution times for the observed tracer profiles vary widely between formations and sites (Table 7.1-1). The longest evolution time (tens of Ma) is obtained for the Toarcian-Domerian at Tournemire (thick low-permeability sequence, low De), while, on the other end of the spectrum, London Clay at Bradwell records only the younger Holocene evolution (thin and surficial low-permeability sequence, high De). The majority of the evolution times for the other sites are in the range of a few Ma. These are the lengths of time since structural changes, usually uplift and erosion, perturbed the ground-water systems and activated the upper and/or lower boundary aquifers, usually with fresh water. They give a broad idea of the time scales of geomorphological and hydrogeological stability in each sedimentary rock system.
- As an illustration, the characteristic times for evolving tracer profiles can be estimated using the equations discussed in Chapter 4. Taking a generic example with typical parameters, a time of 3 Ma can be calculated for the propagation of a signal (i.e. a change in one boundary condition) into the centre of a 200 m thick clay rock sequence with a Dp of 1E-10 m²/s by diffusion. After 13 Ma, the signal has penetrated across the whole sequence, thereby obliterating older signatures that may have been present in the sequence.
- All evolution times for the tracer profiles represent periods of time much shorter than the depositional ages of the respective formations. This does not mean that the systems only started to evolve in the recent past – the opposite is likely the case. However, the earlier history cannot be resolved because 1) the palaeo-hydrogeological evolution is not known well enough and 2) in the tracer profiles, the older events are obliterated by the more recent evolution – see previous bullet. The geochemical evolution of low-permeability sequences embedded between aquifers must be conceived as dynamic over geological time, always adjusting to evolving boundary conditions.
- Opalinus Clay at Mont Terri is exceptional in that there is evidence that the folding of the Jura Mountains (10 – 3 Ma) and subsequent erosion activated the aquifers for the first time.

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22 In the case of the Callovo-Oxfordian shale at Bure, there have not been any structural changes that could be directly linked to the best-fit evolution times. Therefore, the scenarios that underlie the calculations remain hypothetic. Given the absence of discrete events (except external factors, such as climate change), it is possible that a gradual evolution of the bounding aquifers rather than a distinct starting point better represents reality. In this sense, the indication of evolution times has a weak basis for Bure.
Since deposition at 174 Ma, Opalinus Clay in this region was part of a sedimentary basin and was subjected to burial and uplift events, which apparently did not activate ground-water flow in the limestone units, such that the marine signature of the pore water in Opalinus Clay was preserved over most of its history.

- At Tournemire, Essen and Bradwell, a recent signal reflecting Holocene warming is superposed on the water-isotope profiles. This signal reflects a time period of max. 10 ka and is identified in the outermost parts of the low-permeability sequences, i.e. adjacent to the aquifers.

<table>
<thead>
<tr>
<th>Site</th>
<th>Thickness of low-permeability sequence [m]</th>
<th>Evolution time of lower aquifer [Ma]</th>
<th>Evolution time of upper aquifer [Ma]</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Callovo-Oxfordian at Bure</td>
<td>256</td>
<td>Not well defined(^1)</td>
<td>Not well defined(^1)</td>
<td>Refers to the URL site. Based on argumentation combining the CI(^-) and water-isotope profiles</td>
</tr>
<tr>
<td>Couche Silteuse at Marcoule</td>
<td>404, 246, 163</td>
<td>1.5 – 3</td>
<td>1.5 – 3</td>
<td>Based on CI in all three profiles. Initial condition uncertain</td>
</tr>
<tr>
<td>Opalinus Clay at Benken</td>
<td>312</td>
<td>Stagnant over very long time scales</td>
<td>0.7 – 2</td>
<td>Water-isotope profiles define the trend better than the more scattered CI data. Slope towards lower boundary is the important constraint</td>
</tr>
<tr>
<td>Opalinus Clay at Mont Terri</td>
<td>219</td>
<td>6.5</td>
<td>0.5</td>
<td>CI(^-) and water-isotope profiles both have distinctive slopes towards upper and lower boundaries. Asymmetry of the profiles suggests diachronous activation of aquifers. CI(^-) profile best constrains the evolution times</td>
</tr>
<tr>
<td>Opalinus Clay at Mont Russelin</td>
<td>&gt;222</td>
<td>Stagnant over very long time scales</td>
<td>3</td>
<td>CI(^-) and water isotopes both have distinctive slopes towards upper boundary. CI(^-) profile best constrains the evolution time. Water isotopes and He show evidence of a perturbation in a faulted zone</td>
</tr>
<tr>
<td>Toarcian-Domerian at Tournemire</td>
<td>257</td>
<td>&gt;60/2.4</td>
<td>&gt;60/2.4</td>
<td>Evolution times are hypothetical and based on a scenario considering 2 successive changes in boundary conditions. CI(^-) and (^{2})H are useful, (^{18})O data are scattered and are not strong constraints. Young signal adjacent to aquifers due to Holocene warming (since 0.01 Ma) recorded by (\delta) values</td>
</tr>
<tr>
<td>Boom Clay at Mol</td>
<td>103</td>
<td>2</td>
<td>2</td>
<td>CI(^-) is very low throughout and is consistent with out-diffusion from initial sea water; Br(^-) may not be conservative. No water-isotope profile data</td>
</tr>
<tr>
<td>Boom Clay at Essen</td>
<td>127</td>
<td>1.7</td>
<td>1.7</td>
<td>CI(^-) and (\delta) values for water isotopes increase linearly with depth consistent with steady-state diffusion. Young signal adjacent to aquifers due to Holocene warming (since 0.01 Ma) recorded by (\delta) values</td>
</tr>
<tr>
<td>London Clay at Bradwell</td>
<td>45.6 (Borehole B102)</td>
<td>Not well constrained</td>
<td>0.004 – 0.005</td>
<td>Upper boundary of profile is at surface, therefore timescales are short. CI(^-) and water isotopes yield consistent results for borehole B102. Water-isotope data show a cold-climate signal in the centre (due to longer-term diffusion in the Pleistocene) overprinted by higher, Holocene (\delta) values towards the aquifers</td>
</tr>
</tbody>
</table>

\(^1\) No base-case scenario could be defined for Bure, and evolution times based on modelling critically depend on the underlying assumptions. The uncertainty is increased by scattered, not well defined profiles of stable water isotopes.
7.1.3 Scale issues

- In this report, observed tracer profiles were successfully reproduced by transport modelling considering diffusion as the dominant transport process. The obtained evolution times are in the plausible ranges as constrained by independent palaeo-hydrogeological data. This means that the laboratory-derived diffusion coefficients that underlie the model calculations appear to be applicable on the formation scale. This is confirmed independently by detailed studies at the King Site (Saskatchewan, Canada) by Hendry & Wassenaar (1999) and Hendry et al. (2000, 2005b).

- The Toarcian-Domerian at Tournemire is the only low-permeability sequence studied that is heavily fractured in response to deep burial and induration followed by uplift. Considering the hydraulic conductivities measured in boreholes and the measured head difference between the embedding aquifers, a substantial downward advection would be obtained that dominates over diffusive transport (Peclet number around 200). This scenario is inconsistent with the observed curved tracer profiles across the formation. The most likely explanation is that the measured hydraulic conductivities represent local values that cannot be upscaled to the formation scale due to limited connectivity. On the large scale, hydraulic conductivity is probably orders of magnitude smaller.

7.2 Strengths and weaknesses of different pore-water tracers

- Tracer-data quality is variable and reflects the appropriateness of sampling procedures and the adequacy of analytical methods. For certain sites, anions provide most information, whereas for other sites, stable water isotopes yield a more useful data set. This depends on, among others, the signal-to-noise ratio, i.e. the ratio between the observed range of the tracer concentration to the total measurement error. The experience gathered regarding the usefulness of various tracers in pore waters of low-permeability formations is given in detail in Table 7.2-1.

- Anions (Cl-, Br-, I-) typically yield similar profiles. In general, it is sufficient to model Cl-, as the other anions would not bring any additional insights. The Cl-/Br- ratio is a useful indicator of the provenance of salinity (marine or other), making the assumption that Br- is conservative. In some cases this assumption might not be valid, as illustrated by the data from the Boom Clay at Mol. Similarly, Cl-/I- ratios cannot be used to constrain the provenance of salinity, and it is difficult to estimate defendable initial I- contents in the formation before activation of the aquifers. I- contents in pore waters are always much higher than the concentration in sea water, which is considered to be due to I- release from organic matter during diagenesis. For both Br- and I-, care must be taken regarding analytical uncertainties in the quantification of these species.

- Cl- has a large relative (i.e. compared to the analytical error of the analysis) concentration range that is easily related to end-member water sources. It is also easily analysed, though the correction of leaching data for anion-accessible porosity introduces some uncertainty. One should keep in mind that if the (generally not very well constrained) anion-accessible pore fraction is spatially variable, this does not only introduce a systematic error, but can also affect the shape of the profile to some degree. In systems which have had saline initial conditions in clay pore waters and aquifers and have evolved by meteoric water dilution, Cl- is a sensitive indicator of the process.

- δ¹⁸O and δ²H values have more limited ranges and also larger relative measurement uncertainties, though problems with extractions and analyses in clay pore waters are mostly
resolved except for very saline waters. Therefore, $\delta^{18}$O and $\delta^2$H are sometimes less sensitive for tracing pore-water evolution in comparison with Cl$^-$ (Opalinus Clay at Benken being the exception). Nevertheless, stable isotopes may be quite distinctive as natural tracers, and they benefit from an established framework for understanding past variations of initial conditions (i.e. sea water, climate effects on meteoric water compositions). This may be so in systems dominated by only fresh or brackish ranges of salinity where the Cl$^-$ variations may not be so distinctive, and where inferred climatic influences on stable isotopes may provide characteristic variability.

- He is geochemically different from the other tracers in that it is produced radiogenically within the rocks. Therefore, its distribution is determined by the balance between in-situ production and loss or gain by diffusion and/or advection. It may show gradients even if the other tracers have flat profiles. However, the distribution of He has a more complex relationship to time than does the shape of a Cl$^-$ or $\delta^{18}$O profile, and uncertainties in the controlling factors mean that the profile may not be quantitatively interpretable. The fact that the initial He content of a formation at the time of aquifer activation cannot be constrained in most cases is a disadvantage for modelling. For example, the initial He concentration has been treated as a free parameter to adjust model curves to observed data at Mont Terri, and this limits the amount of independent information obtained from this tracer. In contrast, the rate of He transport in the Boom Clay at Essen is so high, reaching steady state with the boundary compositions after only ~0.2 Ma, that the lack of knowledge of the initial condition does not affect the modelled profile for 1.7 Ma, the time of interest. For the same reason, in-situ production at Essen is insignificant for the He distribution across the clay.

- The high diffusion coefficient of He and the orders-of-magnitude variability of its concentration make it potentially a more sensitive qualitative indicator of local perturbations than Cl$^-$ or stable water isotopes. It would, for example, be expected that the hydrogeological effect of a transmissive fault cutting a clay-rock sequence would be indicated as a local anomaly in the He profile.

- $\delta^{37}$Cl is currently of limited use because of the incomplete understanding of the processes that affect this tracer. The systematics of $\delta^{37}$Cl in sedimentary basins are not well characterised, and the available data base is currently small. Therefore, it is difficult to define appropriate initial and boundary conditions. These uncertainties are exemplified by the model for $\delta^{37}$Cl in the Couche Silteuse at Marcoule, from which it has been inferred that the initial $\delta^{37}$Cl distribution was probably heterogeneous, although it is impossible to establish any independent support for that inference. Similarly, the initial $\delta^{37}$Cl value required to make a plausible model of the $\delta^{37}$Cl profile at Benken is not supported by any generic understanding of $\delta^{37}$Cl variations. In certain cases, the shape of the profile can be qualitatively interpreted to result from diffusion. In general, however, the signal-to-noise ratio (i.e. the observed amplitudes of natural $\delta^{37}$Cl profiles divided by the analytical error) is less favourable than for all the other tracers. At present, the modelling of the $\delta^{37}$Cl profiles has to deal with at least double the number of unknowns as compared to the modelling of Cl$^-$ because both the initial and boundary values of both $\delta^{37}$Cl and Cl$^-$ are needed for a quantitative treatment.

- The modelling of $\delta^{37}$Cl and of the characteristically complex dependence on diffusive isotope fractionation suggests that this might be a useful tracer in the future if more could be learned about its long-term hydrochemical evolution. The potential power of $\delta^{37}$Cl originates from the fact that $\delta^{37}$Cl signatures can remain visible for much longer times than those of Cl$^-$. Generic simulations for diffusive transport of Cl$^-$ and $\delta^{37}$Cl for the same palaeohydrogeological scenario are shown in Figure 7.2-1. A 312 m thick low-permeability sequence is considered with an initial Cl$^-$ concentration of 6000 mg/L and $\delta^{37}$Cl = 0‰. Both
Aquitards are assumed to be activated at the same time and have low Cl' contents and $\delta^{37}$Cl = 0‰. For the chosen parameters, the maximum Cl' content in the centre of the sequence drops to about one third of the initial concentration after 10 Ma, and after 20 Ma the Cl' profile is very close to the steady state (flat profile). In contrast, the $\delta^{37}$Cl values steadily increase until 10 Ma and are still very close to the maximum values after 20 Ma. In this sense, $\delta^{37}$Cl values have a much longer memory of events that occurred in the past when compared to the Cl' signature. However, this long memory can also become a disadvantage because in most cases it is not possible to reconstruct the palaeo-hydrogeology of a given site back to several tens of million years, so the choice of initial and boundary conditions for $\delta^{37}$Cl becomes even more uncertain.

- The conclusions regarding the usefulness of various tracers are independently supported by detailed studies in surficial clays at the King Site (Saskatchewan, Canada; Vengosh and Hendry 2001, Hendry et al. 2000, 2005b, Hendry and Wassenaar 1999, 2005, Wassenaar and Hendry 2000, Hendry and Woodbury 2007). There, $\delta^{18}$O, $\delta^2$H, Cl' and Br' proved to be most valuable, with $^4$He providing good verification. Due to the general lack of understanding of the sources and controlling processes, $\delta^{37}$Cl provided limited insight.

- Given the surficial environment of the King site, additional, short-lived radioactive tracers ($^{36}$Cl, $^{14}$CDOC, $^{14}$CDIC) that have not been used for the deep formations treated here provided additional confirmatory data on residence times and transport mechanisms. However, it is unclear at this stage whether the analysis of $^{36}$Cl and $^{14}$C is feasible in compacted shales with porosities much smaller than those of the uncompacted surficial sediments of the King site. Moreover, only in the case where Cl' migrated into the clay rock from the bounding aquifers or from a formation with a markedly different neutron flux (i.e. U and Th concentrations) within the last 1.5 – 2 Ma might $^{36}$Cl yield some interesting data. Within the suite of sites considered here, this could have been the case in London Clay at Bradwell but not at any of the other sites, where the origin of salinity is of Mesozoic or Tertiary age. An analogous argument also applies to $^{14}$C, with an even shorter time scale of ca. 50 ka.

Figure 7.2-1: Generic simulations for the evolution of Cl' and $\delta^{37}$Cl values in a low-permeability sequence

Aquitard thickness: 312 m; Dp = 5E-11 m²/s, Dp ratio of $^{35}$Cl and $^{37}$Cl = 1.002, Cl' init = 6 000 mg/L, Cl' top = Cl' bottom = 500 mg/L, $\delta^{37}$Cl init = $\delta^{37}$Cl top = $\delta^{37}$Cl bottom = 0‰. Numbers adjacent to model curves indicate evolution times since activation of the aquifers. Adapted from Gimmi & Waber (2004)
Table 7.2-1: **Strengths and weaknesses of different conservative pore-water tracers from the perspective of sampling, analysis and interpretation**

<table>
<thead>
<tr>
<th>Tracer</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
</table>
| Cl⁻ | • Simple analytical procedures (aqueous leaching or squeezing of rock, analysis by ion chromatography)  
• Can be performed on old core materials, no need for fresh, saturated samples, no redox sensitivity  
• In certain cases, sea-water Cl⁻ concentration can be used as initial condition  
• In general, favourable signal-to-noise ratio | • Requires knowledge of anion-accessible porosity, which is not straight-forward to derive (e.g. from direct in-situ sampling or from squeezing)  
• Additional uncertainty is introduced if leaching and porosity determination are not made on the same sample (local heterogeneity may be important)  
• Porosity determination may be very uncertain in old sample materials due to mineral reactions (e.g. pyrite oxidation, hydration of anhydrite) |
| Br⁻ | • Can be performed on old core materials, no need for fresh, saturated samples, no redox sensitivity  
• In certain cases, sea-water Br⁻ concentration can be used as initial condition  
• Cl⁻/Br⁻ ratios are useful as indicators of water provenance | • Same as for Cl⁻, plus  
• Difficult to measure by ion chromatography at low concentration due to peak interference; possibly need to use ICP-MS  
• Br⁻ profiles are typically similar to those of Cl⁻, i.e. provide only little additional information |
| I⁻ | • Natural proxy for ¹²⁹I, one of the safety-relevant radionuclides in spent nuclear fuel  
• Numerous measurements of the diffusion coefficient available | • Analytically demanding  
• The small difference in the diffusion coefficients for ³⁵Cl and ³⁷Cl is not well constrained  
• The systematics, relevant processes and the genetic understanding of ³⁷Cl behaviour in pore waters are not well established  
• Initial and boundary conditions often difficult to constrain  
• Typically unfavourable signal-to-noise ratio  
• Modelling depends not only on boundary and initial conditions for ³⁷Cl but also on those for Cl⁻ (i.e. there are 6 instead of 3 conditions) |
| ³⁷Cl | • Can be performed on old core materials, no need for fresh, saturated samples  
• Independent of accurate knowledge of physical and anion-accessible porosity  
• Potentially useful to discriminate between diffusive and advective solute transport  
• Can complement the Cl⁻ modelling due to the dependence on the same assumed boundary and initial conditions that were used for Cl⁻ | • Analytically demanding  
• The small difference in the diffusion coefficients for ³⁵Cl and ³⁷Cl is not well constrained  
• The systematics, relevant processes and the genetic understanding of ³⁷Cl behaviour in pore waters are not well established  
• Initial and boundary conditions often difficult to constrain  
• Typically unfavourable signal-to-noise ratio  
• Modelling depends not only on boundary and initial conditions for ³⁷Cl but also on those for Cl⁻ (i.e. there are 6 instead of 3 conditions) |
| ²H | • Independent of accurate knowledge of porosity  
• Diffusive exchange technique is the established analytical method of choice  
• In general excellent signal-to-noise ratio  
• In certain cases, sea-water ²H can be used as initial condition  
• Genetic information on water provenance from ²H- ³¹⁸O graphs | • Requires fresh, saturated sample materials and proper sample protection  
• Data obtained by vacuum distillation are affected by fractionation due to incomplete distillation. They need to be corrected in order to be comparable with data from ground waters in the embedding aquifers  
• Isotope analysis is more difficult (and less accurate) for waters with salinity exceeding that of sea water  
• δ²H of water infiltrating over geological times scales is not well known (effects of surface temperature, precipitation rate, permafrost, etc.) |

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<table>
<thead>
<tr>
<th>Tracer</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>δ¹⁸O</td>
<td>• Same as δ²H</td>
<td>• Same as δ²H, plus&lt;br&gt;• Signal-to-noise ratio less favourable compared to δ²H</td>
</tr>
<tr>
<td>He</td>
<td>• <em>In-situ</em> production prevents complete out-diffusion and allows study of systems in which other tracers may no longer show any signal&lt;br&gt;• In certain cases, a steady-state situation (rate of out-diffusion = rate of <em>in-situ</em> production) can be inferred, which simplifies modelling and interpretation&lt;br&gt;• He is more mobile than anions and water and therefore records a more recent part of the evolution when compared to the other tracers, which is a welcome complement&lt;br&gt;• ³⁷He/³²He provides additional information on He provenance</td>
<td>• Demanding sampling, gas purification and analysis, requiring purpose-made equipment&lt;br&gt;• Diffusion coefficients difficult to measure, only few data available&lt;br&gt;• Impossibility to independently constrain the initial condition&lt;br&gt;• Only few data sets currently available</td>
</tr>
</tbody>
</table>

The signal-to-noise ratio refers to the variability of the tracer concentration over the profile in the low-permeability sequence ("signal amplitude") divided by the total analytical error for that tracer.

### 7.3 Consistency of results from different tracers

- Interpretative models for the various tracers (Cl⁻ and Br⁻, δ¹⁸O and δ²H, δ³⁷Cl, He) represent different types of dependence on physico-chemical conditions. It is possible to judge the consistency of results and interpretations obtained from different tracers (*e.g.* evolution times based on model calculations) if independent constraints on the initial and boundary conditions for each tracer are available. In practice, these constraints are often not totally independent. Nevertheless, each additional tracer adds confidence to the overall interpretation of site evolution. Opalinus Clay at Mont Terri can be taken as an example: The activation times of the upper and lower aquifers were determined from the Cl⁻ data, whereas the δ¹⁸O and δ²H were only used as supporting evidence. Due to the lack of knowledge of the initial condition, the only independent piece of information added by modelling the He profile is the conclusion that the same palaeo-hydrogeological framework can be used to explain the asymmetric Cl⁻ profile and the symmetric He profile.

- Bearing the restriction of the last bullet in mind, it is concluded that no single major inconsistency among conclusions obtained from different tracers was identified in the present study. Generalised statements on internal consistency are summarised in Table 7.3-1. They are in good agreement with independent evidence from the King Site (Saskatchewan, Canada), where a multitude of tracers were used (Hendry, pers. comm.).

- In some cases, *e.g.* the Opalinus Clay profiles at the Swiss sites, the choice of initial conditions affects the internal consistency of the site-specific data sets. Assuming sea water as the initial condition at Mont Terri and at Mont Russelin yields inconsistencies in the evolution times based on the Cl⁻, δ¹⁸O and δ²H profiles. Consistency is achieved by using negative δ values for both water isotopes as initial conditions. Independent support for this choice is provided by a ground-water sample from Mont Russelin, characterised by marine Cl⁻ but negative δ values. The fact remains that the processes that accounted for this water composition are unknown. This point is perhaps the most intriguing geochemical question remaining in the understanding of these pore-water data, but it does not have any direct consequences for the modelling and interpretations of tracer profiles.
At some sites, a Holocene signal in response to the increased surface temperature is observed in the $\delta^{18}$O and $\delta^2$H data but not in the Cl and He data. Because the latter are not sensitive to surface-temperature variations, the different behaviour of the tracers does not represent an inconsistency but is the consequence of changed boundary conditions.

Table 7.3-1: Consistency of interpretations based on different tracers

<table>
<thead>
<tr>
<th>Site</th>
<th>Conclusions obtained from different tracers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Callovo-Oxfordian at the Bure URL site</td>
<td>Only wide ranges can be given for the evolution times. The range for Cl$^-$ (1.2 – 15 Ma) overlaps with that for $\delta^{18}$O and $\delta^2$H (1 – 4 Ma). He is not in steady state unless its diffusion coefficient is manipulated or alternative scenarios considering upward flux from underlying formations are considered.</td>
</tr>
<tr>
<td>Couche Silteuse at Marcoule</td>
<td>Cl$^-$ and Br$^-$ profiles lead to near-identical conclusions. Cl isotope data do not add independent support because of the limited knowledge of the initial and boundary conditions.</td>
</tr>
<tr>
<td>Opalinus Clay at Benken</td>
<td>The calculated base-case evolution times are &gt;0.7 Ma for $\delta^{18}$O and $\delta^2$H but 1.4 – 2 Ma for Cl$^-$. Given the uncertainties of the initial conditions (which have a strong effect on the evolution times) and due to the limited knowledge of diffusion coefficients over the low-permeability sequence, the evolution times are considered as largely consistent. The interpretation of $\delta^{37}$Cl is qualitatively consistent but cannot be used in quantitative terms.</td>
</tr>
<tr>
<td>Opalinus Clay at Mont Terri</td>
<td>Consistent evolution times are obtained from Cl$^-$ and from stable water isotopes when the initial condition for the latter is slightly adapted. One single palaeo-hydrogeological scenario explains the strong asymmetry of the Cl$^-$ profile, the weaker asymmetry of the water-isotope profiles and the symmetry of the He profile.</td>
</tr>
<tr>
<td>Opalinus Clay at Mont Russelin</td>
<td>The evolution times for Cl$^-$, $\delta^{18}$O and $\delta^2$H are all about 3 Ma. This consistency is considered to be meaningful because the initial and boundary conditions are reasonably well constrained. The profiles of $\delta^{18}$O, $\delta^2$H and He are disturbed in a major fault zone along the contact to underlying Lias limestone, whereas Cl$^-$ shows no disturbance. There is not a ready combination of understood processes that allows this situation to be modelled. Effects of the tunnel (all data were obtained from short boreholes) cannot be excluded.</td>
</tr>
<tr>
<td>Toarcian-Domerian at Tournemire</td>
<td>The palaeo-hydrogeological evolution is complex (at least 2 major stages) and not well constrained. Therefore, no clear statements about consistency among the various tracers can be made.</td>
</tr>
<tr>
<td>Boom Clay at Mol</td>
<td>The current Cl$^-$/Br$^-$ ratio of 37 indicates that the out-diffusion of Cl$^-$ and Br$^-$ was distinctly different (the initial marine Cl$^-$/Br$^-$ ratio of 290 is well constrained), leading to slightly different evolution times of 2.5 – 3 Ma (Cl$^-$) and 2 Ma (Br$^-$). Explanations to this difference (retardation of Br$^-$, lower diffusion coefficient) are hypothetical at the present stage.</td>
</tr>
<tr>
<td>Boom Clay at Essen</td>
<td>Steady-state linear profiles are obtained for Cl$^-$, $\delta^{18}$O, $\delta^2$H and He. All data are consistent with emergence at 1.7 Ma as suggested by palaeo-hydrogeological arguments.</td>
</tr>
<tr>
<td>London Clay at Bradwell</td>
<td>Evolution times for Cl$^-$ (4 – 5 ka) and for stable water isotopes (4 ka) are consistent.</td>
</tr>
</tbody>
</table>

7.4 Choice of initial conditions for modelling tracer profiles

The studied formations, all of marine origin, have ages of tens to hundreds of Ma. The conservative pore-water tracers characterise only the most recent part of the history, about 1 – 10 Ma. The evolution of the low-permeability sequences is complex in many cases, including stages of deep burial in the basin, and/or exposure to meteoric waters during continental periods. Older geochemical disturbances were obliterated by more recent processes and so, in most situations, do not play a role in the interpretation of the present-day profiles. This is fortunate because the palaeo-hydrogeological understanding of the earlier evolution of the formations is generally insufficient for a quantitative treatment. In the transport calculations presented, the early evolution finds its only expression in the choice of
the initial condition, *i.e.* the spatial distribution of the tracers at the time when the most recent activation of the embedding aquifers occurred.

- Together with the time-dependent boundary conditions, the initial condition is one of the least known parameters in the modelling. In some cases, arguments exist that sea-water composition can be used as an initial condition (which does not necessarily imply connate water – sea water may have diffused into the formations at some later stage). With the possible exception of the Couche Silteuse at Marcoule, there are no indications at any of the study sites of evaporation events that would have proceeded anywhere near halite saturation. Therefore, the current Cl⁻/Br⁻ ratio can be used to test whether the pore water can be explained on the basis of an original sea water that was later diluted or lost part of its salinity by out-diffusion.
- In several cases, sea water has been shown not to be a good choice as initial condition, and the highest observed tracer concentrations are used instead. An overview of the applied initial conditions for base-case modelling is presented in Table 7.4-1.
- There is still a degree of uncertainty about the past variations of sea-water salinity, up to a maximum x 2 variation has been suggested in the literature, but this scale of uncertainty is considered to be very unlikely.
- In several cases, alternative models of initial salinity higher than the currently observed maximum are generally not consistent with the shapes of the Cl⁻ profiles. The slopes of the Cl⁻ profiles towards upper and lower boundaries are the most sensitive test of the match for models with varying initial salinities and times that are constrained by palaeo-hydrogeological considerations.

### 7.5 Choice of boundary conditions for modelling tracer profiles

- The choice of boundary conditions generally assumes that present aquifer compositions are representative of past compositions for the period during which the tracer profile has evolved. It is generally supported by the spatial continuity of tracer concentrations adjacent to the interfaces.
- In three cases, the Toarcian-Domerian at Tournemire, the Boom Clay at Essen and the London Clay at Bradwell, there is evidence and reasoning that δ¹⁸O and δ²H at the boundaries of the clays have changed due to Holocene climate effects. In some cases modelling has tested the sensitivity to changing boundary compositions, and the results indicate that these are plausible hypotheses. More discussion of recent climate-related changes follows below.
- Asymmetric tracer profiles are modelled by assuming that the upper and lower boundary aquifers were activated at different times, for example in the modelling of the Opalinus Clay profiles in Switzerland and of the Toarcian-Domerian Cl⁻ profile at Tournemire. The results provide a convincing match to data and strongly support the assumption of asynchronous aquifer activation. Whilst the palaeo-hydrogeological reasoning for this does not have independent support from, for example, different ground-water age structures in the aquifers, there is a qualitative to semi-quantitative match with the site-specific erosion histories (shallower aquifers are activated well before erosion exhumes and activates deeper aquifers).
- The He model for Benken strongly depends on the concentration that is assumed for the upper (Malm aquifer) boundary. Using the measured concentration in the Malm aquifer results in a poor fit to the data in the low-permeability sequence. An acceptable match has to
ignore this measured upper boundary value as an anomaly and instead assume a ca. 
× 0.5 lower value similar to the He value at the lower boundary. Explanations of this 
discrepancy include analytical error or an insufficient understanding of He in the Malm 
aquifer.

Table 7.4-1: Initial conditions chosen for base-case calculations

<table>
<thead>
<tr>
<th>Site</th>
<th>Cl− Justification</th>
<th>δ¹⁸O, δ²H Justification</th>
<th>He Justification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Callovo-Oxfordian at the Bure URL</td>
<td>No base case can be defined due to the lack of independent constraints. Model calculations were performed for the range between the current maximum and the nominal sea-water value.</td>
<td>Same as for Cl−. Strongly positive δ values are unlikely because those in the underlying Triassic aquifer (which possibly affected those in the overlying units via diffusion) are around 0 or only slightly above.</td>
<td>No base case. Chosen so that a match with data was obtained for diffusion time of max. 4 – 6 Ma. There are no independent constraints except the weakly supported maximum evolution time of about 4 Ma based on the water-isotope data.</td>
</tr>
<tr>
<td>Couche Silteuse at Marcoule</td>
<td>Maximum observed value in thickest profile, slightly higher than in current sea water.</td>
<td>Reasonably consistent model ages for all 3 profiles are obtained on this basis, despite the wide range of current salinities in each profile. Current salinity of the Mediterranean is higher than the worldwide average due to restricted mixing.</td>
<td>No model.</td>
</tr>
<tr>
<td>Opalinus Clay at Benken</td>
<td>Maximum observed value in the centre of the low-permeability sequence. Non-marine Cl−/Br− ratios, indicating dilution of sea water in the earlier evolution. Higher initial values yield less good model fits to the data.</td>
<td>Maximum observed value in the centre of the low-permeability sequence. Non-marine Cl−/Br− ratios. Higher values yield less good model fits to the data.</td>
<td>Chosen so that a match with data was obtained after diffusion time of 0.7 – 1 Ma. There are no independent constraints. The current He profile is flat, and the model is also sensitive to boundary concentrations, for which two models were run.</td>
</tr>
<tr>
<td>Opalinus Clay at Mont Terri and at Mont Russelin</td>
<td>Sea water. Maximum current Cl− concentration is only slightly lower than that in sea water. Marine Cl−/Br− ratios at Mont Terri.</td>
<td>Values between current maximum and sea-water values. Initial δ¹⁸O and δ²H values used as fit parameters when applying the same palaeo-hydrogeological evolution as that for Cl−. Independent confirmation of these values from a ground-water sample (interpreted to represent an old water) from Mont Russelin.</td>
<td>Chosen so that a match with data was obtained after diffusion time of 6.5 Ma for top boundary and 0.5 Ma for lower boundary at Mont Terri, and 3 Ma for the top boundary at Mont Russelin. There are no independent constraints. Initial He concentration used as fit parameter when applying the same palaeo-hydrogeological evolution as that for Cl−. At Mont Terri, the only independent piece of information from He is the shape of the profile, not the absolute concentrations. At Mont Russelin, the limited He data set does not provide truly independent information.</td>
</tr>
</tbody>
</table>
### 7.6 Glacial and post-glacial effects recorded by stable water isotopes

- The possibility that shifts in $\delta^{18}$O in the upper parts of some profiles are due to Pleistocene-Holocene climate changes suggests further calibrations of time scales represented by tracer profiles. $\delta^{18}$O and $\delta^2$H values in the uppermost 10 – 20 m of the Toarcian-Domerian at Tournemire, Boom Clay at Essen and London Clay at Bradwell shift towards higher values, while Cl$^-$ contents are not affected. This trend at shallow depth sharply breaks the larger-scale trend across these low-permeability sequences and must be due to a geologically recent change in the upper boundary condition. Based on the model calculations, it is likely that this change reflects Holocene warming, resulting in higher $\delta^{18}$O and $\delta^2$H values in the upper aquifers. The changed boundary condition is then propagated via diffusion into the low-permeability sequence. The model calculations indicate short diffusion times, which are in general agreement with Holocene warming that started at ca. 10 ka.

- Taken together, the sharp $\delta^{18}$O and $\delta^2$H gradients in the upper parts of the low-permeability sequences of the Toarcian-Domerian at Tournemire, Boom Clay at Essen and London Clay at Bradwell clearly indicate that the disturbance must be young and can most likely be linked to warming at the end of the last glacial cycle. Over such a short time scale, the palaeo-hydrogeological situation is better constrained than that for calculations considering much longer evolution times, so there is less ambiguity in the interpretation. From this perspective, the conclusion that diffusion is the dominating transport process and adequately explains the observed tracer distributions is particularly strong and supported by independent studies targeted at clay-rich aquitards (e.g. Desaulniers et al. 1981, Remenda et al. 1996, Hendry & Wassenaar 1999).
The absence of a shift of $\delta^{18}$O and $\delta^2$H at other sites can be explained by the likely presence of permafrost, which limited infiltration during the cold periods during the Pleistocene. These sites are typically located away from the sea in the northern (i.e. colder) part of central Europe (e.g. Opalinus Clay at all three sites).

7.7 Spatial heterogeneity in bounding aquifers

Heterogeneity limits the possibility to extrapolate findings from one borehole to the wider region. Although at some of the sites discussed here, the investigations have enabled us to establish some knowledge of lateral variability in the pore water profiles and in the compositions of the bounding ground waters, there is in general a significant degree of uncertainty about lateral variations and the significance for long-term evolution of pore water compositions at any one point. Essentially, a single borehole will have taken a 1-D sample through a system in which the diffusive evolution may have some 3-dimensionality.

An example of heterogeneous ground-water flow velocities, residence times and chemical compositions is the Malm limestone that constitutes the aquifer overlying the low-permeability sequence at Benken (Switzerland). Due to fracturing and karstification, the salinity and age of the Malm water vary widely over short lateral distances (Figure 7.7-1). At the Benken borehole, the Malm water is essentially stagnant with high salinity (possibly buffered by out-diffusion from the low-permeability sequence), while, only a few km away, it contains $^3$H and is one order of magnitude less saline. As Figure 7.7-1 shows, the lateral variability of salinity shows no clear relationship to the distance to the outcrops of the Malm. The maximum lateral salinity gradient that can be deduced from Figure 7.7-1 (between Benken and Lottstetten) is around 1 g Cl/L per km, which is more than one order of magnitude less than the vertical gradient observed in the Benken borehole (see Table 3.1-1).

Figure 7.7-1: Lateral variability of chemical characteristics of ground waters in the Malm aquifer overlying the low-permeability sequence at Benken

Units: Total dissolved solids TDS [mg/L], $^3$H [TU], $^{14}$C [pmc]. Adapted from Nagra (2002)
Heterogeneity within aquifers also occurs due to the vertical and horizontal variability of sedimentary facies and of diagenetic evolution, which results in local high-porosity horizons. The Oxfordian limestones at Bure (Section 2.1, Figure 2.1-15) provide a good example. The contrary example is the Lower Rupelian aquifer in Belgium, which consists of weakly consolidated sandy sediments. The water in this aquifer is a mixture of sea water and meteoric water infiltrating in the outcrop area in the south. As shown in Figure 2.7-2, there is a more or less smooth trend towards higher salinity when moving away from the infiltration area, indicating that heterogeneity within the aquifer is limited.

7.8 **Vertical and lateral heterogeneity in the low-permeability sequences**

7.8.1 **Lithology and mineralogy**

- The shale unit(s) in low-permeability sequences always show some degree of heterogeneity in the vertical dimension, expressed mainly by variable contents of carbonates (e.g. Callovo-Oxfordian at Bure, Opalinus Clay at all 3 sites) and/or quartz (e.g. Boom Clay at Mol and Essen). This heterogeneity is due to changes in the sedimentary facies over time. At Bure, a number of transgression/regression cycles were identified within the Callovo-Oxfordian (Figure 2.1-3; Andra 2005c).

- In addition to clay-rich lithologies, low-permeability sequences may contain marls, limestones, siltstones and other rock types. Parts of the limestones overlying Opalinus Clay have low permeability at Mont Terri (ca. 15 m) and at Mont Russelin (ca. 45 m) and are part of the diffusion-dominated low-permeability sequence. At Benken, the low-permeability sequence is 312 m thick, i.e. much thicker than Opalinus Clay itself (113 m). At Bure, parts of the overlying Oxfordian and of the underlying Dogger limestones belong to the low-permeability sequence. The transport parameters of these rock types may differ markedly from those of the clay rocks but, typically, have not been investigated to the same level of detail.

- If sufficient data are available, vertical heterogeneity can be modelled explicitly by distinguishing a number of layers with different transport and other parameters. Heterogeneity of the argillaceous unit(s) in the horizontal dimension is generally more limited at the sites in this study. Only minor lithological changes were identified in Boom Clay and Opalinus Clay over distances of several tens of km.

- The important points are that 1) the boundaries of low-permeability sequence do not necessarily coincide with the boundaries of the shale unit(s) and have to be derived from borehole and core measurements, and 2) transport parameters (diffusion coefficient, porosity, hydraulic conductivity) should be studied for all lithologies within a low-permeability sequence.

7.8.2 **Lateral variability of tracer contents**

- While tracer profiles are generally well characterised in the vertical dimension, only a limited amount of data is available that is pertinent to lateral heterogeneity, as this requires information from a set of adjacent boreholes or from different positions along a tunnel. At Tournemire, distinctly different Cl\(^-\) contents were observed over a lateral distance of 220 m, as shown in Figure 7.8-1, whereas stable water isotopes do not show any lateral variation. The lateral Cl\(^-\) gradient is ca. 100 mg/L per 100 m, compared to about 320 mg/L per 100 m in the vertical dimension. Considering an anisotropy factor of the diffusion coefficient of 2,
the diffusive fluxes in the vertical and horizontal directions are of comparable magnitude. Therefore, in principle, Cl⁻ transport should be modelled in 2, if not 3 dimensions. This is currently not possible because the differences in the chemical evolution of the embedding aquifers that most likely are the cause of lateral heterogeneity within the low-permeability sequence cannot be resolved. However, it has to be borne in mind that modelling in 1 dimension may be an oversimplification.

- Another example of lateral tracer variability is the Callovo-Oxfordian at Bure. On a regional scale, Cl⁻ contents are variable. Cl⁻ concentrations >3 000 mg/L are observed in boreholes EST311/EST312 some 13 km away from the URL (with Cl⁻ = 1 000 – 2 000 mg/L) and are most likely due to the higher salinity in the underlying Dogger aquifer (Figure 2.1-6).

- In the Couche Silteuse at Marcoule, highly contrasting Cl⁻ contents were observed over lateral distances of a few km (Figure 2.2-2, Figure 2.2-3). In this case, the preferred explanation is that the tracer distributions represent snapshots of the ongoing out-diffusion process and that the heterogeneity is due to the lateral variation of the thickness of the low-permeability sequence (factor of 2.5 over 5 km distance).

- The only case where both Cl⁻ and stable water isotopes change drastically over short distances is documented for Bradwell (Figure 2.9-2, Figure 2.9-3). This is a special situation in that the upper boundary is the surface, and that one borehole is dominated by a marine signal, while a second borehole 600 m farther inland records meteoric conditions. Such a substantial heterogeneity would not be expected if the upper boundary were a deep aquifer because mixing would attenuate the high chemical gradients to some degree.

Figure 7.8-1: Lateral heterogeneity of Cl⁻ contents in the Toarcian-Domerian at Tournemire

7.8.3 Conclusions

- In summary, lateral heterogeneity on scales of hundreds of metres to tens of kilometres was observed in all cases where multiple observation points were available, so it appears that this is more the rule than the exception. In particular, the available data indicate that lateral
heterogeneity may be substantial for Cl\(^-\). The lateral gradients are generally much smaller than those in the vertical direction. Still, because diffusion coefficients in the horizontal direction (parallel to bedding) are typically 2 – 5 times higher when compared to the vertical direction, possible effects of lateral diffusion on the vertical tracer distribution in a given borehole cannot be discounted \textit{a priori}. All modelling in this report is, however, only in 1-D, essentially due to the fact that a full parameterisation in 2-D would require more data that are not currently available.

- According to the limited evidence that is available, the stable-isotopic composition of water shows only a small variability on horizontal scales of hundreds of metres (Tournemire, Bure), except in surficial situations where the upper boundary condition varies drastically (Bradwell).

7.9 Constraints on vertical advection velocities

7.9.1 General aspects

- Modelling provides illustrations of how tracer profiles would look if advection dominated over diffusion. This shows that advection has a piston-displacement effect, with the compositional step change being spread out by limited hydrodynamic dispersion. If advective velocity is comparable to the diffusive transport rate, modelling shows that the effect is a relatively minor change of concentration distribution. If advection velocity greatly exceeds the diffusive transport rate (\textit{i.e.} for high hydraulic conductivity and/or high hydraulic gradient), then the piston displacement effect prevails with total flushing of pore water in the course of time. This is not seen in any of the sequences here.

- The likely situation in which advection would dominate would be a silty formation with sufficient large-scale vertical permeability (>1E-8 m/s) to be advective under normal gradient, or a slightly less permeable silty clay rock with anomalously high gradient, \textit{i.e.} much greater than 1 (\textit{e.g.} a cap rock above an overpressed hydrocarbon reservoir or deep aquifer). Across the studied low-permeability sequences, current hydraulic gradients are always ≤0.5 m/m, and hydraulic conductivities are orders of magnitude lower (Table 7.9-1).

- Vertical advection could also be significant in clay rocks that have fracture networks so that the upper and lower bounding aquifers are connected. Examples of these would be indurated shales and carbonate-cemented marly siltstones that have undergone brittle fracturing. The distributions of solutes through the pore waters and between pore waters and fracture waters are expected to be complex. The general regularity of the tracer profiles studied here and the scarcity or absence of fractures at most of the sites speak against fracture control.

7.9.2 Insights obtained from modelling

- The consideration of vertical advection in the model calculations leads to predicted tracer profiles that are comparable or less good than models with diffusion alone. Not a single case was identified in which advection would actually improve the model fits\(^{23}\).

\(^{23}\) For the Cl\(^-\) data of borehole EST311/312 near Bure, a specific value for the vertical advection velocity does slightly improve the fit of the model. However, the data are somewhat scattered and, more importantly, only available for the central part of the low-permeability sequence, whereas data close to the boundaries would be more diagnostic for discriminating transport processes. Therefore, this case is not given much weight for the general conclusions.
Model calculations were made to identify threshold values for vertical advection velocities beyond which the modelled profiles are no longer in agreement with the data. These calculations were performed in the sense of “what if” scenarios, i.e. they relate to situations that are not supported by (or even in contradiction with) independent evidence. The resulting hydraulic gradients are always higher than what is observed today in the formation. Also, it was assumed that Darcy's law applies even in the low-permeability sequences and that no threshold gradients exist in the clay-rich units below which no flow occurs. Therefore, the calculated hydraulic gradients must be treated *cum grano salis*.

The results of all site-specific calculations are summarised in Table 7.9-1. It turns out that the resulting Peclet numbers are mostly below 10. Peclet numbers in the range 1 – 10 correspond to systems in which diffusion and advection are both important, and only values >10 relate to advection-dominated systems. It is concluded that none of the studied low-permeability sequences can be considered as advection-dominated. Or, reversing the argument: Even when assuming hypothetical and sometimes extreme scenarios that are not supported by palaeo-hydrogeological evidence, advective effects on the observed tracer profiles must be limited and, more probably, do not exist.

Opalinus Clay at Benken is exceptional in that upward advection with velocities up to about -7E-12 m/s yield modelled profiles that are broadly consistent with the tracer distributions at evolution times that are not in clear contradiction to independent evidence. The obtained maximum Peclet number of about 25 is in the advection-dominated range. This does not mean that advection actually occurred at Benken (pure diffusion still yields the better fit to the data), but it shows that in the case of upward advection, the system is not very sensitive to discriminating between advective and diffusive transport. This is because of the strong asymmetry of the profile, in which only the lower limb shows a strong geochemical gradient. The piston effect of upward advection accelerates the decrease of tracer concentrations in the lower limb, but, in the model calculation, this can be counterbalanced to a certain degree by choosing a shorter evolution time. Because of the small geochemical gradient in the upper limb and due to the absence of tracer data in the uppermost part of the sequence, a clear misfit in this region is only identified at high advection velocities (Figure 5.3-10). However, the hydraulic gradients of up to 40 that would be needed to generate such velocities appear unrealistic – there are no plausible mechanisms to create such gradients between the two embedding aquifers. For this reason, the calculated maximum upward velocity is considered as the result of a numerical experiment with little practical relevance.

The other exception is downward flow across the low-permeability sequence at the Bure URL site, which can reach relatively high advection velocities and Peclet numbers without contradicting the data. The reason is the absence of tracer data in the Dogger limestone above the Dogger aquifer and the aberrantly high and not well understood Cl- content in the Dalle Nacrée limestone just below the Callovo-Oxfordian shale. This is another example of how data gaps limit the sensitivity of the model calculations to discriminate between transport processes.

In the Couche Silteuse at Marcoule, the relatively high calculated Peclet numbers of 5 – 10 are due to the fact that, for analytical reasons, the tracer data have a substantial scatter. This uncertainty propagates into the determination of the maximum advection velocities that are still consistent with the data. If the Cl- data had been obtained using current best practice procedures, the resulting advection velocities and Peclet numbers would most probably be smaller.

At Mont Terri and at Tournemire, the Cl- profiles are asymmetric, with maximum concentrations well below the centre of the respective low-permeability sequence. In the
base cases, the asymmetry is explained by different evolutions of the embedding aquifers. In alternative scenarios, the asymmetry can also be well reproduced by considering identical evolutions for both aquifers but adding some degree of downward advection. At Mont Terri, the palaeo-hydrogeological scenario that underlies this case is in contradiction to independent information on the erosion history. Due to the more limited knowledge of the palaeo-hydrogeological evolution at Tournemire, such a discrimination is not possible at this site.

Table 7.9-1: Bounding values of vertical advection velocities and Peclet numbers for all study sites

<table>
<thead>
<tr>
<th>Site</th>
<th>Tracer</th>
<th>Flow porosity [-]</th>
<th>Input parameters</th>
<th>Current hydraulic state</th>
<th>Results of model calculations: Bounding values</th>
<th>Current hydraulic state</th>
</tr>
</thead>
<tbody>
<tr>
<td>Callovo-Oxfordian at the Bure URL site</td>
<td>Cl</td>
<td>0.09</td>
<td>3E-13</td>
<td>5.6E-11</td>
<td>256</td>
<td>0.05 0.8 5.6E-12 -5.6E-13 1.6 -0.2 2.5 – 26</td>
</tr>
<tr>
<td>Couche Silteuse at Marcoule, MAR203</td>
<td>Cl</td>
<td>0.049</td>
<td>1E-13 (2)</td>
<td>4.4E-11</td>
<td>404</td>
<td>0 0 5.5E-13 -1.1E-12 0.3 -0.5 5 – 10</td>
</tr>
<tr>
<td>Opalinus Clay at Benken</td>
<td>δ¹⁸O, δ²H</td>
<td>0.12</td>
<td>2E-14</td>
<td>5.3E-11</td>
<td>312.1</td>
<td>-0.2 0.2 8.3E-13 -6.7E-12 5 -40 3 – 25</td>
</tr>
<tr>
<td>Opalinus Clay at Mont Terri</td>
<td>Cl</td>
<td>0.096</td>
<td>5E-14</td>
<td>4.8E-11</td>
<td>231.8</td>
<td>small small 4E-13 -4E-13 0.8 -0.6 1.5 – 2</td>
</tr>
<tr>
<td>Opalinus Clay at Mont Russelin</td>
<td>Cl</td>
<td>0.096</td>
<td>5E-14</td>
<td>4.8E-11</td>
<td>&gt;222(3)</td>
<td>n.a. n.a. 5.2E-13 -1E-12 1 -2 &gt;3(3)</td>
</tr>
<tr>
<td>Toarcian-Domerian at Tournemire</td>
<td>Cl</td>
<td>0.026</td>
<td>1E-12(6)</td>
<td>2.5E-11</td>
<td>257.4</td>
<td>0.5 204 No results due to ambiguities in model scenarios</td>
</tr>
<tr>
<td>Boom Clay at Mol</td>
<td>Cl</td>
<td>0.16</td>
<td>2.4E-12</td>
<td>1.7E-10</td>
<td>102.6</td>
<td>0.02 0.18 No results due to flat profile</td>
</tr>
<tr>
<td>Boom Clay at Essen</td>
<td>Cl</td>
<td>0.25</td>
<td>5.8E-12</td>
<td>2.5E-10</td>
<td>127.1</td>
<td>0 0 4E-12 -5E-13 0.2 -0.02 0.4 – 3</td>
</tr>
<tr>
<td>London Clay at Bradwell</td>
<td>Cl</td>
<td>0.24</td>
<td>6.5E-12</td>
<td>4.3E-10</td>
<td>45.6</td>
<td>0.1 0.3 2.3E-11 -4.5E-11 0.9 -1.7 3 – 6</td>
</tr>
</tbody>
</table>

Flow porosities and pore-diffusion coefficients are thickness-weighted arithmetic means of layer-specific values and relate to the chosen tracer. If not specified otherwise, hydraulic conductivities are thickness-weighted harmonic means of layer-specific values. Positive hydraulic gradients and advection velocities relate to downward flow, and vice versa. Note that the calculated gradients assume the validity of Darcy’s law, which is not necessarily the case (see Section 4.3.1).

(1) Calculated using the site-specific correction of Dp for in-situ temperature; rounded values
(2) Estimation based on range of K (parallel to bedding) of 1.8E-13 – 1.6E-12 m/s
(3) Minimum values because the location of the lower boundary of the low-permeability sequence is not known
(4) Estimation based on range of K (parallel to bedding) of 1E-13 – 1E-11 m/s
In all calculations that consider vertical advection, it is assumed that water flow occurs constantly over the entire evolution time of the calculated profiles. It was concluded above that even small fluxes are unlikely because such scenarios contradict the observations and because the hydraulic gradients over the low-permeability sequences that would be needed for such fluxes are typically higher than what is observed today or what can be expected in general for the hydrogeological settings of the studied sites. However, there remains the possibility of transient episodes of fluid flow in which advection operates over a limited period of time. Such events would probably be localised in specific structures, such as faults, and would correlate with tectonic events. Because only a limited volume of pore water adjacent to the flow zones would be affected by such events, subsequent diffusion would obliterate the transient signal. Whether such transient flow events have occurred at the study sites in the past, or whether they may occur in future, is therefore a question to be addressed by studies of tectonics, structural geology and mineralogy.

7.10 Comparing results and insights gained from different sites

- The clay-rich formations discussed in this report cover a wide range of induration. Boom Clay and London Clay have always remained in superficial positions, whereas, at the other end of the spectrum, the Toarcian-Domerian at Tournemire was buried several kilometres deep before being uplifted again. These different geodynamic evolutions led to highly contrasting properties, as discussed in Chapter 3. In particular, transport parameters such as porosities, diffusion coefficients and hydraulic conductivities strongly depend on the degree of induration. In contrast, the mineralogical variability appears to be less important from the perspective of conservative-tracer transport.

- Higher diffusion coefficients and permeabilities in weakly indurated clay rocks result in shorter propagation times of external perturbations (i.e. changed tracer concentrations at the boundary). This means that the memory of such rocks to the palaeo-hydrogeological evolution is shorter when compared to indurated shales where propagation times are much longer. This fundamental difference becomes evident in the model calculations: Boom Clay records the evolution since emergence at 1.7 – 2 Ma, and all older signals are obliterated. In London Clay, the memory is even shorter (tens of ka), but here the limited formation thickness L also plays a role (note that the propagation time is proportional to L²). The other extreme is the Toarcian-Domerian at Tournemire, in which it takes tens of Ma to reduce the original sea-water salinity to the current level.

- A lot is learned from comparisons for the cases where the same clay rock formation has been investigated at different sites, as is the case for the Opalinus Clay at Benken, Mont Terri and Mont Russelin and for the Boom Clay at Mol and Essen. The different structural settings for the former three sites have influenced how their pore waters have evolved both in their long-term evolution and in the periods since activation of adjacent aquifers in the most recent phase of hydrogeological evolution. Higher Cl- and He contents, and also more positive δ¹⁸O and δ²H values, in pore waters at Mont Russelin than at Mont Terri are probably reflecting the more limited perturbing effects of Jura folding and erosion on the pore waters at Mont Russelin than at Mont Terri.

7.11 Role of faults and other brittle structures

- The role of faults and fractures as conduits for fluid flow in clay-rich formations is a matter of current debate. Evidence exists that such structures can be seals or conduits for at least episodic fluid flow. A general discussion is provided by Dewhurst et al. (1999b).
With the exception of Opalinus Clay at Mont Terri and Mont Russelin, all sites considered are located in near-horizontally bedded basins. Boom Clay at Mol and Essen, London Clay at Bradwell, the Callovo-Oxfordian at Bure and Opalinus Clay at Benken are essentially devoid of brittle discontinuities and so not suited to explore their hydraulic and geochemical effects.

The Couche Silteuse in boreholes MAR402 and MAR501 contains fractures and faults, but there is no evident correlation with variations of tracer contents. Admittedly, the tracer-data base in these boreholes is limited.

The Toarcian-Domerian at Tournemire is highly indurated and fractured. On a large scale, there is no clear link between tracer concentrations and brittle structures. On a scale of up to 1 metre, local disturbances were identified, even though it is not evident to what extent these anomalies can be related to the disturbance created by the construction of the tunnel. It was shown above that enhanced hydraulic conductivities measured in borehole tests are not applicable on the scale of the formation, probably due to limited connectivity on a large scale.

The tracer profiles for Cl -, $^{18}$O, $^2$H and He across Opalinus Clay at Mont Terri cross the Main Fault, a ca. 1 m thick thrust containing abundant crushed fault rock, but there are no anomalies in tracer contents that could be related to this fault (Figure 2.4-4, Figure 2.4-5). Together with the known hydraulic insignificance of this fault, it is concluded that the transport properties of this fault are not markedly different from those of the rock matrix, and that this has been so for extended periods of time in the past.

In the Mont Russelin anticline, the tunnel runs subparallel to a major thrust fault for about 100 m. This fault correlates with marked negative anomalies of $^{18}$O, $^2$H and He, whereas Cl- shows no signal. Model calculations indicate that the age of the disturbance would be tens of ka, but there is no supporting evidence for deformation and fluid-flow processes at such recent times. Alternatively, the anomalies could be related to a disturbance due to tunnel construction (all data originate from 4 m deep boreholes drilled through the tunnel lining). In either case, the underlying mechanisms and scenarios remain hypothetical at the present stage and would require a dedicated study, including the collection of new data.

In summary: Five study sites are essentially unfractured, whereas four contain various types of brittle structures. In the latter, contents of pore-water tracers are not disturbed by the discontinuities. The only exception is a major fault at Mont Russelin, whose evolution is currently not well understood.

### 7.12 Recommendations for future investigations and open questions

#### 7.12.1 Planning of field campaigns

*A priori*, the depth locations of water-conducting horizons that can be taken as the boundaries of the low-permeability sequence (*e.g.* porous horizons within limestone units) are not known before drilling a new borehole. Due to lateral heterogeneity, it may also be difficult to extrapolate the information from an existing borehole to the new one. This means that core sampling for pore-water studies will inevitably take place at times when the system geometry, in particular the extent of the low-permeability sequence, is not yet known. Therefore, it is advisable to take samples not only from the clay-rich formation itself but also from the embedding units. In several cases considered in this report, limestones and other lithologies are also part of the low-permeability sequence and embed the clay-rich unit. Due to their proximity to the boundaries, these units may have the highest geochemical
gradients in pore water. Not sampling these would mean a major loss of information about solute transport.

- The data needed for a quantitative interpretation of tracer profiles are discussed throughout this report and are summarised in Appendix A1, which can be used as a checklist.

- Sampling for pore-water studies requires special core-protection measures. Proper communication with the field sampling team is necessary, ideally including having a dry run of procedures prior to borehole drilling.

- Multi-tracer studies allow a better constrained interpretation compared to that based on a single tracer. Which tracer turns out to be best suited for interpretation is not clear a priori, and complementary information can be obtained from other tracers.

- The modelled evolution times for the tracers in this report varied widely (Table 7.1-1), with the majority in the range of a few Ma. Hendry et al. (2000) successfully applied $^{36}$C to provide insight into systems with residence times of up to 2 Ma in Cretaceous clays. Thus, $^{36}$Cl (half life = 0.3 Ma) could be used in future studies at sites where Cl$^{-}$ migration into the low-permeability sequence occurred within the last 1.5 – 2 Ma, provided $^{36}$C is measurable in pore waters of clays and shales.

- Boron and boron isotopes have been successfully used to distinguish between marine and non-marine fluid sources (e.g. Vengosh & Hendry 2001) and could be used as additional constraints in future studies.

- In the case of Holocene-aged profiles in near surface clay aquitards, $^{14}$C$_{DIC}$ and $^{14}$C$_{DOC}$ (half life of $^{14}$C = 5730 a) have proven successful in defining residence times (Wassenaar & Hendry 2000, Hendry & Wassenaar 2005). Holocene effects on pore waters are evident in the $\delta^{18}$O and $\delta^{2}$H values in Boom Clay at Essen (Section 5.8.2), London Clay at Bradwell (Section 5.9.2) and, less clearly, in the Toarcian-Domerian at Tournemire (Section 5.6.2).

- Analytical procedures for the tracers, including sample processing to extract water, solutes or gases, require specialist laboratory facilities and expertise. Procedures that have been used to collect the data considered in this report include mainly leaching of solutes, squeezing of pore waters with a purpose-designed extraction cell in a high-load rig, diffusional exchange of water followed by isotope ratio mass spectrometry, and vacuum extraction of gases into a mass spectrometer. In addition, great care is necessary, as is evident from the discussions here of sources of error, to specify appropriate measurements of supporting parameters such as water-content porosities and diffusion coefficients.

- The sampling strategy needs to be defined well before drilling starts, based on predicted lithological and hydrogeological profiles of the site. A list of planned samples needs to be prepared and can be adapted in case the real situation differs from the prediction. All tracers should be studied on immediately-adjacent sample materials from homogeneous sections of the core. Water-loss porosity and mineralogical compositions should also be analysed on each sample. Denser sampling is recommended in zones where higher chemical gradients are expected.

- In case successive field campaigns are conducted in the same area, it is advisable to compile the lessons learned from previous campaigns and to integrate them in the planning process.

- Due to lateral heterogeneity, pore-water studies on core materials and ground-water sampling should be made on samples from the same borehole. Combining pore- and ground-water data from different boreholes should be avoided wherever possible.
The data base on the hydraulic and geochemical significance of faults in shales is currently very limited. It would be worthwhile to conduct pore-water studies targeted at the influence of faults and fractures, e.g. by sampling at very closely-spaced intervals (dm-scale) away from the fault or fracture.

In situations where one or both embedding aquifers contain a young meteoric component, the effect of Holocene warming on the stable-isotope composition of pore water in the low-permeability sequence could be studied in detail. This would require a dense sampling (one sample every 1 – 2 m) of the core adjacent to the aquifer.

7.12.2 Missing data

To understand the evolution of pore water in clay rocks, a large number of data and system characteristics need to be constrained. Some gaps in our knowledge may remain even when major efforts are invested, e.g. when it comes to better understand palaeo-hydrogeology. The fact remains that the waters that affected the system in the past are no longer in place, and so their evolution can only be reconstructed indirectly. The following bullets list data that are frequently missing but, in principle, could be realistically obtained and would reduce the uncertainty of the interpretation of pore-water evolution.

- In many of the investigation programmes, transport parameters (porosities, diffusion coefficients, hydraulic conductivity) and tracer contents in pore water have been thoroughly characterised for each clay-rich formation. However, the low-permeability sequences frequently contain other lithologies, such as limestones (e.g. Callovo-Oxfordian at Bure, Opalinus Clay at all 3 locations). In some cases, tracer data in these units are scarce or absent, and the formation properties are not well known. As stated above, it should be borne in mind that a low-permeability sequence may contain a number of lithologies adjacent to the clay rock, and that its extent is not precisely known before drilling a borehole.

- Noble gases are potentially useful pore-water tracers. Whereas in-situ production and release from the rock to pore water can be constrained, only few data exist on diffusion coefficients in clays and shales. Therefore, these need to be estimated either from the atomic masses or from the ratios of noble-gas to water diffusion coefficients in pure water. Rock-specific measurements, even though not trivial to perform, would be beneficial.

7.12.3 Concepts that need further development

- Anion-accessible (or "geochemical") porosity in shales is smaller than physical porosity (the water-filled space between minerals) because, in regions close to negatively charged clay-mineral surfaces, access for anions is restricted. The fraction of porosity that is accessible to anions has been determined based on macroscopic evidence (e.g. by comparison of Cl- contents determined by leaching and by squeezing). However, these determinations are purely empirical and subject to uncertainties. The dependence on pore-water salinity and on mineralogy (namely the clay-mineral content) is not known. Most geochemical models consider one single value for porosity in a specific media and so do not take into account the complexity of the microscopic pore-space distribution. An improved understanding of the mobility of ions in the pore space of clays and shales on a microscopic scale would be a logical step forward and could also lead to a more realistic representation of porosities in geochemical and transport models.

- Once the understanding of porosities is improved, these should also be implemented in **geochemical and transport codes**. At the present stage, codes typically consider one single
value of porosity, irrespective of the nature of the solute (neutral species such as water vs cation vs anion) and the process (e.g. diffusion-accessible vs flow porosity).

- Some off-diagonal Onsager processes, such as osmosis and ultrafiltration, have been invoked to explain certain macroscopic features of clay and shales, such as hydraulic overpressures. However, the experimental basis to quantify the membrane properties, such as osmotic efficiency, was very limited. In recent times, the basis has been enriched for deep clay and shale formations by several in-situ works in Opalinus Clay (Noy et al. 2004), in Boom Clay (Garavito 2006, Garavito et al. 2007) and in the Callovo-Oxfordian shale (Gueutin et al. 2007, Rousseau-Gueutin et al. 2007).

- Diffusion coefficients measured in the laboratory are mostly tracer-diffusion coefficients, i.e. values for ions that are present in solution in trace amounts and so are not affected by charge-balance constraints. An example is the measurement of the diffusion coefficient for Cl using a radioactive isotope (36Cl) – even though there is much more Cl in the artificial pore water, the measurement refers only to the mobility of the radioactive isotope that is present in trace amounts. In the natural system, the relevant parameter is the salt-diffusion coefficient, which refers to the transport of bulk Cl and the co-diffusion of its positively charged counter-ion, typically Na+. Because the Na+-accessible porosity is larger than anion-accessible porosity (cations are not repelled at clay surfaces and can enter even the interlayer space of swelling clays), its diffusion coefficient is typically larger than that for Cl. On the other hand, Na+ transport could be retarded by sorption on clay surfaces, depending on the mineralogical composition.

- In many cases, the diffusion coefficient for anions is measured for I and assumed to be valid for all other anions (Cl, Br) as well. Even though major and systematic differences between the values for these species have not been identified, the adequacy of this extrapolation is yet to be shown.

- Transport of Br and I can be potentially retarded by sorption, e.g. on organics. The degree to which this actually happens is not well known because it is difficult to experimentally identify the effects of weak sorption. Sorption of I is described for the Callovo-Oxfordian at Bure but considered to be irrelevant in the Boom Clay at Mol.

- The validity of Darcy’s law in low-permeability rocks is not established for natural hydraulic gradients. In laboratory and in-situ experiments, gradients are typically >1 000 m/m, in order to obtain measurable responses over short time scales. The natural situation, where gradients are <10, if not <1 m/m, has not been tested experimentally. Because a substantial part of the pore water is more or less strongly bound to clay-mineral surfaces, it is conceivable that a certain activation energy may be required to mobilise the water molecules. In such a case, no flow may take place below a certain threshold gradient, the value of which depends on the pore structure of the argillaceous media. The well established overpressure in the Callovo-Oxfordian at Bure is currently explained as an effect of the osmotic potential of this formation, but this hypothesis is not well established due to the limited knowledge on the osmotic efficiency of the media. An alternative explanation would be that the overpressures were "frozen in" at the point when the hydraulic gradient fell below the threshold.

- The otherwise well-defined term "flow porosity" requires closer attention in clays and shales. It was argued above that, similar to the porosity that governs diffusion, there is a dependence on the species whose transport is considered. Flow porosity may also change with hydraulic gradient and fall to zero below the threshold gradient mentioned above. In geochemical and transport models, these features are typically not taken into account.
Constraints on several of the previous points could be obtained by an improved understanding of the **microscopic pore structure**. Current information on the pore structure in clay and shales is only indirect (Hg injection, ad-/desorption isotherms, *etc.*). With the advent of new microscopic techniques, such as focussed ion-beam (FIB) nano-tomography, high-resolution transmission electron microscopy (TEM) and related techniques (including cryogenic systems to preserve the natural water content), more direct geometric information is becoming available at the pore scale of clays and shales. These techniques can potentially visualise at least the larger pores in shales directly, as shown in Figure 7.12-1 and Figure 7.12-2.

Knowledge on the **systematics of δ$^{37}$Cl** in sedimentary formations is currently incomplete. On the one hand, the ratio of the diffusion coefficients for $^{35}$Cl and $^{37}$Cl is not well constrained but important for the quantitative interpretation of $\delta^{37}$Cl profiles. On the other hand, the processes that lead to isotope fractionation during long-term evolution of relatively deep crustal fluids are not completely understood. For example, the wide range of $\delta^{37}$Cl values observed in brines is difficult to explain by physical fractionation by diffusion alone, and it may be necessary to consider fractionation with Cl in minerals.

In most cases, anions are considered to behave in a conservative way, *i.e.* water-rock interaction is considered unimportant. On the other hand, the nature of the **anion reservoirs in the shale/pore-water system** is not well characterised. At Tournemire, it was found that the solid rock contains much more Cl than its pore water, and that not all Cl in the rock is bound in apatite. As long as the sites where Cl occurs in the solid rock are not known, there are uncertainties regarding the reactivity of Cl in the rock over geological time scales.

Finally, a more explicit **link between the scientific conclusions based on tracer profiles and aspects related to performance assessment and to the safety case methodology of deep geological repositories for radioactive waste** (*e.g.* the GEOTRAP and AMIGO projects, see NEA 2002, 2004, 2007) is yet to be established. Practical examples of topics to be addressed include scale issues, understanding of long-term transport processes, timing of aquifer activation and geochemical stability. In a more general context, the contribution of tracer-profile studies to the following steps common to most safety cases would deserve a closer evaluation:

- Phenomenological analysis, overall process understanding and interactions between processes
- Identification of uncertainties and limitations
- Impact of uncertainties on the qualitative and quantitative system analysis and on safety
- Completeness check
- Quantitative evaluation of performance (assessment cases)
- Synthesis and overall confidence in the results.
Figure 7.12-1: Scanning electron microscope images showing the preparation of a ca. 100 nm thick lamella of Opalinus Clay using a focussed ion beam (FIB)

Left: Side view; right: view from top. Courtesy of L. Holzer, EMPA, Switzerland

Figure 7.12-2: Transmission electron microscope image across a ca. 100 nm thick lamella of Opalinus Clay

A: Macropore between clay-mineral aggregates; B: Nanopores within clay-mineral aggregates. Courtesy of L. Holzer, EMPA, Switzerland
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Waber, H.N., 2005. Laboratoire de recherche souterrain Meuse/Haute Marne – $\delta^{18}$O, $\delta^{2}H$ and Cl in pore water of the Callovo-Oxfordian and surrounding rock formations. Nagra Arbeitsbericht NAB 05-02, Nagra, Wettingen, Switzerland.


METHODOLOGY OF DATA COLLECTION: EXAMPLE OF A DATA TRACKING DOCUMENT

An example of a Data Tracking Document is shown below for borehole MAR203 at Gard/Marcoule, France. The empty forms were sent to the organisations who supplied information on their site(s) and also used the forms as checklists and general guides to what is needed. The Core Group then evaluated all information received and filled in the Data Tracking Document for each site (areas shaded grey in the example below). For each item, the name of the underlying electronic document was noted (if applicable), together with the references to sources of the information. Very importantly, screening procedures and all changes done to the data were recorded, together with comments.

In the next step, the completed draft Data Tracking Document was sent back to the data suppliers for review. Once this process was finalised, the document was used as the basis for a formal data release and freeze, in which the data suppliers confirmed their agreement to the selection and screening of the relevant data. Only once this procedure was finalised, evaluation and modelling work was initiated.

CLAYTRAC Data Tracking Document: Gard MAR203 (Marcoule, France)

Author: Martin Mazurek
Date of last changes: 11. 7. 06

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| 1    | Anion contents (Cl, $\delta^{37}$Cl, Br, I) in pore water | MAR 203.dat | Reeder et al. 1997a, Reeder et al. 1999, Eggenkamp & Coleman (1998), Andra report CRP O UNR 98-01 (leaching data: Cl, Br, $\delta^{37}$Cl), Andra 1998c. Andra report D RP O ANT 97-068. (water sampling at 770 m) | • Cl and Br contents based on leaching were multiplied by a factor 2.5 to account for anion exclusion. The factor was derived from the comparison between contents based on leaching and squeezing.  
• Eggenkamp et al. Cl, Br data: Recalculation from mg/kg rock to mg/L pore water done differently than in the original report, using more realistic porosity values. Results are significantly different. | • Very nice profiles for Cl, Br with highest contents slightly higher than in sea water  
• I profile unclear - ignore due to limited amount of data  
• Regular profile of Cl/Br but with different shape - plateau with a value 400-500 in the centre, lower close to rims  
• Complex $\delta^{37}$Cl profile; water sample at 770 m fits well into leaching data |
<table>
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<td>3</td>
<td>Noble gas contents (He, $^3$He/$^4$He, Ar, $^{40}$Ar/$^{36}$Ar) in pore water</td>
<td></td>
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</table>
| 4    | Anion contents (Cl, $^37$Cl, Br, I) in the upper and lower aquifers (boundary condition) | MAR 203.dat | Andra 1998c (ground-water samples), Eggenkamp & Coleman (1998), Andra report CRP O UNR 98-01 (leaching data: Cl, Br, $^37$Cl) | none - no scaling for anion exclusion | • Values used for modelling - upper aquifer: Cl $= 102.5$ mg/L, Br $= 0.67$ mg/L (ground-water sample)  
• Values used for modelling - lower aquifer: Cl $= 167.5$ mg/L, Br $= 0.58$ mg/L (ground-water sample)  
• Consistently low anion concentrations compared to the Couche Silteuse  
• Ground waters were pumped from somewhat long packer intervals  
• Cl isotopes based on leaching and water samples are inconsistent, the overall pattern is inconclusive. Eggenkamp & Coleman and Aranyossy et al. 1999 ignore the ground-water samples. |
| 5    | Isotope data ($\delta^{18}$O, $\delta^2$H) in the upper and lower aquifers (boundary condition) |  | no data | no data | |
| 6    | Noble gas contents (He, $^3$He/$^4$He, Ar, $^{40}$Ar/$^{36}$Ar) in the upper and lower aquifers (boundary condition) |  | no data | no data | |
| 7    | Definition of the bulk geometry |  | Andra (1998a, Fig. 6.1-1 to 6.1-3) | Couche Silteuse: 377 - 781 m, sandwiched between thick sandstone units | |
| 8    | Definition of lithological sub-units of the low-permeability formation(s) between the aquifers |  | Andra (1998a, Fig. 6.1-1 to 6.1-3) | Unité sup. alternante: 377 - 484 m  
Unité médiane homogène: 484 - 700 m  
Unité inf. laminée: 700 - 781 m | |
| 9    | Structural discontinuities (fracture zones, faults) |  | Andra (1998a, ch. 5.4.2.3) | Essentially no tectonic features except two fractures at 570 and 593 m | |
| 10   | Pore or effective diffusion coefficient for anions (Cl, I, Br) |  | Data of Vitart et al. (1999) are screened out | Data of Vitart et al. (1999) are very scarce and yield surprisingly low, if not inconsistent values. Experimental conditions are not documented. These data are not considered here. Instead, De(anions) is calculated from De(HTO), dividing the latter by 4 (average for other shale formations). Thus:  
De (anions) Unité sup. alternante: 3.58E-12 m²/s  
De (I) Unité médiane homogène: 1.90E-12 m²/s  
De (I) Unité inf. laminée: 1.33E-12 m²/s  
• It is unclear if the data are parallel or normal to bedding  
• Porosity values and therefore Dp calculated from De should not be used - Vitart’s lab does not correct for artefacts (Mont Terri experience) | |
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<td></td>
<td>Pore or effective diffusion coefficient for water (often measured by $^3$H diffusion experiments)</td>
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<td>Vitart et al. 1999</td>
<td>De (HTO) Unité sup. alternante: 1.43E-11 m$^2$/s De (HTO) Unité médiane homogène: 0.76E-11 m$^2$/s De (HTO) Unité inf. laminée: 0.53E-11 m$^2$/s • It is unclear if the data are parallel or normal to bedding • Porosity values and therefore Dp calculated from De should not be used - Vitart’s lab does not correct for artefacts (Mont Terri experience)</td>
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<td>Pore or effective diffusion coefficient for He</td>
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<td>Salinity of pore water</td>
<td>Andra (1998c)</td>
<td>Squeezing and leaching data: Na-Cl water, slightly above present sea-water salinity in the centre, trending towards very low salinity along the contacts to other aquifers</td>
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<td>Hydraulic conductivity</td>
<td>Andra (1998b. p. 53-54)</td>
<td>• $K_h = 1.6E-12 - 1.8E-13$ m/s for the whole Couche Silteuse; the coverage by packer tests is not complete • 756.0 - 756.8 m: sandstone bed with $K_h = 2E-8 - 2E-9$ m/s • $K_v$ measured on core samples in the lab: 1 - 4E-14 m/s</td>
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<td></td>
<td>&quot;Total&quot; porosity (derived e.g. from density or water-content measurements, or from diffusion experiments)</td>
<td>Blackwell et al. (1995), Reeder et al. (1999)</td>
<td>Moisture contents (relative to dry mass) are recalculated to water-loss porosities assuming a bulk dry density of 2.5 g/cm$^3$ • Moisture contents (drying to 110 °C) referring to dry mass reported • Substantial decrease of porosity with depth, roughly correlating with a decrease of clay content Unité sup. alternante: mean 0.181 Unité médiane homogène: mean 0.106 Unité inf. laminée: mean 0.093 • There are other sources for porosity but they are either not trustworthy or not well documented (e.g. Andra 1998a, Figs. 6.2-9 to 6.2-11; Gard book, p. 193)</td>
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<td>Fraction of &quot;total&quot; porosity accessible to anions</td>
<td>Reeder et al. (1997a)</td>
<td>The comparison of leaching and squeezing data from borehole MAR203 indicates a fraction of 40% of total porosity that is accessible to anions</td>
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<td>U and Th contents of the rocks</td>
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<td>No data available and, in the absence of He data, not needed</td>
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<td></td>
<td>In-situ temperature</td>
<td>Mouroux &amp; Brulhet (1999)</td>
<td>• 21.9 °C (top CSM) - 35.2 °C (base CSM); mean 29.6 °C</td>
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<td>Hydraulic pressure in upper and lower aquifers</td>
<td>Andra (1998b, p. 61)</td>
<td>The overlying Cenomanian aquifer has a head of 45 m NGF all over the Marcoule area. The underlying Albian sandstones in MAR203 also have 45 m, resulting in a zero gradient across the Couche Silteuse.</td>
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<td>20</td>
<td>Palaeo-hydrogeologic evolution of the low-permeability formation</td>
<td></td>
<td>Andra (1998a,b)</td>
<td>• Complex evolution with many unknowns. Area close to coast line over geological periods of time, thus several switches between marine and continental conditions. Base case scenario: - 100 - 50 Ma: Marine conditions, undeformed beds - 50 - 5.8 Ma: Predominantly continental; very little sedimentation; Pyrenean deformation at 50 Ma -&gt; erosion of anticlines begins. - 5.8 - 5.35 Ma: Incision of canyons during Messinian crisis, continental - 5.35 - 3.0 Ma: Transgression, canyons are marine but flats remain continental - 3.0 Ma - present: Continental</td>
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<tr>
<td>21</td>
<td>Evolution of boundaries over time</td>
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<td></td>
<td>see 20</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>Erosion / exhumation history</td>
<td></td>
<td></td>
<td>see 20</td>
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</tr>
<tr>
<td>23</td>
<td>Tectonic evolution</td>
<td></td>
<td></td>
<td>see 20. MAR203 is located on the crest of an open anticline</td>
<td></td>
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Appendix A2

EXPERIMENTAL TECHNIQUES AND ANALYTICAL METHODS TO CHARACTERISE TRACER CONTENTS IN ARGILLACEOUS FORMATIONS

A2.1 Introduction

The mass of pore water present in an argillaceous rock formation is significant and varies between a few % to several tens of % depending on the geologic history of the formation. Due to the low permeability of argillaceous formations, pore water cannot be sampled by conventional groundwater sampling techniques. Thus, information about tracer concentrations in pore water can only be obtained by applying indirect extraction techniques based on fresh, saturated rock material, or directly by long-term and cost-intensive in-situ experiments in underground facilities. Indirect techniques are described in Sections A2.4 to A2.9, and direct techniques follow in Section A2.10.

Many of the indirect techniques commonly yield only partial information pertinent to solute concentrations, isotope ratios or gas contents and so have to be applied in a complementary way in order to obtain a more comprehensive characterisation of the pore water. Several indirect extraction techniques have in common that they deliver solute concentrations per mass of rock, and these have to be converted to concentrations per mass of pore water. This requires knowledge of the porosity that is accessible to the tracer of interest under in-situ conditions. The determination of the tracer-specific porosity in argillaceous (and other) rocks is one of the key issues, and a number of perturbing effects (stress release, desaturation, mineral reactions, etc.) need to be considered. The potential of such perturbations differs from location to location and depends on mineralogy, geological evolution and diagenesis, and the local tectonic setting. Established protocols for the extraction of different tracers and their corresponding porosities under in-situ conditions need to be evaluated and possibly modified for each new locality where pore-water investigations are planned.

Over the past two decades, various indirect extraction techniques for chemically conservative compounds in the pore water have been tested and continuously improved. Sacchi & Michelot (2000) and Sacchi et al. (2001) give a comprehensive general review about various extraction techniques, and Pearson et al. (2003) report more specifically on techniques applied for Opalinus Clay in Switzerland. This Appendix gives an update on existing and newly developed techniques for pore-water extraction since the comprehensive review by Sacchi & Michelot (2000). This update does not aim at completeness but is focussed on those extraction techniques by which the tracer data evaluated in this report were obtained. It serves as a basis for the evaluation of the pore-water data, their screening and for the justification of correction schemes aimed at obtaining information representative of in-situ conditions.
A2.2 Concepts and terminology of porosity and pore fluids in argillaceous rocks

Different types of porosity measurements characterise different parts of the pore space of an argillaceous rock, and the accessible porosity in a clay or shale is also solute-specific. For all indirect techniques of pore-water characterisation, appropriate porosities are needed for the recalculation of \textit{in-situ} solute concentrations. The terminology used here is based on reviews by Horseman \textit{et al.} (1996), Pearson (1999), Pearson \textit{et al.} (2003) and Nagra (2002).

The \textbf{physical or total porosity} of a rock describes the total pore space in a rock that is defined by the ratio of void volume to the total volume of the rock and can be calculated from the bulk density of a dry sample and its grain density (Norton & Knapp 1977). The physical porosity includes the volume not occupied by mineral grains, such as pore spaces between mineral grains, dead-end pores, microfractures, porous minerals (\textit{e.g.} altered or secondary minerals) and fluid inclusions.

The \textbf{connected porosity} of a rock describes the volume of connected pore space and is smaller than or equal to physical porosity. In argillaceous rocks, it is most commonly based on weight-loss measurements of a sample due to drying at a specific temperature until stable weight conditions are reached. This method requires the availability of fresh, saturated drillcore samples that were processed using protocols to minimise artefacts (see below). More recently, the water content of rocks has also been determined using isotope mass-balance relationships with data obtained by the vacuum distillation technique (\textit{e.g.} Moreau-Le Golvan \textit{et al.} 1997, Rübel & Sonntag 2000), by the radial diffusion method (Van der Kamp \textit{et al.} 1996) and by the isotope diffusive-exchange technique for water isotopes (Rogge 1997, Rübel \textit{et al.} 2002). Each of these techniques has its uncertainties due to a number of possible artefacts. Most favourably, different techniques are applied to the same rock sample. For the dilute pore water of the Toarcian-Domerian at Tournemire, it was shown that water contents obtained from vacuum distillation at 50 °C are significantly lower than those obtained by vacuum distillation or heating at 105 and 150 °C. The highest water contents were obtained from the diffusive-exchange technique for water isotopes (Altinier \textit{et al.} 2007).

The \textbf{flow porosity} relates the Darcy flux to the linear velocity of a tracer in a rock environment where advective flow and transport prevail (Pearson 1999). As discussed in Section 4.3.5, its magnitude also depends on the substance whose transport is considered. Flow porosity is smaller than physical porosity, or equal to physical porosity in cases where the contribution of fluid inclusions is negligible and the pore network is fully connected.

The \textbf{diffusion porosity} can be measured by various types of in-, out- and through-diffusion experiments and is specific to the solute by which it was determined. For water, the magnitude of diffusion porosity is typically similar to that of connected porosity determined by weight loss at 105 °C (or even slightly higher because heating at 105 °C does not liberate all pore water). Diffusion porosity of anions in argillaceous media is smaller than that of water and cations (by a factor 2 – 3 in the formations studied here, see Table 3.2-1) due to anion exclusion effects.

The term \textit{“geochemical porosity”} as defined by Pearson (1999) for low-permeable argillaceous rocks describes the fraction of physical porosity in which a specific solute occurs. This fraction is well below 1 for anions, such as Cl$^-$ or Br$. By its definition, geochemical porosity is essentially identical to diffusion porosity.

The term \textit{“pore water”} as used here refers to the water in the connected pore space of the rock matrix in which transport, \textit{e.g.} via diffusion or advection, can occur. It includes bound water on external surfaces as well as interlayer water of swelling clay minerals. In the argillaceous rocks studied here, pore water is the dominating fluid and salinity reservoir, and potential other reservoirs, such as
disconnected pores and fluid inclusions in detrital and diagenetic minerals, are generally negligible. Nevertheless, care must be taken to identify the relative sizes of fluid and salinity reservoirs in every formation that is investigated by destructive techniques, such as aqueous leaching. In principle, low-salinity pore water could be contaminated if highly saline fluid inclusions are liberated during crushing. Indications in this direction have been found in the highly compacted shales at Tournemire and in limestone units within the low-permeability sequence at Bure, *i.e.* lithologies with relatively low porosities. At both sites, the pore water has a low salinity and is therefore particularly sensitive to contamination from fluid inclusions.

### A2.3 Sample treatment for indirect pore-water extraction techniques

Reliable data about natural tracer concentrations in pore water of low-permeability rocks can only be obtained from drillcore material of newly drilled boreholes. The adequacy of pore-water data generated from such material by indirect extraction techniques relies on the preservation of the *in-situ* conditions in the rock sample, in particular on the minimisation of induced chemical reactions between minerals, pore water and atmosphere. The preservation of full saturation is a key element because only in saturated samples the gravimetric water content can be measured, which in turn provides the basis for calculating porosity that is needed for the recalculation of measured data to concentrations in pore water. Moreover, desaturation is also linked to a chemical disturbance that may lead to precipitation of dissolved salts. The need to preserve saturation calls for a sophisticated treatment and handling of the samples on site and in the laboratory, as well as a good co-ordination between the personnel on the drill site and in the laboratory – even when considering only chemically conservative pore-water constituents.

The on-site treatment of drillcore samples foreseen for pore-water investigations is similar for most indirect methods except for noble gases. Contact times of the fresh core with the atmosphere should be minimised to minutes wherever possible. To preserve saturation, the sample is immediately wiped clean with a dry towel, wrapped into a heavy-duty, transparent PVC bag, which is repeatedly flushed with nitrogen or argon, then evacuated and heat-sealed. At this stage, the field geologist can immediately perform core logging and macroscopic sample description. Then the packing procedure is repeated with a second PVC bag, and finally with a bag made of plastic coated Al foil. Alternatively, two plastic coated Al foils with the same procedure may serve the same purpose, in case core logging is not foreseen. Once tightly packed, the core should be stored cool, shipped to the laboratory and processed for the various measurements and extraction techniques within days.

The unavoidable impact of air exposure on the fresh drill core depends on core diameter, on characteristics of the material (*e.g.* hydraulic conductivity, diffusion coefficient, porosity, air-entry value) and on the ambient climate (*e.g.* air humidity, temperature). The results of a design calculation by Gimmi (2005) targeted at the quantification of desaturation in cylindrical samples are shown in Figure A2.3-1. The chosen diffusion coefficient $D_{H_2O} = 1E-10 \text{ m}^2/\text{s}$, the hydraulic conductivity at saturation $K_s = 1E-13 \text{ m/s}$ and the porosity of 0.1 are typical values for the clay and shales studied in this report (Table 3.2-1). A desaturated zone about 0.3 cm thick develops along the rim of the sample within 12 min and penetrates to about 1 cm within 2.4 h. In the case of a drillcore radius of 2.5 cm, this means that it is difficult, if not impossible, to separate the still-saturated core of the sample from the desaturated rim after an air exposure of about 2 h, so the sample essentially lost its value for an reliable porosity determination. In the case of a core with a radius of 5 cm, more time is available. For a higher hydraulic conductivity of 1E-12 m/s, the effects are clearly more drastic (right diagram in Figure A2.3-1). It should be noted that these scoping calculations were performed assuming a homogeneous medium, but desaturation would be enhanced if natural or induced microfractures were present in the sample. Therefore, rapid sample processing on the drill site and in the laboratory,
including a minimisation of transport and storage times, is instrumental for successful pore-water tracer investigations.

In the laboratory, about 1 – 2 cm of the rim of the drillcore should be removed by hand or by dry sawing, in order to avoid the effects of desaturation and chemical contamination. The central part of the sample is then immediately processed for the planned experiments. For the determination of the water content and water-loss porosity, this includes immediate weighing of an aliquot of the saturated rock material and subsequent drying in an oven until stable weight conditions are attained. Drying may take days to weeks, depending on the characteristics of the material. For argillaceous rocks, the most commonly used drying temperature is 105 °C. The further sample preparation depends on the planned extraction technique and is described in the following sections.

Figure A2.3-1:  Design calculations for the development of an unsaturated zone in drillcores exposed to the atmosphere

Water-content profiles are shown in drillcore samples with 25 mm (red) or 50 mm (blue) radius after various exposure times (0 = centre of core). Atmospheric water potential = -100 MPa (corresponds to a relative humidity of ca. 50 % at 20 °C), air-entry value 1/a = 10 MPa, pore-size index n = 1.6; other parameters specified in text. From Gimmi (2005)

A2.4  Aqueous leaching

A2.4.1  Basic description

Aqueous leaching is the simplest destructive method for indirect pore-water characterisation based on drillcore material. It is commonly performed on crushed rock material, dried under ambient conditions or – less frequently – under an oxygen-free atmosphere (see scheme in Figure A2.4-1). During drying, the dissolved constituents in the pore water will precipitate as highly soluble salts following complex evaporation cycles. Crushing and grinding of the rock material will additionally liberate fluid trapped in mineral fluid inclusions. The mineralisation of a leach solution is thus the sum of 1) the constituents originally dissolved in the pore water, 2) the constituents present in fluid inclusions, and 3) water-rock interaction during the leaching process. In clay-rich rocks, the contribution of 1) dominates, whereas 2) is in general negligibly small, and 3) is only relevant for reactive species but not for anions that are typically studied by aqueous leaching.

Aqueous leach solution data provide information about the concentrations per mass of rock of chemically conservative (free) elements such as chloride and possibly bromide and iodide originally dissolved in the in-situ pore water. To convert these concentrations to concentrations per mass of pore
water, adequate (i.e. geochemical) porosity data of the sample need to be known. This requires, among others, the preservation of the original saturated state of the sample to derive the in-situ water content and water-loss porosity, respectively.

In principle, it is also possible to analyse older, desaturated core materials by aqueous leaching, as the anion contents are not affected by storage. However, the problem lies in the determination of porosity that is needed to relate the measured contents to concentrations per kg pore water. The most appropriate measurement, namely water loss upon drying, cannot be performed on desaturated materials, so what remains is the characterisation of porosity from bulk dry and grain densities. Namely the former may be affected by recurrent changes of ambient humidity and by chemical reactions such as pyrite oxidation. In general, the information obtained from dry core materials is of limited use in the context of understanding tracer profiles.

### A2.4.2 Experimental setup

Following arrival at the laboratory, at least 1.5 cm of the rim of the drill core sections are removed by hammer or dry sawing, in order to minimise artefacts induced by evaporation and possible drilling-fluid contamination. Saturated material from the centre of the drill core is then used for immediate determination of the gravimetric water content and for aqueous extraction. For each lithology, aqueous extraction should be performed on different grain-size fractions and on different solid:liquid ratios. Aqueous leaching is performed using water that was de-ionised in two cycles. Depending on the grain size, leaching is performed by shaking the rock material and solution end-over-end for 24 hours or longer in polypropylene tubes. Finally, the solution is separated from the rock material by centrifugation, and the supernatant solution is filtered before chemical analysis.

**Figure A2.4-1:** Schematic representation of an aqueous leaching test performed on rock material

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A2.4.3 Data and information obtained

Chemically conservative tracers, such as chloride and possibly bromide and iodide, will display a linear correlation between their concentrations per mass of rock as obtained from the leach solutions and the solid:liquid ratio used in the extractions if the pore water is their only source. Also, leach solutions of different grain-size fractions should yield equal concentrations per mass of rock for chemically conservative components. In such a case, the determined concentration per mass of rock of a leached compound can be converted to a concentration per mass of pore water using its geochemical porosity. If only water-loss porosity is available but the fraction that is accessible to anions is not known, the general shape of a tracer profile can still be characterised, even though not the absolute values.

The analytical error on the concentrations of the leach solutions is commonly less than ±5 % for most techniques. The cumulative error taking into account the heterogeneity of the rock can be obtained from the leach experiments conducted on different grain-size fractions and different solid:liquid ratios. For Opalinus Clay at Mont Terri, this cumulative error for chloride concentrations per mass of rock was estimated to be 10 – 15 % (Waber et al. 2003a). If gravimetric water-loss data are not available and porosity must be based on density measurements, the error on the chloride concentrations per kg pore water is typically dominated by the error on porosity.

A2.4.4 Possible artefacts

Possible artefacts during aqueous leaching of pore-water tracers include a chemically non-conservative behaviour of the compound of interest (e.g. iodide in organic-rich sediments) and multiple sources of the tracer during leaching. Such artefacts are indicated by a non-linear behaviour of concentrations per mass of rock when plotted against solid:liquid ratio. Leaching the rock at different grain sizes will identify different sources of a leached component, because the relative contribution of other reservoirs (such as fluid inclusions or soluble solids) is expected to vary with grain size. The conversion of solute concentration per L leach solution to concentration per kg pore water can only be performed if the solute has been shown to be conservative and to occur only in pore water. Additional artefacts might originate from an inadequate sample treatment on site or in the laboratory, e.g. incomplete removal of rim portions that are desaturated or contaminated by drilling fluid.

A2.5 Squeezing under high pressure

A2.5.1 Basic description

Pore-fluid extraction from unconsolidated and consolidated sediments by squeezing under high pressure has been successfully applied in the past (see e.g. summaries by Chiligarian et al. 1994, Reeder et al. 1998, Sacchi & Michelot 2000). To some extent, squeezing of an argillaceous rock sample is analogous to the natural process of consolidation, caused by the deposition of material during geological time, but at a greatly accelerated rate. The successful expulsion by squeezing of a pore-water volume sufficient for chemical and isotopic analysis from saturated argillaceous rocks depends primarily on the water content and the rock properties (fabric and mineralogy), the squeezing pressure applied, the squeezing time and the size of the squeezing apparatus (volume and diameter). The representativity of the analysed composition of the squeezed water for in-situ pore water depends on various factors concerning the rock sample itself (water content, mineralogy, fabric), the experimental conditions and the procedures used for squeezing (sample preservation, applied pressure, pressure history of the total squeezing procedure, atmosphere and temperature during the squeezing,
etc.). As for aqueous leaching, procedures used to preserve the core sample and to handle it in the laboratory have a key influence on reliability of the results (see, e.g., Fernandez et al. 2003).

**A2.5.2 Experimental setup**

Squeezing rigs generally comprise a compaction chamber, an automatically controlled hydraulic ram and a collection system for the squeezed water (Figure A2.5-1). Most commonly, the hydraulic ram squeezes the contents of the cell vertically upwards and the expelled pore water passes through a stainless-steel filter support at the upper end of the cell where it is collected in a polypropylene syringe after passing through a micro-filter. Depending on the design of the squeezing rig, maximum squeezing pressures of more than 500 MPa can be reached and the collection of squeezed water may occur under ambient or anaerobic conditions.

Over the last few years, squeezing tests within the framework of pore-water investigations related to low-permeability argillaceous rocks were mainly carried out at BGS, UK (max. pressure = 70 MPa), CIEMAT, Spain (200 MPa) and CRIEPI, Japan (512 MPa). Squeezing is performed on saturated rocks samples that are conditioned by dry cutting for the specific compaction chamber. Temperature and atmosphere are kept constant and the volume of the expelled water is continuously monitored. The rate of pressure increase and the pressure holding time may vary from sample to sample according to its water content and rock properties. Commonly, a few milliliters of water can be squeezed from a rock sample of about 7 – 10 cm in length and 4 – 6 cm in diameter. Fernandez et al. (2003) provide a detailed description of the individual squeezing rigs used in these studies.

Figure A2.5-1: **Squeezing apparatus used at CIEMAT for water extraction under high pressure**

From Fernandez et al. (2003)
A2.5.3 Data and information obtained

Under favourable conditions, squeezing of an argillaceous rock may yield sufficient water to perform a complete chemical analysis except pH, but including isotopic data. Generally it was observed that for rocks affected by a weak to moderate diagenetic overprint and with water contents >10 wt%, the composition of the squeezed water is comparable to that of the in-situ pore water for many components. However, even under such favourable conditions, the concentrations of the most reactive components, such as of the carbonate and sulfur systems, can be modified during squeezing, e.g. by pressure solution or oxidation. More commonly, squeezing delivers partial information about the in-situ pore water, especially on concentrations of chemically conservative components and on the stable-isotope composition of the water. In combination with the results of aqueous leaching, squeezing data of conservative tracers are instrumental for the determination of the anion-accessible fraction of physical porosity.

A2.5.4 Possible artefacts

Besides the possible modification of the pore water associated to drilling and sample conditioning, some potential perturbations are specific to squeezed waters. For chemically conservative tracers, the most prominent artefacts are ultrafiltration and evaporation. Ultrafiltration will lead to a decrease in the concentration of solutes with increasing pressure as the pore sizes decrease and ions are progressively immobilised due by the effects of the charged clay-mineral surfaces. This phenomenon depends on mineralogy, fabric and the time-pressure history of the squeezing process.

For the Opalinus Clay at Mont Terri, it has been shown that under loads varying from 25 to 200 MPa, no significant differences in concentrations of chemically conservative components occurred, but substantial chemical differences have been found between successive fractional samples squeezed at much higher loads up to 512 MPa. The chloride and bromide concentrations of the squeezed water decreased with increasing pressure and reached only 75 % of the initial (<200 MPa) concentrations at 512 MPa (Figure A2.5-2).

Figure A2.5-2: Decrease of measured chloride concentrations in water squeezed with increasing squeezing pressure

![Decrease of measured chloride concentrations in water squeezed with increasing squeezing pressure](image)

Data refer to two samples of Opalinus Clay from the same borehole at Mont Terri. The decrease in chloride is explained by ultrafiltration at pressures above 200 MPa. From Waber et al. (2003b)
Additional uncertainty in squeezing data relates to the fact that the amounts of squeezed water are commonly very small (about 1 – 5 mL). Such small volumes are susceptible to evaporation in the sample collection system during squeezing and during sampling. Partial evaporation will considerably modify the isotopic signature of the squeezed water (beginning Rayleigh distillation). For chemical components, the necessity of filtering and diluting aliquots of water samples prior to analysis introduces additional uncertainties. The analytical uncertainties are around ±10 % for major species and up to ±25 % for species or elements with concentrations close to the respective detection limits.

A2.6 Vacuum distillation

A2.6.1 Basic description

The extraction of water from solids containing water by distillation under vacuum has been applied since the beginning of isotopic measurements by mass spectrometry. Vacuum distillation allows the measurement of the isotope composition of the water but provides no data on other pore-water constituents because these are not volatilised. Originally, the method was developed for soil samples with high permeabilities and water contents. At later stages, there were numerous attempts to adapt the method to argillaceous and other low-permeability rocks with low water content. Sacchi & Michelot (2000) give a detailed review of the development of the technique and an evaluation of its applicability to argillaceous rocks.

A2.6.2 Experimental setup

The basic design has not changed much over the last decades, but some procedures were modified and adapted to the different needs and interests. In the most common setup, originally saturated rock pieces are crushed to a grain size of less than 1 cm and placed in glass vessels that are connected to a vacuum extraction line. The glass vessels are heated at constant temperature and the water is removed from the rock sample by simultaneous pumping. Along the extraction line, the water vapour is trapped in one or several cold traps. The collected water is then transferred to and analysed by a conventional ion-ratio mass spectrometer. A modification of this setup applies an in-line grinding of the rock sample to minimise de-saturation during preparation (Figure A2.6-1). Other variations include the temperature to which the sample is heated (50 to 200 °C), the duration of extraction (minutes to days), the grain size of the rock material (mm to cm) and the cooling temperature in the cold traps (-7 to -195 °C).

A2.6.3 Data and information obtained

Based on the numerous comparative studies conducted, it can be concluded that the isotope compositions obtained for pore water extracted from low-permeability argillaceous rocks by vacuum distillation are invariably depleted in $^{18}$O and $^2$H in comparison to the values obtained by other techniques and so are not representative of in-situ pore water (Figure A2.6-2, Figure A2.7-2). The strongest argument against the adequacy of the distillation method comes from the fact that in all argillaceous rocks investigated to date, the $\delta^{18}$O and $\delta^2$H obtained for pore water are discrepant from those of the flowing ground water in the adjacent aquifer or fracture even if the distance is only centimetres to decimetres. This discrepancy can only be explained as an artefact of the technique (see below). In the fortunate case of a very homogeneous argillaceous rock formation and a consistent and strictly followed protocol for vacuum distillation, it may be possible that the error is systematic. This means that the shapes of the $\delta^{18}$O and $\delta^2$H profiles are correctly reproduced, but with inadequate absolute values that create difficulties in interpreting the data in conjunction with the $\delta^{18}$O and $\delta^2$H
values in the aquifers (see, e.g. Patriarche et al. 2004a,b). If a direct comparison with data based on other techniques (e.g. squeezing, isotope diffusive-exchange method) is available, a correction may be feasible (as done for the data from Tournemire in Section 2.6.2).

Figure A2.6-1: **Example of different setups of vacuum-distillation lines at CNRS-Université de Paris-Sud**

Left: Conventional extraction line using rock material ground outside the line; right: stainless-steel cell with ball grinder where the rock material is milled in-line and extracted by vacuum distillation (from Altinier 2006)

Figure A2.6-2: **Comparison of pore-water isotope data obtained by different types vacuum distillation and other techniques**

Data refer to samples from the Toarcian-Domerian at Tournemire. Modified vacuum distillation indicates in-line grinding of the rock as compared to the conventional off-line preparation. Modified from Altinier et al. (2007)
A2.6.4 Possible artefacts

Artefacts leading to non-representative isotope compositions in the vacuum-distillation technique can be induced at several stages of the process. As for all indirect methods, the first perturbation is induced by processing partially desaturated drillcore material. Additional desaturation may occur during the crushing of the rock material and during manipulations with the glass vessels. It should be noted that the technique requires rather fine-grained material, so the fact that new surfaces are created during crushing leads to enhanced desaturation even for short exposure times to the atmosphere. As shown by Altinier et al. (2007), an in-line grinding of the rock sample indeed yields different results compared to off-line preparation (Figure A2.6-2).

The most important artefact appears to be the incomplete distillation and/or the incomplete water recovery in the cooling trap(s), as shown in the detailed work by Moreau-Le Golvan (1997), Moreau-Le Golvan et al. (1997) and Altinier et al. (2007) for the Toarcian shale at Tournemire. In both cases, incomplete volatilisation results in a Rayleigh fractionation process of the water isotopes, and the measured $\delta^{18}$O and $\delta^2$H values become lower compared to the in-situ pore water. Commonly, the data plot above the Global Meteoric Water Line in diagrams of $\delta^{18}$O vs $\delta^2$H (Figure A2.6-2, Figure A2.7-2). The incompleteness of the distillation is highlighted by the fact that lower water contents are obtained from the vacuum-distillation technique when compared to water contents measured by drying aliquots of the same sample at the same temperature for a longer period of time, i.e. until stable weight is attained. Rübel (2000) and Rübel et al. (2002) made the same observations for Opalinus Clay at Mont Terri and at Benken.

Other artefacts include exchange with and liberation of different types of bound water in the clay-rich rocks depending on the extraction time and temperature. Such processes are difficult to quantify and also depend on the mineralogy of each sample (e.g. France-Lanord 1997, Giannesini 2006). Further, the precipitation of secondary minerals (e.g. hydrated salts, carbonate) during the extraction was identified as a source of fractionation of stable water isotopes in pore water during vacuum distillation (Giannesini 2006). While such effects may be small in low-salinity environments, they become significant at high salinity.

A2.7 Isotope diffusive-exchange technique

A2.7.1 Basic description

The isotope diffusive-exchange technique was designed for the determination of $\delta^{18}$O and $\delta^2$H in pore water. In addition, the method delivers a value for the water content of the rock sample, and this value is independent from that obtained from the gravimetric water content. The method is based on the premise that the known isotopic composition of a test water will equilibrate with the unknown isotopic composition of the pore water in a rock sample via the vapour phase. The technique has been originally developed at IUP Heidelberg (Rogge 1997, Rübel 2000) and has been applied to various argillaceous rocks in the meantime (e.g. Rübel & Sonntag 2000, Rübel et al. 2002, Waber 2005, Altinier et al. 2007).

A2.7.2 Experimental setup

The experimental setup is relatively simple but requires completely saturated rock samples. From the centre of a well-preserved drillcore, rock pieces about 1 – 2 cm in diameter and a small Petri dish filled with test water are stored together in a vapour-tight glass container (Figure A2.7-1). The mass
and the initial isotopic composition of the test water need to be known. Condensation of test water on the rock fragments and on the glass container walls is inhibited by lowering the water-vapour pressure above the test water. This lowering of the water activity in the vapour phase is achieved by the addition of salt to the test solution.

The Petri dish with the test water and the whole container are weighed before and after the exchange experiment to make sure that no water was lost from the container and that there is no transfer of test water to the sample by condensation on the rock material. Isotopic equilibrium in such a system is achieved in about 20 to 30 days at room temperature, depending on the size and water content of the rock fragments. After complete equilibration, the test water is removed and analysed by conventional ion-ratio mass spectrometry. It should be noted that during the entire experiment, the rock material is never in direct contact with the test water, in contrast to radial diffusion techniques.

The water content of a rock sample and the stable isotope composition of its pore water can be calculated from the mass balance relationship of the exchange experiment according to:

\[
M_{PW} \cdot C_{PW} |_{t=0} + M_{TW} \cdot C_{TW} |_{t=0} = (M_{PW} + M_{TW}) \cdot C_{TW} |_{t=\infty}
\]

where
- \(M\) = mass
- \(C\) = isotope ratio
- \(PW\) = pore water
- \(TW\) = test water.

\(t = 0\) (left side) refers to the initial situation, and \(t = \infty\) (right side) refers to times at which isotopic equilibrium is achieved. It should be noted that at complete equilibration, the mass balances remain correct even if a small amount of test water is transferred to the sample during the experiment. Each equilibration experiment yields two independent equations as shown above, one for \(C_{PW} = \delta^{18}O\) and another for \(C_{PW} = \delta^2H\). To solve these equations for the three unknowns \((M_{PW}, \delta^{18}O_{PW}, \delta^2H_{PW})\), two different exchange experiments have to be performed for each sample. By applying Gauss' law of error propagation, Rübel (2000) showed that the error of his method is minimised if a) the two exchange experiments are conducted with test solutions that have an isotopic composition similar to and greatly different from that of the expected pore water and b) the ratio of the masses of test water to pore water is close to unity.

### A2.7.3 Data and information obtained

The isotope diffusive-exchange method directly yields the isotopic composition of the pore water. In addition, the water content of the rock sample is obtained from the mass-balance equations. There is still some uncertainty related to the fact that the water contents obtained by this method are commonly slightly higher than the gravimetric water content derived by drying at 105 °C (e.g. Pearson et al. 2003 [Annex 10], Waber 2005, Altinier et al. 2007). This could reflect the fact that not all pore water is removed at 105 °C. Indeed, in Opalinus Clay, weight loss upon drying is 16 and 22 % higher at 150 and 200 °C when compared to 105 °C (Nagra 2002). The comparison of pore-water isotope signatures obtained by the isotope diffusive-exchange method with the signature of formation water collected over years in packed-off borehole intervals at the Mont Terri Rock Laboratory and water squeezed from rock samples indicates that the diffusive-exchange method delivers isotopic compositions very close to those of the \(in-situ\) pore water (Figure A2.7-2). In addition, data obtained by this method from pore waters in aquifers are consistent with the respective ground-water data, which adds further confidence to this approach.
Figure A2.7-1: **Experimental setup of the isotope diffusive-exchange method**

Saturated rock material is placed into two vapour-tight glass containers together with two Petri dishes containing isotopically different test waters.

Figure A2.7-2: **Comparison of δ^18O and δ^2H values obtained by different methods in Opalinus Clay at Mont Terri and at Benken**

The methods include the isotope diffusive-exchange technique, vacuum distillation, squeezing and long-term in-situ sampling in packed-off intervals. The error of the indirect methods is ca. ±1 ‰ for δ^18O and ±3 ‰ for δ^2H. Data from Pearson *et al.* (2003), Rübel & Sonntag (2000) and Waber *et al.* (2003b).
A2.7.4 Possible artefacts

The isotope diffusive-exchange method requires originally saturated rock material and is sensitive to evaporation of pore water during sample preparation and to condensation of test water during the experiment because these processes are linked to large isotopic fractionations. For highly saline pore waters, the activity of the test water needs to be reduced accordingly by addition of salt. The isotopic analysis of highly saline test water is difficult due to the very large isotopic fractionation between volatilised water and water bound to the solid salt residue, in particular to CaCl$_2$. The impact of the resulting analytical errors on the derived $\delta^{18}$O and $\delta^2$H of pore water is substantial and subject of ongoing investigations (Waber et al. 2007). The same problem also applies to the vacuum distillation technique, but there the error is not further propagated and so less critical to the resulting $\delta^{18}$O and $\delta^2$H of pore water.

The mentioned small difference between the water contents obtained by the isotope diffusive-exchange technique and the gravimetric water content derived by drying at 105 °C is not completely clarified, but the effect on the calculated $\delta^{18}$O and $\delta^2$H of pore water is limited and well within the analytical error of the isotope analysis (Pearson et al. 2003). Nevertheless, further studies are needed to better quantify the uncertainties.

A2.8 Advective displacement

A2.8.1 Basic description

The method is forcing displacement of the original pore water contained in a drill core sample by advection of a traced artificial pore water. The feasibility of the method hinges on the well connected porosity and homogeneity of the rock sample that result in approximate one dimensional advective-dispersive flow when applying a large hydraulic gradient across the length of a cylindrical sample. The objective is to obtain a true sample of pore water subject to relatively minor artefacts. Pre-requisites are the availability of a saturated core sample processed and stored protected from atmosphere, the absence of preferred flow paths, and the ability to induce a relatively homogeneous advective-dispersive displacement front between the injected artificial pore water and the displaced in-situ pore water. Passive tracer components contained in the artificial pore water serve as a monitor for the proportion of artificial pore water contained in the extracted pore water (e.g. Br$^-$, NO$_3^-$, D$_2$O). The induced fluid fluxes are low (0.1 – 0.5 mL/day). Experience indicates that 10 – 30 mL of little disturbed original pore water can be extracted from shales with a porosity of 0.1 – 0.2. The method is illustrated in Figure A2.8-1 and summarised in Mäder et al. (2004).

The strength of the method is to transfer approximate in-situ conditions to the laboratory and minimise unwanted effects due to stress relief, redox processes (pyrite, organics), and reactions within the carbonate system. A single carefully prepared long-term experiment can thus yield a comprehensive data set to constrain rock-water interaction processes as well as transport and retardation properties.

A2.8.2 Experimental setup

The heart of the apparatus is a pressure vessel that subjects the rock core to a hydraulic confining pressure (Figure A2.8-1, left). The core is sealed from the confining medium by a sleeve (Teflon–rubber–shrink tubing) and two coupling pieces made of titanium. Porous disks (Teflon, Ti, PEEK) separate the top and base of the core from the couplings to allow for distribution or collection of
infiltrating or extracted fluid. The spindle allows adjustment to the length of a rock core. Fluid infiltration is driven from a He-pressurised tank. Typical confining pressures are 50 – 100 bars (the possible maximum is around 500 bars), and chosen infiltration pressures are frequently chosen around 50 bars in argillaceous rocks. The infiltration system guides the gas-pressurised artificial pore water to the surface of the core sample. The pore water forced out of the core sample is collected by a porous disc and guided through PEEK capillary tubing to a sampling device.

The apparatus allows choosing from a wide range of physical conditions for a pore-water extraction experiment. The lower practical limit of hydraulic conductivity for a core sample for the method to work is approximately 1E-14 m/s. Only small sample aliquots (0.5 – 2 mL) are commonly sampled from low-permeability rocks. This is especially true when flow porosity is small and therefore a relatively fast breakthrough of the injected artificial pore water is to be expected. Typical durations for extracting a few samples from low-permeability rocks are weeks to months.

Measurement of pH and Eh can be performed in-line with micro flow-through cells. The sample aliquots are typically being stored refrigerated as is (in syringes), or may be diluted and/or preserved if required. The analytical programme has to be tailored to the objectives of the experiment, the expected chemical composition, the tracers used in the artificial pore water, and to the possibly very small sample size.

Figure A2.8-1: Illustration of the apparatus for advective displacement of pore water

A2.8.3 Data and information obtained

Under favourable conditions, the method provides pore-water aliquots of sufficient volume for analysis of major ions and stable water isotopes. It also offers the possibility to perform in-line measurements of electrochemical parameters such as pH, Eh and electric conductivity. Ideally, a time
series of extracted aliquots of *in-situ* pore water should initially yield pure pore-water samples and then display an increasing proportion of admixed artificial pore water with increasing time.

The hydraulic conductivity of the sample can be calculated for each sampling interval using Darcy's law if porosity is known and the flow rates are recorded (note that at the very high gradients applied, the validity of Darcy's law is undisputed).

### A2.8.4 Possible artefacts and technical difficulties

The composition of the artificial pore water should be as close as possible to that of the pore water in terms of its major constituents Cl, SO₄, Br, Na, Ca, and Mg, so information from other techniques of pore-water characterisation is a pre-requisite for a successful experiment. Deviating compositions of the artificial pore water may lead to ion-exchange reactions, mineral dissolution or precipitation, which may lead to plugging of porosity and therefore to drastic decrease of hydraulic conductivity that prevents further fluid movement.

Very low hydraulic conductivity, in conjunction with a very small mass of pore water contained in a given volume of a rock core, will lead to difficulties when attempting to extract aliquots of pore-water samples not significantly contaminated by the artificial pore water. Also, working at the lower limits of hydraulic conductivities makes the system vulnerable to small imperfections in sample confinement that may lead to preferential flow along interfaces (rock / resin, resin / Teflon sleeve). If very small sample volumes can be collected, only a partial chemical and/or isotopic characterisation may be feasible.

Overall, a single successful experiment may provide an excellent characterisation of the pore water in the sample. However, the method is manpower-intensive, and a single experiment runs over weeks to months. It is not possible to use this method to generate data from a large suite of samples (as would be needed for a full profile across a low-permeability sequence).

### A2.9 Core outgassing of noble gases

#### A2.9.1 Basic description

Noble gases are chemically inert and serve as valuable tracers in rocks of low permeability. Under ambient conditions, the solubility of noble gases is low (Weiss 1971), and so water infiltrating into the underground has low noble-gas concentrations (see summary by Kipfer et al. 2002). In the underground, the concentrations namely of He and Ar increase with time due to the continuous production of radiogenic He and Ar by various nuclear processes in the rock. Once released to the pore water, the dissolved noble gas is transported by diffusion or advection into the ground water of neighbouring aquifers and will be eventually released to the atmosphere. By comparing measured He and Ar concentrations and isotope ratios in the rock, in pore water and in ground water with the calculated *in-situ* production rate, it is possible to study and quantify transport processes over geological time scales.

The core-outgassing technique for noble gases takes advantage of the chemical inertness of these gases and their low solubility in water under atmospheric conditions, so dissolved gas will be liberated into the free volume of a high-vacuum container. The technique was originally developed at IUP, University of Heidelberg (Osenbrück 1996), where it has been first applied to evaporitic rock environments of low permeability (Osenbrück et al. 1998) and later to argillaceous rocks, such as Opalinus Clay (Rübel & Sonntag 2000, Rübel et al. 2002). More recently, a more robust and newly
designed field-sampling equipment with new sample containers have been developed at KUP, University of Bern, and the slightly modified method has been applied to the Callovo-Oxfordian at Bure (Bigler et al. 2005), the Boom Clay at Essen (Bigler & Mazurek 2006) and the Toarcian-Domerian at Tournemire (ongoing work).

Figure A2.9-1: Illustration of the on-site sampling equipment for noble gases in pore water

A2.9.2 Experimental setup

A sophisticated sampling technique is needed to minimise the effects of rapid outgassing of dissolved noble gases to the atmosphere during handling (Bigler et al. 2005). This includes on-site conditioning of drillcore samples immediately after core recovery. Each core sample is cut dry to an octagonal prism to remove the rim that may already have suffered degassing or is contaminated with drilling fluid. Subsequently, the sample is weighed and sealed in a high-vacuum container. The time of exposure to the atmosphere needs to be minimised to less than about 10 minutes.

The high-vacuum containers are made of stainless steel and comprise a copper sealing ring and a copper tube attached to their top flange through which the container is flushed twice with nitrogen and evacuated with a vacuum pump to remove atmospheric helium (Figure A2.9-1). After the final evacuation, the copper tube is crimped and closed with a steel clamp while pumping. The noble gases are then allowed to degas from the rock sample to the void volume of the container until equilibration. The time needed for quantitative extraction of noble gases has been determined in laboratory experiments and varies with sample size and rock type (Osenbrück et al. 1998, Bigler et al. 2005). A typical time for He is about 1 – 2 weeks but up to 5 times longer for the heavier noble gases because of their lower diffusion coefficients. Therefore, samples are commonly allowed to equilibrate over a period of 2 – 3 months.

After equilibration, the gas is transferred from the container to a purification line that is directly linked to the mass spectrometer. The design of the purification line may vary depending on which gases and/or isotope ratios are of interest, but the line commonly used contains titanium and/or zircon getters and charcoal traps to separate and remove undesired gases from the noble gases of interest.
Mass-spectrometric measurements were performed on a VG1200 mass spectrometer by Osenbrück et al. (1998) and Rübel et al. (2002), and on a Pfeiffer QMS422 quadrupole by Bigler et al. (2005). In all cases, gas abundances were calibrated by measuring known amounts of atmospheric air.

For the calculation of the in-situ production rate of noble gases, the concentrations of U, Th, Li, K, Gd, Sm, and of the noble gases in the solid rock need to be known. The concentrations of Gd and Sm are important for the exact calculation of the local neutron flux in the rocks of interest. These investigations can be carried out on the rim material of the drill core because the artefacts of concern when dealing with dissolved gas are irrelevant for the characterisation of the solid rock. For the case studies in this report, U, Th, Li, and K were analysed by flame photometry (K, Li), laser fluorescence (U) and X-ray spectrometry (Th) at the Kola Science Centre, Russia (Tolstikhin et al. 1996) and by X-ray fluorescence techniques (Gd, Sm) at Actilabs, Canada. Other analytical techniques may exist that provide similarly accurate data.

Abundances and isotope ratios of He and Ar in solid rock samples are needed to quantify the release rate of He and Ar from rock to pore water. They were measured at the Kola Science Centre, Russia, according to the method described in (Tolstikhin et al. 1996). This technique includes heating the rock sample in an all-steel double vacuum furnace at several steps for the initial purification of the sample, followed by crushing the rock sample and extracting the noble gases at 1 700 °C under high vacuum. Following that, the gases released from the minerals are purified with a titanium-zirconium getter system, separated using charcoal traps, cooled with liquid nitrogen and finally analysed by static mass spectrometry.

**A2.9.3 Data and information obtained**

The technique delivers noble-gas concentrations per volume of gas. For the conversion to concentrations of cubic centimetres gas at standard pressure and temperature (STP) per gram of pore water (cm³ STP/gwater), the weight and water content of the sample must be known. Ideally, this value is obtained from the same sample used for outgassing by measuring its wet weight just before sealing in the high-vacuum container and again after heating to stable weight at 105 °C after the experiment. A diffusion coefficient for He can also be derived by measuring the concentrations of He degassed from the rock sample as a function of time (Bigler et al. 2005).

The abundance of He in pore water and solid rock combined with the in-situ production and release rate allows to identify and quantify He transport across a low-permeability rock formation. Together with the $^{3}$He/$^{4}$He ratio and preferably supported by Ar isotope data, different sources of He can be potentially identified (Waber et al. 2003a). Similar information as for He can also be obtained for Ar and Xe (only one single case study documented by Osenbrück et al. 1998 is currently available for the latter). The release rate of Ar from minerals to pore water is much smaller than for He (Lehmann et al. 2001, Rübel et al. 2002), and this also forms the basis for the K-Ar age dating method of minerals and rocks. Together with the contrasting diffusion coefficients, this leads to a behaviour during diffusive transport that is strongly different from that of He. Concentration profiles of He and Ar may therefore record information about different time spans in the past (see Figure 2.3-6 and Figure 2.3-7).

**A2.9.4 Possible artefacts**

The only relevant source of error is the loss of gas from the rock sample at the various stages, either during drilling and core handling or due to leaks in the high-vacuum containers. Because no noble gases can be added to the sample from an external source, this results in an asymmetrical error.
for the measured noble gas concentrations. The error reflects the analytical uncertainty towards lower concentration and the combined uncertainty related to gas loss and analytical procedure towards higher concentrations. With the original sampling equipment Rübel et al. (2002), the estimated error is +30/-5 %. The error was subsequently reduced with the new equipment to +15/-5 %, as shown by Bigler et al. (2005).

A2.10 Direct pore-water extraction and equilibration techniques

The term “direct pore-water extraction techniques” as used here applies to the in-situ collection of water that seeps from an argillaceous rock formation into a borehole interval that is sealed off by packers. A priori, it is unclear how well the collected water represents the undisturbed in-situ pore water in the rock, and so the term 'borehole water' is recommended for such type of water (Pearson et al. 2003).

A2.10.1 Basic description

The collection of borehole water for pore-water characterisation takes a long time and is commonly only feasible in underground research laboratories. From argillaceous rock formations, such type of water has only been obtained to date from the Opalinus Clay at Mont Terri (Pearson et al. 2003) and from the Callovo-Oxfordian shale at Bure (Vinsot & Mettler 2007).

The in-situ collection of seepage water from an argillaceous rock is performed in isolated borehole intervals over long periods of time. Various designs of borehole drilling, installations and sampling techniques exist depending on the desired information. The experience from the Opalinus Clay and the Callovo-Oxfordian showed that it is very challenging to derive the complete in-situ pore water composition (including e.g. pH, pCO₂ and Eh) from borehole water, but there is good confidence that the obtained concentrations for chemically conservative components represent true pore-water concentrations (e.g. Pearson et al. 2003).

A2.10.2 Experimental setup

The experimental setup has greatly evolved over the last decade. The first campaign in the Mont Terri URL started with boreholes air-drilled at an angle into the tunnel ceiling (Figure A2.10-1, Griffault et al. 2003). Care was taken that the sampling intervals were located deep enough to avoid any kind of perturbation by the excavation disturbed zone (EDZ). One mechanical and one inflatable packer sealed off the lower side of an interval, with the annulus between the two packers being filled with epoxy resin to further increase tightness. The inflatable packer had a conical end piece (funnel) covered with Teflon to avoid corrosion, allowing collection of very small quantities of water. This funnel was linked to the sampling line by a stainless steel tube, 2 mm in diameter. Additional inlet and outlet nylon tubing allowed the interval to be flushed with nitrogen. A pressure sensor monitored the build-up of water pressure in the sampling line of each borehole. Water sampling from such boreholes occurred by natural outflow and/or was forced by applying a nitrogen-gas overpressure. Water samples for specific analyses were processed as required (i.e. filtration, acidification, etc.) on site and placed in bottles for direct transfer to analytical laboratories. On-site measurements of sensitive parameters such as pH, Eh, and alkalinity were continuously improved (e.g. analysis under ambient or controlled conditions). Water samples were also collected from boreholes for the analysis of dissolved gases. The water samples were collected and transferred to the laboratory in gas-tight containers.

At later stages, drilling was performed with nitrogen to reduce oxidation of rock and pore water. Sampling and gas lines made of stainless steel and nylon were replaced by PEEK tubing, which is
Further developments included borehole equipments using ceramic screens, all-PEEK tubing and in-line measurements of sensitive parameters such as pH, CO₂ and Eh using specially designed measuring devices (e.g. Wersin et al. 2004b, Vinsot et al. 2006, Vinsot & Mettler 2007).

An alternative design for characterising the pore-water composition using in-situ experiments has been developed at Mont Terri and was subsequently optimised and used for the PAC experiment at Bure (Figure A2.10-2; Vinsot & Mettler 2007). In this design, about 8 – 15 L of artificial pore water (i.e. water with a composition as close as possible to that expected for the pore water) was circulated in a borehole interval isolated by packers. In order to minimise contamination, the boreholes were drilled with nitrogen, and all equipment and the water itself were thoroughly sterilised to limit microbial activity. No metallic components were in direct contact with the circulated water. Inflow of pore water into the circulation system was enhanced by the hydraulic potential difference of about 30 bars between pore water and circulated artificial pore water. The total mass of circulated water was monitored to constrain the amount of inflowing water. Conservative tracers, such as HDO or Br⁻, were added to this water to determine the mixing ratio of natural and artificial pore water over time. In contact with the rock, the synthetic pore water slowly adjusted its composition to match that of the natural pore water residing in the rock. Such adjustment is expected to occur mainly via cation-exchange reactions and reactions in the carbonate system. Non-reactive species, such as halogens, are expected to completely adjust to the pore-water composition via diffusion and inflow. The evolution of the circulated water over time was monitored by regular analysis of pH, Eh and electrical conductivity.

Figure A2.10-1: Experimental scheme for first-generation direct pore-water sampling at Mont Terri

From Pearson et al. (2003)
A2.10.3 Data and information obtained

The Main Fault (see Section 2.4.1) and undisturbed Opalinus Clay at Mont Terri produced 4 L and 65 mL of water over one year, respectively (Griffault et al. 2003). In twelve sampling campaigns between 1996 and 2000, totals of about 6–23 L were collected from three boreholes drilled perpendicular or at an angle to the bedding, whereas one borehole that was drilled parallel to bedding remained dry for more than 7 years.

Complete chemical and isotopic analyses could be obtained from the sampled waters. During some campaigns, samples for dissolved and head-space gases were also taken and analysed for chemical and isotopic composition. A thorough examination of the collected data concluded that for conservative elements and isotopes, the concentrations measured on the borehole water indeed represent in-situ pore-water concentrations (Pearson et al. 2003). The concentrations of reactive
components may be close to the in-situ concentrations, depending on the degree of observed perturbations (see below), with the exception of dissolved carbon and, in most cases, redox-sensitive parameters.

Therefore, the concentrations and isotope compositions derived from borehole water for conservative components and their isotopes, such as Cl, Br, δ\(^{18}\)O, δ\(^{2}H\), δ\(^{37}\)Cl, are used as benchmarks to test the capability of various indirect pore-water extraction techniques to provide concentrations of conservative tracers that represent in-situ conditions.

### A2.10.4 Possible artefacts

The most important artefacts that affected the resulting chemical and isotopic data included effects induced by the excavation-disturbed zone, microbial activity, and – in the initial phases – corrosion, in addition to artefacts common to all conventional ground-water sampling techniques, such as de- or in-gassing of CO\(_2\) and O\(_2\). In the air-drilled boreholes, the borehole-disturbed zone (BDZ) strongly perturbed the redox system in the early sampling campaigns until the induced oxygen was completely consumed. Microbial activity was induced in all boreholes in spite of all precautions taken (e.g. including sterilisation of the equipment). Such activity strongly perturbed (and still perturbs) the carbon and sulfur systems and, as a consequence, also the other reactive ions.

Initially, it was suspected that the collection of seepage water from a borehole could mimic a large-scale squeezing experiment, and it was unknown to what degree processes such as ultrafiltration could affect the composition even of conservative components. For the Opalinus Clay at Mont Terri, such a perturbation can be excluded based on the measured range of pore-water pressures, which is far below pressures required to induce ultrafiltration.

In the circulation-type setup for pore-water sampling as used in the PAC experiment at Bure, major deviations between the chemical compositions of the natural and artificial pore waters would induce reactions that may disturb the system, so some information on the expected composition is needed a priori, based either on data obtained from other methods or from geochemical modelling. If circulation is maintained over long times, microbial activity becomes important and will seriously affect the results, namely for sulfate and alkalinity (Vinsot & Mettler 2007, Wersin et al. 2004b).
A3.1 Temperature dependence of diffusion coefficients

Most values for diffusion coefficients were obtained on the basis of laboratory experiments conducted at ambient temperature. *In-situ* temperatures may deviate significantly from the laboratory temperature. In the case studies considered here, the most significant deviations are identified in borehole MAR501 in the Couche Silteuse de Marcoule (29.5 °C) and in Opalinus Clay at Benken (34.5 °C). In a generic way, the temperature dependence of diffusion coefficients can be described by the Stokes-Einstein equation (Li & Gregory 1974)

\[
\frac{D_{\text{ref}} \eta_{\text{ref}}}{T_{\text{ref}}} = \frac{D_1 \eta_1}{T_1},
\]

where

- \(D_{\text{ref}}\) = diffusion coefficient at reference temperature
- \(D_1\) = diffusion coefficient at temperature 1
- \(\eta\) = water viscosity
- \(T\) = absolute temperature.

Van Loon *et al.* (2005) studied the temperature dependence of diffusion coefficients in Opalinus Clay from Benken and Mont Terri by means of laboratory experiments. They found that in the investigated range of 0 to 70 °C, the dependence can be described as an Arrhenius function and that the temperature dependence is stronger than predicted by the Stokes-Einstein equation because the structure (and therefore the viscosity) of pore water in Opalinus Clay differs from that of free water. Figure A3.1-1 illustrates the temperature dependence of the self-diffusion coefficients for HTO and Cl⁻ and compares them with that based on the Stokes-Einstein equation.

In the absence of formation-specific data on the temperature dependence of diffusion coefficients, the experimental data by Van Loon *et al.* (2005) for Opalinus Clay are used for all other formations considered in this report as well. The temperature dependence of Cl⁻ is assumed to be valid for all anions.

A3.2 Diffusion coefficient for He

A very limited number of values for diffusion coefficients of dissolved He are available for Opalinus Clay at Mont Terri and for the Callovo-Oxfordian at Bure but not for any of the other formations considered. On the other hand, abundant data are available for HTO. Available data for both tracers are summarised in Table A3.2-1.
Figure A3.1-1: Temperature dependence of diffusion coefficients according to the Stokes-Einstein equation and the experimental data of Van Loon et al. (2005) for Opalinus Clay

![Graph showing temperature dependence of diffusion coefficients](image)

Table A3.2-1: Comparison of self-diffusion coefficients of He and water

<table>
<thead>
<tr>
<th>Formation</th>
<th>Method</th>
<th>Substance</th>
<th>(D_p) [m (^2)/s]</th>
<th>(D_e) [m (^2)/s]</th>
<th>Direction</th>
<th>Physical porosity [-]</th>
<th>Reference</th>
<th>(\frac{D_e(\text{He})}{D_e(\text{HTO})})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free water</td>
<td></td>
<td>He</td>
<td>7.28E-9</td>
<td></td>
<td>Isotropic medium</td>
<td>1.0</td>
<td>Cook &amp; Herczeg (2000)</td>
<td>3.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HTO</td>
<td>2.27E-9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Callovo-Oxfordian at Bure**

|                                   | Out-diffusion of spherical samples | He        | 7.5E-10               | (1.4E-10)             | Mainly || | 0.18 | Bigler et al. (2005) | 3.8 (||)                                      |
|----------------------------------|-------------------------------------|-----------|-----------------------|-----------------------|-----------|-----------------------|---------------------------------------------------|-----------------------------------------------|
|                                  | Through diffusion                   | HTO       | (2.1E-10)             | (3.7E-11)             | ||        | 0.18 | Andra (2001, p. 61 ff.), Andra (2005b, Tome 1, vol. 3, ch. 19, p. 75) |                                               |
|                                  | Through diffusion                   | HTO       | (1.4E-10)             | 2.6E-11               | ↓         | 0.18 | Andra (2005b, Tome 1, vol. 3, ch. 19, p. 75) |                                               |

**Opalinus Clay at Mont Terri**

|                                   | In-situ experiment                  | He        | (7.0E-10)             | 2.1E-10               | ||        | 0.3 | Gomez-Hernandez (2000) | 3.5 (||)                                      |
|----------------------------------|-------------------------------------|-----------|-----------------------|-----------------------|-----------|-----------------------|---------------------------------------------------|-----------------------------------------------|
|                                  | Through diffusion                   | HTO, \(_2\)H_2O | (3.2E-10)             | 6.0E-11               | ||        | 0.19 | Nagra (2002, Tab. 5.10-1) |                                               |

**Notes:**
- \(||\) = parallel to bedding, \(\perp\) = normal to bedding
- Values for \(D_e\) and \(D_p\) are shown as reported in the original documents. Calculated values are in brackets.
- Values for diffusion coefficients of HTO in the Callovo-Oxfordian at Bure as reported in Andra (2005b) were all measured perpendicular to bedding. The anisotropy factor of 1.4 was used to calculate the corresponding values parallel to bedding and is based on data reported in Andra (2003).
- The He diffusion coefficient \(D_{p,\text{He}}\) = 6E-11 m\(^2\)/s at 50 °C derived for the Callovo-Oxfordian at Bure in laboratory experiments by Rebour et al. (1997) is in conflict with more recent laboratory and field-derived data and is not considered here.
Based on the evaluation of the natural He concentration profile across the low-permeability sequence at Mont Terri, Rübel et al. (2002) derived an effective diffusion coefficient for He normal to bedding of \((3.5\pm1.3)\times10^{-11}\) m\(^2\)/s. However, the calculation assumed steady state between He out-diffusion and He production due to the decay of U and Th. Because the activation of the aquifers embedding the low-permeability sequence took place much more recently, the He concentration profile most likely does not represent steady state but is transient (Section 5.4). Moreover, the reported diffusion coefficient for He would be smaller than that for HTO, which appears unlikely. For this reason, we do not consider Rübel et al.’s (2002) value.

In a clay or shale, the pore volume and pore geometry accessible to He is very similar to that for water. Therefore, the diffusion coefficient for HTO can be taken a proxy for that of He if an appropriate scaling factor is applied that accounts for the different molecular masses. As shown in Table A3.2-1, the self-diffusion coefficient for He in free water is 3.2 times larger than that of HTO. The available data for the Callovo-Oxfordian at Bure and for Opalinus Clay at Mont Terri yield comparable ratios. It is concluded that the effective diffusion coefficient for He in argillaceous formations can be estimated as 3 times that for HTO in the same material, and this factor is used throughout this report.
ASPECTS PERTINENT TO THE EVOLUTION OF BOUNDARY AND INITIAL CONDITIONS OVER TIME

A4.1 Stable isotopes in precipitation

A4.1.1 Relationship between temperature and isotopic composition of precipitation

In order to constrain the evolution of the boundary conditions for the clay pore waters over time, the stable isotopic composition of meteoric recharge that feeds the aquifers needs to be known over the considered evolution time. The temporal variability of the stable isotopic signature of recharge water at a given site depends mainly on temperature and therefore on climate. Provided the evolution of surface temperature can be constrained on the basis of independent evidence and the relationship between temperature and isotopic composition of recharge is known, the evolution of the latter can be estimated for the periods of interest. For this purpose, previous works (e.g. Marivoet et al. 2000) used the world-wide correlation between mean annual temperature and O, H isotope compositions in precipitation (Dansgaard 1964, Frick & O’Neil 1999):

\[
\delta^{18}\text{O} \text{[‰ V-SMOW]} = 0.695 \times T \text{[°C]} - 13.6 \\
\delta^{2}\text{H} \text{[‰ V-SMOW]} = 5.6 \times T \text{[°C]} - 100 ,
\]

together with temperature evolutions over geological time derived from independent evidence (e.g. Savin et al. 1975, O’Connell et al. 1996, Van Weert & Hassanizadeh 2000). There are a number of shortcomings to this approach:

- The Dansgaard relationship represents a spatial correlation at present time. An ergodic substitution needs to be applied by transforming it to a temporal correlation at a specific location, but a justification for the validity of this substitution is not at hand (Alley & Cuffey 2001).
- Latitude effect: The slope in Dansgaard’s correlation is mainly defined by high-latitude information from Greenland and Antarctica. Taking the temperate and warm climate regions alone provides a less well defined correlation with distinctly different slopes. Indeed, some authors use different slopes for different parts of the curve (e.g. Clark & Fritz 1997, Fig. 3-1).
- Other site-specific effects due to the source and path of precipitation (i.e. processes between evaporation in the source region and transport to the region where precipitation occurred), and to continentality or seasonality, are not considered (Alley & Cuffey 2001, Clark & Fritz 1997).

In summary, it appears inappropriate to use Dansgaard’s relationship for the reconstruction of stable isotope compositions in precipitation in the geological past. Most likely, this relationship greatly overestimates the dependence of isotopic compositions of precipitation on temperature at low to intermediate latitudes (Alley & Cuffey 2001).
An alternative approach to characterise the relationship between temperature and water isotopic compositions is based on infiltration temperatures derived from noble gas contents of the ground waters (Pearson et al. 1991, Stute & Schlosser 2000). For Central Europe, recent studies are available from Belgium (Philippot et al. 2000) and southern France (Huneau 2000, Huneau et al. 2002) and yield the following relationships:

Belgium (Philippot et al. 2000):
\[ \delta^{18}O \, [\text{‰ V-SMOW}] = 0.26 \, T \, [\text{°C}] - 9.5 \]
\[ \delta^2H \, [\text{‰ V-SMOW}] = 2.08 \, T \, [\text{°C}] - 66 \]

Southeastern France (Huneau 2000):
\[ \delta^{18}O \, [\text{‰ V-SMOW}] = 0.22 \, T \, [\text{°C}] - 10 \]
\[ \delta^2H \, [\text{‰ V-SMOW}] = 1.76 \, T \, [\text{°C}] - 70 \]

Older studies are also available for Europe, namely for northwestern Austria (Andrews et al. 1985, Andrews 1993), Germany (Rudolph et al. 1984, Andrews 1993), northern Switzerland (Beyerle et al. 1998), Hungary (Stute & Deak 1989, Andrews 1993) and the UK (Bath et al. 1979, Andrews 1993). The available relationships between temperature and \( \delta^{18}O \) are shown in Figure A4.1-1. They all have in common that the dependence of \( \delta^{18}O \) on temperature is substantially smaller (slope = 0.19 – 0.49 ‰/°C) than that of the Dansgaard relationship (slope = 0.695 ‰/°C). The factors that explain this difference between long-term temporal changes over the glacial-interglacial timescale and spatial variability at a given time (as in Dansgaard’s approach) have been discussed by Andrews (1993) and Darling (2004). Because the noble-gas approach is based on data from the region of interest and because it relates directly to temporal variability in ground-water recharge at specific locations, it is considered here as the method of choice. However, uncertainties remain, mainly due to the fact that the relationships are extrapolated to much larger time scales when compared to the periods recorded by the measurements. In considering the stable isotope compositions of ground waters in the boundary aquifers for the clay rock sequences during their Quaternary and Tertiary palaeo-hydrogeological evolutions, the temperature coefficient from Philippot et al.’s (2000) study of Belgian ground waters, 0.26 ‰ \( \delta^{18}O \) per °C, has been used here.
A4.1.2 Stable isotopes of precipitation during the Plio-/Pleistocene glacial cycles

Major glaciations in Europe started at 2.4 Ma (Frakes et al. 1992), resulting in cycles of temperate, boreal, periglacial and glacial climates. Over the last six cycles (0.62 Ma) in central Europe, temperate climate prevailed over ca. 20% of the time, boreal over ca. 30%, periglacial over ca. 40% and glacial over ca. 10% (Boulton et al. 1997). This means that about 80% of the time was characterised by temperatures below modern values.

The last glacial cycle (0.126 – 0 Ma)

Based on climate modelling on supra-regional (ca. 1 000 x 1 000 km²) and regional (ca. 80 x 80 km²) scales, Marivoet et al. (2000) quantified the evolution of surface temperature and of precipitation and infiltration rates over the last glacial cycle (126 – 0 ka) in central Europe and Belgium (Figure A4.1-2). Using Philippot et al.'s (2000) relationship, the isotopic composition of precipitation (and therefore of infiltrating water) can be calculated from surface temperature. In Table A4.1-1, two bounding cases are shown:

- Case 1 assumes that precipitation and infiltration rates were constant over the glacial cycle, irrespective of surface temperature. The resulting average δ¹⁸O and δ²H values are 3.2 and 25.7 ‰ below present-day, temperate-climate values. This simple calculation ignores the fact that precipitation rate is generally lower during cold periods, and in addition infiltration is limited by the presence of permafrost. This means that the calculated average δ¹⁸O and δ²H values for ground-water recharge are most likely too low.

- Case 2 considers variable precipitation rates over the glacial cycle and assumes that infiltration only occurred during periods with surface temperature ≥0 °C, i.e. in the complete absence of permafrost. This case is the one considered by Marivoet et al. (2000) and is illustrated in Figure A4.1-2. The calculated average δ¹⁸O and δ²H values are 0.9 and 6.7 ‰ below present-day values. The much smaller shift than in Case 1 is due to the fact that no infiltration is assumed to occur during very cold times within the glacial cycle. Compared to case 1, case 2 is the other extreme and probably underestimates the deviation of the δ¹⁸O and δ²H values from modern values because local infiltration may occur even at negative surface temperatures (discontinuous permafrost).

Realistic values for average δ¹⁸O and δ²H values of precipitation infiltrated over a full glacial cycle (i.e. over a cold period and the successive interglacial stage) probably lie between the two extremes. A relatively moderate shift of glacial waters from modern values is consistent with observations in natural systems. For example, glacial waters in the Muschelkalk aquifer of northern Switzerland show δ¹⁸O values of ≥-12.3 ‰, compared to modern values in the range -11 to – 8.5 ‰ (Pearson et al. 1991). Another factor that limits the negative shift in cold-climate δ values is the slightly higher δ value of sea water from which precipitation is sourced.

Glacial cycles predating the last glaciation (2.4 – 0.126 Ma)

The climatic evolution during the last glacial cycle is better known and documented than for all older cycles. Over the last 1 Ma, about 10 glacial cycles, all dominated by the 100 ka Milankovitch period, occurred. According to existing knowledge, it appears that the climatic conditions during the older cycles were not substantially different from the most recent cycle (see, e.g., Boulton et al. 1997, text and Figure 2.3). In the absence of more specific data, we extrapolate the findings from the last glacial cycle to the last 1 Ma and consider the ranges given in Table A4.1-1 as realistic.
The oldest part of the glacial period (2.4 – 1 Ma) was more strongly affected by climate oscillations with shorter periods. The data base to constrain temperature evolution is limited, and we assume that the average isotopic composition of infiltrating water was identical to the one in the last 1 Ma.

Table A4.1-1: Isotopic composition of precipitation in Belgium, averaged over the last glacial cycle

<table>
<thead>
<tr>
<th></th>
<th>Average $\delta^{18}$O [%$_{\text{V-SMOW}}$]</th>
<th>Average $\delta^2$H [%$_{\text{V-SMOW}}$]</th>
<th>Difference in $\delta^{18}$O to the present value [%$_{\text{V-SMOW}}$]</th>
<th>Difference in $\delta^2$H to the present value [%$_{\text{V-SMOW}}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present value</td>
<td>-7.0</td>
<td>-46.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Case 1: average value</td>
<td>-10.2</td>
<td>-71.9</td>
<td>-3.2</td>
<td>-25.7</td>
</tr>
<tr>
<td>Case 2: average value</td>
<td>-7.9</td>
<td>-52.9</td>
<td>-0.9</td>
<td>-6.7</td>
</tr>
</tbody>
</table>

Data calculated from the modelled temperature evolution (Figure A4.1-2) using the temperature – $\delta^{18}$O / $\delta^2$H relationship of Philippot et al. (2000)

Figure A4.1-2: Results of climate modelling over the last glacial cycle in Belgium

From Marivoet et al. (2000)

A4.1.3 Late Miocene to middle Pliocene (11.6 – 2.4 Ma)

Information exists on global sea-surface temperature and for mid-latitude continents (e.g. Crowley & Kim 1995, Savin et al. 1975, Frakes et al. 1992). Overall, temperatures in the time period 11.6 – 2.4 Ma were somewhat higher than at present. However, global trends are not necessarily representative of specific regions due to the non-linearity of the processes that determine climate.

Data pertinent to western Europe are mostly based on the evaluation of pollen or other botanical archives. For the Pliocene in the northern Mediterranean region (mainly southern France), Fauquette et al. (1999) derived temperatures 1 – 6 °C higher than today for most of the Pliocene (5.3 – 3.3 Ma). These data are in general agreement with the palaeo-climate modelling by Chandler et al. (1994). Haywood et al. (2000) concluded on the basis of atmospheric modelling that temperature in Europe
and in the Mediterranean at 3 Ma was 5 °C higher than at present. All authors identified higher precipitation rates in the Pliocene. For northwestern Germany, Gebka et al. (1999) and Utescher et al. (2000) used palaeo-botanical data to derive mean annual temperatures of 14 – 15 °C for the late Miocene and Pliocene (11.6 – 2.5 Ma), which is ca. 5 – 6 °C above the present values. Similar differences were obtained by Ivanov et al. (2002) for the late Miocene (ca. 11.6 – 5.3 Ma) in the Bulgarian Paratethys.

It is concluded that the late Miocene and the Pliocene were warmer by about 5 °C than today. Using Philippot et al.’s relationship leads to δ¹⁸O and δ²H values of precipitation of ca. 1.3 and 10 ‰ above modern values.

A4.1.4 Summary

For the purpose of defining time-dependent boundary conditions for stable water isotopes in aquifers embedding the argillaceous formations, three different stages are distinguished in the last 11.6 Ma (Table A4.1-2):

- Holocene (0.01 – 0 Ma): Current values of meteoric recharge are used as boundary conditions. The reason for explicitly considering this short period is the fact that, at least in formations with high diffusion coefficients, some effects could be seen at least close to the aquifers.
- Late Pliocene – Pleistocene (2.4 – 0.01 Ma): The period of extensive glaciations is represented by lower δ values for infiltrating meteoric water. In spite of the large climatic variability during this period, constant average values are used, i.e. the individual cycles are not considered explicitly. Reasons for this simplification include 1) limitations in our knowledge of the detailed climate evolution and of time-dependent infiltration rates, and 2) the limited penetration depths of signals from individual glacial cycles into the lower-permeability formations (see formal treatment in Section 4.9). The quantification of the shift of the δ values is based on a modelling study targeted at the climate of the last glacial cycle in central Europe (and Belgium in specific).
- Late Miocene – middle Pleistocene (11.6 – 2.4 Ma): The late Neogene period predates the extensive glacial cycles and is characterised by higher temperatures.

Table A4.1-2: Stable isotopic composition of precipitation since the late Miocene

<table>
<thead>
<tr>
<th>Epoch</th>
<th>Period, from [Ma]</th>
<th>Period, to [Ma]</th>
<th>δ¹⁸O [% V-SMOW]</th>
<th>δ²H [% V-SMOW]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Holocene</td>
<td>0.01</td>
<td>0</td>
<td>Present value</td>
<td>Present value</td>
</tr>
<tr>
<td>Late Pliocene – Pleistocene</td>
<td>2.4</td>
<td>0.01</td>
<td>Present value minus 0.9 to 3.2</td>
<td>Present value minus 6.7 to 26.7</td>
</tr>
<tr>
<td>Late Miocene – middle Pliocene</td>
<td>11.6</td>
<td>2.4</td>
<td>Present value plus 1.3</td>
<td>Present value plus 10</td>
</tr>
</tbody>
</table>

A4.2 Composition of sea water over geologic time

A4.2.1 Site-specific depositional conditions and ages

The clay-rich sediments which evolved to the argillaceous formations described here were all laid down in marine conditions. They have geological ages ranging from Lower Jurassic to mid-Tertiary, i.e. 185 to 29 Ma. Their depositional pore waters were contemporaneous sea waters. Therefore, as
background information for interpreting and modelling the present-day evolved pore waters, it is necessary to consider what the compositions of sea water were at the times of sediment deposition. In many cases, it is also possible that sea water of post-depositional age has entered the adjoining aquifers and may have influenced the chemical and isotopic evolution of pore water in the clay formation.

**A4.2.2 Salinity, chloride and bromide variations over Phanerozoic time**

First, it should be noted that there is some degree of variability of sea-water composition even today. As shown in Figure A4.2-1, sea-surface salinity varies between 31 and 39 g/L, with an average of 35 g/L. Note that current surface salinity of the Mediterranean of 37 – 39 g/L is 6 – 11 % above the global average. The reason of this anomaly is the fact that evaporation greatly exceeds the inflow from rivers, and mixing with sea water from the open Atlantic is limited because the Straits of Gibraltar is the only connection.

It has been widely concluded that the overall salinity of sea water in the open oceans has been remarkably constant through Phanerozoic time. There is no definitive evidence of systematic change of salinity or of Cl\(^-\) concentrations with time through 550 Ma. The estimated residence time of Cl\(^-\) and Br\(^-\) in the oceanic system is 100 Ma, which is strong evidence for general uniformity of sea-water salinity (Holland 1984, 2005, Holland et al. 1986). There is evidence of transient fluctuations in some of the components that are connected with global environmental changes, specifically the relative concentrations of the alkaline earth cations Ca and Mg and of SO\(_4\). The paradigm that sea water composition has fluctuated within rather narrow limits is also supported by models that simulate the evolution of sea water through Phanerozoic time also (Demicco et al. 2005, Arvidson et al. 2006). These models take into account river inputs, cycling of sedimentary materials, and alteration of sea water during convection through oceanic crust at ocean ridges, ridge flanks and in general ocean floor, though the relative contributions of sediment cycling and ocean basalt alteration to the maintenance of chemical stability in the oceans is a matter of debate (Demicco et al. 2005, Arvidson et al. 2006).

Additional inferences about the constancy of sea-water salinity are made on the basis of evidence from sedimentary mineral assemblages, diagenetic alteration, fluid inclusions, isotopic ratios, and so on, as well as on more general consideration of sea-level variations, ice volumes and global geochemical budgets for weathering, run-off to oceans and chemical sedimentation. From small variations of the Cl\(^-\)/Br\(^-\) ratio in basal halites in evaporite formations and of compositions of fluid inclusions in halites, Holland (1984) inferred that major solutes in sea water have varied by no more than \(x 2\) and \(x 0.5\) with respect to modern sea water. Considering the evidence overall, it seems likely that variations of Cl\(^-\) in the open oceans have been considerably less than this, though a surprising degree of uncertainty remains.

With regard to the specific locations of the clay sequences being considered in this report, open-ocean marine conditions prevailed at the times of deposition. There is no evidence for local salinity anomalies related to closed-basin conditions leading to higher (e.g. sabkha environments) or lower (e.g. environments affected by enhanced fresh-water input from rivers) salinity. At later stages post-dating deposition, some areas were exposed to fresh-water conditions at least in the near-surface aquifers. In addition, in the Couche Silteuse at Marcoule, the marine transgression related to the refilling Mediterranean Sea in post-Messinian late-Tertiary times may have been related to more saline conditions over a certain period. Therefore the uncertainty in sea water salinity suggested by Holland (1984), i.e. variations between no more than \(x 0.5\) and \(x 2\), and probably much narrower limits, seems to be a well-based assumption.
A4.2.3 Variations of other major solutes

The main chemical variations in sea water have been in Ca, Mg and SO$_4$ due to changing budgets of chemical sediments, carbonates and evaporite minerals in the stratigraphic column (Berner 2004). Ca is controlled primarily by its removal in carbonate and sulfate minerals, Mg by its uptake in dolomitisation of calcite and aragonite and also by exchange for Ca in basalt-sea water interaction, and SO$_4$ by its removal into gypsum/anhydrite and by reduction to or oxidation of pyrite. These sources and sinks have resulted, for example, in low Mg/Ca concentration ratios in Jurassic-Cretaceous sea waters relative to modern sea water (Lowenstein et al. 2001, 2003, 2005, Stanley et al. 2005, Dickson 2002). Mg/Ca was rather higher during the Permian and Tertiary periods, though still being lower than the present-day ratio.

Though there is still much debate about absolute concentrations, Horita et al. (2002) have suggested that Mg concentrations have varied from around the present-day value (53 mmol/kg) to 30 – 40 mmol/kg, that Ca concentrations have been x 2 – 3 higher than present-day value (10.3 mmol/kg), that SO$_4$ concentrations have been as low as x 0.2 – 0.3 of the present-day value (28 mmol/kg), and that K concentrations have varied about 10 % either side of the present-day value (10.2 mmol/kg).

A4.2.4 Stable isotopic composition

Alongside the variability of Cl, the fluctuations of $^{18}$O/$^{16}$O in sea water over time are equally important for interpreting natural tracers in the pore waters of clay rocks. The main source of evidence for variations of $^{18}$O/$^{16}$O in past sea water is the interpretation of marine carbonate compositions.
However, the interpretation of fossil carbonate isotopic data in terms of sea-water compositions is contentious in view of the co-dependence on temperature and the possibilities for post-depositional diagenesis in water with different isotopic composition. For example, there is an overall variation in carbonate fossils from the Cambrian to the present day of $\delta^{18}O$ from -8‰ to 0‰ versus PDB (Veizer et al. 1999). These authors contend that this primarily reflects the variation of $\delta^{18}O$ for depositional sea water, which is controlled mainly by the magnitude of circulation and hydrothermal isotopic exchange in ocean crust. An alternative interpretation is that isotopic variability in carbonates is mainly due to temperature and mineralogical effects. $^{18}O/^{16}O$ data from Jurassic and Cretaceous fossils have been interpreted as reflecting primarily secular variations of general ocean temperature or local variations of temperature in deep or shallow seas, rather than variations of contemporaneous sea water $\delta^{18}O$.

Isotopic data for a large global collection of belemnite guards from Jurassic to Lower Cretaceous sediments have been interpreted to indicate an average sea water value of -1‰ $\delta^{18}O$ (Podlaha et al. 1998). Fluctuations of the belemnite data over a range of 3–4‰ were attributed to local environmental fluctuations and not to global sea water variation. Jenkyns et al. (2002) concluded that compiled $\delta^{18}O$ data for Jurassic carbonates are unlikely to provide worthwhile information on local environmental conditions or sea-water composition variations.

Isotopic data for Cretaceous carbonates have been interpreted in terms of temperature variations and it has been assumed that $\delta^{18}O$ for contemporaneous sea water was similar to that at present. A climatic optimum at the Cenomanian-Turonian boundary and a cooling trend through the Valanginian followed by a warming trend in the Hauterivian have been inferred from $\delta^{18}O$ variations in carbonates (Clarke & Jenkyns 1999, Huber et al. 2002, Van de Schootbrugge et al. 2000). Similarly, high temperatures in the late Cretaceous and Eocene have been interpreted from $\delta^{18}O$ data for foraminifera calcite (Pearson et al. 2001).

From the Middle Eocene or earliest Oligocene (ca. 43–34 Ma) onwards, the $\delta^{18}O$ for sea water has been affected by fluctuating ice sheet volumes during glacial and interglacial periods (Lear et al. 2000). The maximum change to global average $\delta^{18}O$ for deep sea water through this period is $+1.0 \pm 0.1$‰ (Schrag et al. 2001).

### A4.2.5 Conclusions

As a starting point for interpreting natural tracer profiles in marine sedimentary rocks, it is reasonable to assume that anion concentrations in water in the open oceans were close to present values through the Mesozoic and Cenozoic periods. Concentrations in sea water in closed basins would have been variable, depending on the balance between inputs of fresh water and evaporative losses. However, none of the depositional environments of the argillaceous sediments considered here are thought to have been particularly influenced by these closed-basin processes.

There are uncertainties in the assumption of uniform sea-water compositions and these have been reinforced by reappraisals of the interpretations of the various lines of indirect evidence. Most research on this topic has focused on secular variations of cation concentrations, and there is no firm knowledge of the likely magnitude of uncertainties and variations in anion concentrations and overall salinity. The maximum variability on either side of present salinity has been judged to be x 2 and x 0.5. The consensus of present interpretations is that the variability was less than this, but this is a topic of ongoing research and debate, so a cautious approach to uncertainty is justified.

Stable isotopic compositions ($^{18}O/^{16}O$) of sea water through the Mesozoic and the major part of the Cenozoic periods are considered to have been similar to present water. A small difference from
modern composition, much less than 1‰ δ¹⁸O, would be expected due to absence of polar ice. Thus, an assumption of present-day isotopic compositions for initial conditions in pore waters is reasonable. There are uncertainties in this assumption, arising for similar reasons as uncertainties in salinity and also from the interpretations of marine carbonate compositions which are the main source of evidence. Isotopic compositions of carbonates depend on both ¹⁸O/¹⁶O of sea water and temperature, and the respective contributions cannot be unambiguously distinguished. The magnitude of uncertainty is probably <1‰ δ¹⁸O.

At the onset of global ice ages and polar glaciations at the end of the Cenozoic and through the Quaternary, the isotopic composition of sea water became slightly heavier. It is well established that, at the peak of ice sheet build-up in the late Pleistocene, the ¹⁸O/¹⁶O of sea water was +1‰ δ¹⁸O relative to modern sea water.

A4.3 Helium in the Earth’s crust and in argillaceous rocks and pore waters

A4.3.1 Crustal radiogenic He

Helium abundance (He) and the ³He/⁴He ratio in the Earth’s crust have been studied for three interdependent objectives: the relationship with heat production and heat flow (⁴He is produced by radioactive decay of the U and Th decay chains, and this process also generates heat), outgassing of the mantle, and residence times of shallow crustal fluids (i.e. ground waters and natural gases). Early measurements of He abundance at varying depths were interpreted in terms of a ubiquitous diffusive flux of radiogenic He (4.65E-14 mol/m²/s). This was considered to be consistent, within reasonable uncertainties, with the average crustal heat flow (O’Nions & Oxburgh 1983).

There are fluxes of radiogenic ⁴He and ³He through crustal rocks towards release at the Earth’s surface. Radiogenic crustal He typically has ³He/⁴He ratios between 2E-9 and 2.5E-8, depending on rock composition. There may also be a minor contribution to the flux from primordial helium in the mantle, probably associated with a dominant flux of CO₂ (O’Nions & Oxburgh 1988). This mantle component can be detected as minor deviations from the expected ³He/⁴He isotopic ratio for crustal radiogenic He. Mantle He is enriched in ³He and has a ³He/⁴He ratio of (1.10 ± 0.03)E-5 (Andrews 1985, O’Nions & Oxburgh 1988). Dispersion of these mantle gases within the crust could be convective or diffusive, but the common association of anomalous ³He/⁴He with specific localisations of igneous activity and/or crustal weakness suggests that deep thermal convection may be important. Helium anomalies and geothermal anomalies may not be exactly correlated, spatially or temporally, as is the case in the central European Rhine graben (Clauser et al. 2002). This indicates that helium transport through the crust may occur by various mechanisms – episodic thermal convection, normal fluid advection through discrete pathways, or a large-scale quasi-diffusive process. Measurements of He concentrations in rock and mineral samples from the metamorphosed basement rocks in the ultradepth KTB borehole in NE Bavaria, Germany, have led to an estimated bulk transport coefficient for He through crystalline basement of between 1E-10 and 1E-7 m²/s (Bach et al. 1999). Because this coefficient is much larger than typical He diffusion coefficients in rocks (see Appendix A3.2), He mobility in the deep crust tends to be greater than would be accounted for by diffusion alone. The degassing flux for crustal He inferred from the KTB data is (3-5)E-14 mol/m²/s (Drescher et al. 1998).

The argillaceous rocks and pore waters considered in the present context are from relatively shallow depths in tectonically stable regions and, in most cases, are expected to have He contents that have no distinguishable component of mantle helium and thus can be considered to be totally radiogenic and crustal. What fraction of the radiogenic He is produced in situ and what fraction is transported into the sampled ground water from production in adjacent or remote formations is the key
issue in using He measurements to understand ground-water movements and residence times and to illustrate the maximum rate of diffusive transport.

A4.3.2 In-situ production and loss of He from minerals

$^4$He is produced in all rocks by radioactive decay of U- and Th-series nuclides. For $p_{4\text{He}}$, the production rate of $^3$He per mass of rock, Ozima & Podosek (1983) give the relation

$$p_{4\text{He}} = \left(1.19 \cdot 10^{-13}[U] + 2.88 \cdot 10^{-14}[\text{Th}]\right) \frac{\text{cm}^3\text{STP} \ ^4\text{He}}{\text{g}_{\text{rock}}}$$

where

$[U]$ = uranium content of the rock in ppm

$[\text{Th}]$ = thorium content of the rock in ppm.

Converting this relation to an accumulation rate $A_{4\text{He}}$ per mass of pore water yields

$$A_{4\text{He}} = \Lambda_{4\text{He}} \frac{\rho_s}{\rho_w} \left(1.19 \cdot 10^{-13}[U] + 2.88 \cdot 10^{-14}[\text{Th}]\right) \frac{1 - n}{n} \left[\frac{\text{cm}^3\text{STP} \ ^4\text{He}}{\text{g}_{\text{pore water}}}\right]$$

where

$\rho_s$ = grain density

$\rho_w$ = water density

$\Lambda_{4\text{He}}$ = release efficiency of He from the rock to the pore water

$n$ = porosity.

$^3$He is produced in crustal rocks predominantly from $\beta$-decay of $^3\text{H}$ which has been produced nucleogenically by the $^6\text{Li}(n,\alpha)^3\text{He}$ reaction. The in-situ production rate of radiogenic $^3$He, $p_{3\text{He}}$, is given by Andrews (1985) as the rate of neutron production multiplied by the fraction of neutrons which are captured by Li in the rock matrix:

$$p_{3\text{He}} = n' F_{Li} = f([U],[Th],[Na],[Mg],[Al],[Si],[Ca]) \frac{\text{cm}^3\text{STP} \ ^3\text{He}}{\text{g}_{\text{rock}}}$$

where

$n'$ = neutron production rate, dependent on the production of $\alpha$ particles from U and Th and their interaction by $(\alpha, n)$ reaction with light nuclei

$F_{Li}$ = fraction of neutrons which are captured by $^6\text{Li}$ in the rock matrix

$f([U],[Th],[Na],[Mg],[Al],[Si],[Ca])$ = neutron production rate as a function of the production of $\alpha$ particles by U and Th, their $(\alpha, n)$ interaction with nuclei of the light elements Na, Mg, Al, Si, Ca, and the spontaneous fission of U.

This production rate can be converted to an accumulation rate $A_{3\text{He}}$, by applying data for release efficiency of $^3$He, grain and water densities and porosity, as shown above for $^4$He.

The release efficiency $\Lambda_{3\text{He}}$ describes the degree to which He produced in minerals by the decay of U and Th is released into pore water. A value $\Lambda_{3\text{He}} = 0$ means full retention of He in minerals, and
$\Lambda_{He} = 1$ means total release of all produced He into the pore water. In previous studies conducted in surficial, unconsolidated sediments (sands-silts or clay-rich tills; Solomon et al. 1996, Sheldon et al. 2003, Hendry et al. 2005b), it was concluded that minerals and not the pore water are the main reservoir of $^4$He, which is inherited from the protolith and so was produced at times predating sediment deposition. These studies concluded that the high $^4$He contents in minerals record the long-term retention of $^4$He in grains derived from the crystalline protolith, and therefore a limited release efficiency $\Lambda_{He}$. Similarly, Lehmann et al. (2003) and Tolstikhin et al. (2005) analysed $^4$He contents of pore waters and quartz grains from Permo-Carboniferous sandstones in Switzerland and concluded that quartz is an important $^4$He reservoir, and that $^4$He concentrations in quartz and pore water equilibrate after ca. 0.1 Ma at the specific site studied.

In contrast, data from Opalinus Clay at Mont Terri and Benken and from the Callovo-Oxfordian at Bure indicate that He essentially resides in pore water, whereas the contents in minerals are small. He contents were measured in pore water by core outgassing (see Appendix A2.9) and in the total saturated rock (complete fusion at 1700 °C). The comparison of the resulting data sets indicated that 94 – 98 % of $^4$He and 94 – 97 % of $^3$He in Opalinus Clay samples from Mont Terri reside in pore water (Rübel & Lehmann 2003). In the Callovo-Oxfordian at Bure, the fraction amounts to 95 % (Bigler et al. 2005). Therefore, the release efficiency $\Lambda_{He}$ is close to 1 in these formations.

The explanation of these seemingly contradictory interpretations lies in the differences of the sedimentary facies and in grain size. Glacial tills are typically not well sorted and contain, apart from clay-size particles, coarser-grained fractions. Sheldon et al. (2003) report 30 – 40 % silt, 5 – 10 % sand and <5 % gravel-sized particles in their "clay till". The studies of Solomon et al. (1996), Lehmann et al. (2003) and Tolstikhin et al. (2005) were targeted at sandy lithologies. In contrast, Opalinus Clay and the Callovo-Oxfordian are, as all other formations considered in this report, marine sediments deposited in a low-energy environment and therefore fine grained, well sorted and essentially devoid of sand-size quartz particles. For these reasons, it is assumed that the release efficiency $\Lambda_{He}$ is 1 for all formations considered in this report.

### A4.3.3 Solubility in pore water and redistribution by diffusion and advection

He in pore water redistributes by diffusion and by advection if the system is sufficiently permeable. In theory, it could form a discrete gas phase if the cumulative amount exceeds the solubility at the ambient fluid pressure. The Henry’s Law constant for dissolution of He in water is 0.07E-4 moles He per mole water at 10 °C and $P_{He} = 1$ bar and is fairly constant with temperature up to at least 50 °C (Wilhelm et al. 1977). This is reduced only slightly due to ‘salting out’ in saline water – about 25 % reduction in solubility per mole of NaCl (Smith & Kennedy 1983). Therefore, for example, at 300 m depth and hydrostatic pressure, a solubility of 1.2E-5 mol$_{He}$/cm$^3$$_{water}$ (0.27 cm$^3$ STP/g$_{water}$) would have to be exceeded for bubbles of He to form. Typical pore-water concentrations of He are several orders of magnitude less than this (see below). If a discrete gas phase of another gas, e.g. CO$_2$ or CH$_4$, exists, then He would partition into that. However, it is likely that He disperses by diffusion or advection in many systems before the threshold concentration for gas solubility is exceeded.

The diffusion coefficient of He is higher than that of other aqueous solutes, so its rate of diffusive redistribution in low permeability rocks is faster than normal hydrochemical mixing (see Appendix A3.2). Higher-permeability rocks in which advective ground-water movement occurs are likely to have lower $^4$He concentration because the water is relatively younger. Thus, $^4$He concentration gradients in sedimentary rocks develop between low-permeability ‘source’ layers and higher-
permeability ‘sink’ layers. He redistribution locally between waters in low- and higher-permeability formations will lower and raise apparent He accumulation ages, respectively.

### A4.3.4 He fluxes, accumulation and pore-water ages

At a large scale, He is being redistributed through the crust and lost from the Earth’s surface to the atmosphere. A plausible conceptual model for the distribution is the consideration of a steady-state combination of mantle flux, \textit{in-situ} production and advective/diffusive fluxes. At greater depths, the fluxes of $^3$He and $^4$He are likely to be controlled by diffusion, and thus concentration gradients must be sustained by in-diffusion of He from greater depths to drive the diffusive upward movement of He – hence the analogy with heat transfer. This simplistic pattern of diffusion along a uniform vertical concentration gradient is interrupted by zones of higher permeability and horizontal advective movement, \textit{i.e.} aquifer layers, which act as sinks for the flux from below and also, possibly, for He produced in the overlying aquitard layer. The overlying layers are completely or partially isolated from the deeper He flux.

Four conceptual models for He accumulation in an argillaceous formation sandwiched between aquifers can be envisaged and are illustrated in Figure A4.3-1:

1. **Influx from underlying units.** In this model, the He contents of pore waters in the argillaceous formation will suggest accumulation ages that are probably too high because the He concentration in the argillaceous unit is enhanced by the flux from below and lateral removal of He by the lower aquifer is insignificant. The concentration of He represents a maximum pore water age which can be adjusted to a more realistic age if the upwards flux of He can somehow be measured.

2. **He removal in the upper aquifer.** He contents of pore waters in the argillaceous formation are greatly reduced by diffusive loss into the upper aquifer in which the concentration is kept low by lateral flushing. Upwards flux of He from underlying units may be a significant part of the He budget in the argillaceous formation. The accumulation age in the argillaceous formation may be higher or lower than pore-water age, depending on the proportion of He coming from underlying units and the degree of out-diffusion towards the upper aquifer. The loss of He by diffusion is only slightly faster than the movement of other solutes and the diffusive mixing of water (as shown by $^{18}$O and $^2$H). Therefore the He accumulation age in the upper parts of the argillaceous formation may be a useful lower estimate of water age and solute residence times.

3. **In-situ production and out-diffusion to both aquifers.** In this model, \textit{in-situ} production and out-diffusion control the He contents. The peak He concentration will be lowered to some degree from total accumulation by out-diffusion towards upper and lower bounding aquifers. Therefore He content at the peak represents a minimum age of pore water.

4. **Out-diffusion and \textit{in-situ} production, with the upper aquifer being less active hydrodynamically than the lower aquifer.** He in the upper aquifer is controlled by out-diffusion from the argillaceous formation and \textit{in-situ} production. He content at the top of the argillaceous formation and in the aquifer represents a water age and solute residence time for this part of the sequence. This is the case in the eastern Paris Basin sequence, discussed below.

These conceptual models for He in thick argillaceous formations bounded by aquifer layers are rather similar to the 2-D numerical models for He in regional scale sedimentary basins that have been developed by Zhao \textit{et al.} (1998).
Figure A4.3-1: Illustrative depth profiles for different conceptual models of He distribution through argillaceous formations with different boundary conditions.

He in aquifer sequences

He data from several studies in deep aquifers indicate patterns of progressively increasing concentrations with depth, i.e. combinations of models (1) and (2). The depth variations within aquifers are indicative of hydrodynamic dispersion coupled with lateral advection and with varying contributions from underlying formations.

The excess of He over in-situ production with increasing depth in an aquifer (<300 m depth) in Michigan, USA, is interpreted to be sourced from the underlying sedimentary sequence (Ma et al. 2005). The He flux from the underlying fractured low-permeability formations is estimated to be 2.26E-14 mol/m²/s, and the corresponding flux of $^3$He is many orders of magnitude lower at 1.4E-21 mol/m²/s. In this case, vertical He migration is coupled with advective cross-formational movement of saline ground water in fractures. The He flux is similar to the general He flux in the crust, 4.65E-14 mol/m²/s, estimated by analogy with heat flow by O’Nions & Oxburgh (1983).

The He upwards flux at the base of layered aquifers of Mesozoic age in the central Paris Basin is estimated to be 1.27E-13 mol/m²/s, rather higher than the average crustal flux (Castro et al. 1998a, b). Within the same aquifer sequence, the He flux out of the Jurassic Dogger aquifer is estimated to be 6.3E-15 mol/m²/s, indicating that He is removed by advective lateral flow in the deeper Triassic aquifer (Marty et al. 1993). In the eastern part of the Paris Basin, the He flux from the crystalline basement into the aquifer sequence is estimated to be 1.6E-13 mol/m²/s, with He concentrations increasing with depth to 2.8E-8 mol/g_water (6.3E-4 cm³ STP/g_water) in the Triassic aquifer (Marty et al. 2003). Corresponding $^3$He concentrations in the Triassic aquifer are 1.3E-15 to 1.1E-14 mol/g_water, enhanced by a component of mantle-derived He in this tectonically-active area adjacent to the Rhine graben. $^3$He in the overlying Dogger aquifer is much lower at 1.3E-17 to 2.3E-16 mol/g_water, proving that it is effectively isolated from the Triassic aquifer. He content of ground water in the Dogger aquifer where it is remote from the basin edge and deeper is 7.27E-9 mol/g_water, which is higher than
contents in the Triassic aquifer at similar depths in other locations. This is evidence that the Dogger aquifer is less active hydrodynamically than the Triassic aquifer, and is isolated from it by the intervening sequence of Upper Trias and Lias shales and clays (which includes the Callovo-Oxfordian formation). A migration time of several million years through the 600 m thick aquitard is estimated from the accumulation ages for He in Dogger ground waters (Marty et al. 2003). This may be a case of model (4) in Figure A4.3-1, although there is not a set of data for He in a single borehole profile through both aquifers and the aquitard.

In sedimentary sequences which directly overlie crystalline basement rocks, the estimated He flux may be considerably higher due to the locally higher U and Th contents of such rocks. For example, the upwards diffusive flux of He into the Molasse basin sediments in Austria has been estimated as about 1.3E-7 mol/m²/s (Andrews et al. 1985). The maximum He concentrations measured in ground-water samples from the Molasse aquifers was 2.6E-9 mol/cm² water (5.8E-5 cm³ STP/gwater), from the Jurassic Malm at >1 000 m depth.

The deep basinal aquifers of the eastern Pannonian Basin in Hungary also have He contents which are enhanced by migration from underlying rocks. He contents range from 1.8E-12 to 1.8E-9 mol/g_water (4.0E-8 – 4.0E-5 cm³ STP/g_water) and the estimated vertical He flux is 1.2E-15 to 7.5E-15 mol/m²/s (Martel et al. 1989, Stute et al. 1992). As in the case of the eastern Paris Basin, there is evidence from ³He that a proportion of the He flux has a much deeper source. Using ³He/⁴He measurements, it is estimated that 10 – 50 % of the He flux is attributable to a mantle origin, probably related to ongoing or recent tectonic activity at the base of this extensional basin.

**He in low-permeability rocks**

The great majority of He studies have been carried out in ground waters from aquifers, so there are few examples to illustrate the above conceptual models considering low-permeability formations. One of the few studies has been carried out in Triassic claystones overlying limestones of Muschelkalk age at Morsleben, Germany (Osenbrück et al. 1998). The He profile over a 700 m depth interval is shown in Figure A4.3-2. He concentrations extracted from drillcores increase with depth to 8.4E-7 mol/g_water (1.9E-2 cm³ STP/g_water). The He flux through the Triassic claystones is estimated to be 2.8E-15 mol/m²/s, i.e. generally smaller than in the aquifer sequences described above. In this case, Zechstein (late Permian) salt probably underlies the whole sequence (below the section shown in Figure A4.3-2) and the lower He flux is thought to be due, amongst various factors, to the very low diffusion coefficient of He in halite.

He concentrations in ground waters in Permo-Triassic formations at 859 to 1 408 m depth in the Permo-Carboniferous trough of northern Switzerland, underlying the Jurassic formations including the Opalinus Clay, range from 8E-11 to 2E-7 mol/cm² water (1.8E-6 – 4.5E-3 cm³ STP/g_water) (Pearson et al. 1991, Tolstikhin et al. 1996). Ground waters in the crystalline basement at 1 500 – 2 200 m depth contain He at about 1E-7 mol/cm² water (2.2E-3 cm³ STP/g_water), so the upwards flux of He towards the Opalinus Clay appears to originate in the deep sedimentary rocks rather than in the crystalline basement. This interpretation is contrary to that of ³He/⁴He data from ground waters in the Permo-Triassic formations which have been interpreted as having a crystalline signature (Pearson et al. 1991). Whatever the origins of the helium, the varying concentrations illustrate the discontinuous nature of He flux through the crust, with vertical fluctuations between sources and sinks, depending on the in-situ production rates and lateral advective dispersion in each formation in the crustal sequence.

The flux of He through a Tertiary tuffaceous and argillaceous sequence at Rokkasho in the Shimokita peninsula in northern Japan has been estimated to be 7E-15 mol/m²/s (Mahara & Igarashi 2003). Ground-water samples from exploratory boreholes to 352 m depth have He concentrations up
to 7E-9 mol/gwater (1.6E-4 cm³ STP/gwater) (Figure A4.3-3). The depth profile shape suggests that this is an example of model (2) in Figure A4.3-1. The excess of ³He over expected crustal radiogenic concentration increases regularly with depth and overall the ³He/⁴He measurements indicate that the regional flux of He consists of 94 % radiogenic and 6 % mantle components, which presumably reflects the location on the periphery of a volcanic province.

The flux of He into the base of the sedimentary sequence of aquifers and aquitards in the Great Artesian Basin in Australia has been estimated at 6E-14 mol/m²/s, which is very similar to the crustal production rate based on the heat flow analogy (Torgersen & Clarke 1985). Deep in the basin, the basal Jurassic aquifer has He contents up to 2.2E-8 mol/cm³ water (4.9E-4 cm³ STP/gwater) in which the flux from below is a significant component (Torgersen et al. 1992, Bethke & Zhao 1999).

He distribution through a more shallow clay system is illustrated by a study of dissolved gases in the upper 90 m of a 180 m thick Pleistocene till and Cretaceous clay-rich aquitard in Saskatchewan, Canada (Hendry et al. 2005b). Gas samples were collected from in-situ diffusion cells and also by water sampling from piezometers. He concentrations increased with depth to about 3E-10 mol/gwater (6.7E-6 cm³ STP/gwater) at 76 m depth. Using a 1-D diffusion model, the best fit to observed data is given by a model with 87 % of He produced in situ and 13 % coming from upwards diffusion from putative higher concentrations in the deeper Cretaceous aquitard. The flux into the Pleistocene till from the Cretaceous clay is estimated to be 5E-16 mol/m²/s which is about 2 orders of magnitude lower than the average crustal flux. From this and from the fact that these are shallow clays, it is logical to conclude that underlying aquifers have diverted the major part of the crustal flux.

Helium fluxes from the case studies discussed above are summarised in Table A4.3-1.

Figure A4.3-2: Depth profile of He in Triassic sedimentary rocks at Morsleben, Germany

Adapted from Osenbrück et al. (1998)
A4.3.5 Implications for the quantitative treatment of He concentration profiles

Unlike the other natural tracers of interest in this report, He originates from production within the rocks. It does not derive from, and therefore does not “trace”, the sedimentary depositional environment. He content of ground water in an aquifer or pore water in an argillaceous formation derives from in-situ production or by transport (by diffusion or by fluid advection) of He within the formation or from other formations. Production and distribution of helium vertically through a sedimentary rock sequence has occurred since deposition and is expected to be at steady state if the system has remained stable and unperturbed for long enough. Steady state refers to the situation in which in-situ He production from the U and Th decay chains and He loss due to out-diffusion cancel out each other, leading to a time-invariant, smooth He concentration profile. The time since the last perturbation that it takes for steady-state He distribution to be re-established via diffusion depends on the size and properties of the system and is typically in the range of several Ma or more. A perturbation that is evident as a deviation from steady-state vertical distribution of He could have been a transient tectonic episode in the past that affected He migration or it could be a sharp change of concentration and of the concentration gradient of He due to lateral migration in an aquifer layer.
The in-situ origin, high steady-state concentrations in pore waters relative to concentrations in the atmosphere and in young ground waters in aquifers, and the sensitivity to perturbations of He as a dissolved gas, make He a good diagnostic tool of diffusion in low-permeability rocks. The shape and continuity of the profile and the consistency of maximum concentrations with in-situ production (possibly with an additional component of He that has migrated from greater depth) are the main indicators. External boundaries needed for a quantitative interpretation are generally an upper low concentration boundary which may be a shallow aquifer or be controlled by direct exchange with the atmosphere, and a deeper high concentration boundary which is at the base of the clay rocks and has either no vertical He flux, i.e. zero concentration gradient, or a known upwards flux of He from rocks at greater depth. The boundaries that are detected in the He profile and used to build the He model should also be considered for incorporation in the other natural tracer models, if not already apparent. In many cases, He might be the more sensitive indicator of boundaries and advective processes.

Table A4.3-1: Summary of crustal fluxes of He based on literature data

<table>
<thead>
<tr>
<th>Site</th>
<th>Vertical He flux [mol/m²/s]</th>
<th>Reference</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average crust</td>
<td>4.65E-14</td>
<td>O’Nions &amp; Oxburgh (1983)</td>
<td>Estimated from correlation with heat flow</td>
</tr>
<tr>
<td>Superdeep KTB borehole, Bavaria, Germany</td>
<td>3E-14 – 5E-14</td>
<td>Drescher et al. (1998)</td>
<td>Crustal flux at KTB site</td>
</tr>
<tr>
<td>Michigan Basin, USA</td>
<td>2.26E-14</td>
<td>Ma et al. (2005)</td>
<td>Flux from underlying fractured shales into aquifer at &lt;300 m depth</td>
</tr>
<tr>
<td>Central Paris Basin, France</td>
<td>1.27E-13</td>
<td>Castro et al. (1998a,b)</td>
<td>Flux at base of Mesozoic (Triassic-Jurassic) aquifers</td>
</tr>
<tr>
<td>Eastern Paris Basin, France</td>
<td>6.3E-15</td>
<td>Marty et al. (1993)</td>
<td>Flux from Jurassic Dogger aquifer</td>
</tr>
<tr>
<td>Eastern Paris Basin, France</td>
<td>1.6E-13</td>
<td>Marty et al. (2003)</td>
<td>Flux at base of Mesozoic (Triassic-Jurassic) aquifers</td>
</tr>
<tr>
<td>Triassic argillaceous / limestone sequence at Morsleben, Germany</td>
<td>2.8E-15</td>
<td>Osenbrück et al. (1998)</td>
<td>Flux through Triassic claystones; underlying salt limits deep He flux</td>
</tr>
<tr>
<td>Molasse Basin, Austria</td>
<td>1.37E-7</td>
<td>Andrews et al. (1985)</td>
<td>Flux from underlying basement which has high U, Th contents</td>
</tr>
<tr>
<td>Pannonian Basin, Hungary</td>
<td>1.2E-15 – 7.5E-15</td>
<td>Martel et al. (1989), Stute et al. (1992)</td>
<td>Flux from basement into the sedimentary sequence</td>
</tr>
<tr>
<td>Tuffs at Rokkasho, Japan</td>
<td>7E-15</td>
<td>Mahara &amp; Igarashi (2003)</td>
<td>Flux through volcanic tuffs and argillaceous rocks</td>
</tr>
<tr>
<td>Great Artesian Basin, Australia</td>
<td>6E-14</td>
<td>Torgersen et al. (1992), Bethke &amp; Zhao (1999)</td>
<td>Flux from basement into the sedimentary sequence</td>
</tr>
<tr>
<td>Pleistocene till in Saskatchewan, Canada</td>
<td>5E-16</td>
<td>Hendry et al. (2005b)</td>
<td>Flux into till from Cretaceous clay; underlying aquifers remove He laterally</td>
</tr>
</tbody>
</table>
A4.4 Chlorine isotopes: Systematics of $\delta^{37}\text{Cl}$ values in natural water and modelling approaches

A4.4.1 Values of $\delta^{37}\text{Cl}$ in natural waters

Standard Mean Ocean Chloride: Standard for Cl isotopes

The relative abundance of $^{37}\text{Cl}$ is expressed in $\delta$ notation relative to sea-water chloride (SMOC, standard mean ocean chloride), where

$$\delta^{37}\text{Cl} = 1000 \left( \frac{R}{R_{\text{SMOC}}} - 1 \right),$$

where

- $R = \text{molar ratio } ^{37}\text{Cl} / ^{35}\text{Cl} \text{ in the sample}$
- $R_{\text{SMOC}} = \text{molar ratio } ^{37}\text{Cl} / ^{35}\text{Cl} \text{ in the standard}.$

There is an ongoing debate on how homogenous the $\delta^{37}\text{Cl}$ value of sea water is. Coplen et al. (2002) note in an overview paper that sea water is generally considered to be isotopically homogeneous to within about ±0.15 ‰, but that values as high as +0.94 ‰ were also reported. Godon et al. (2004) conclude from their analysis of 24 sea-water samples from worldwide locations that, within the analytical error of ±0.1 ‰, sea water is in fact a homogeneous reservoir with a mean value of 0 ‰, and that the unusually high values reported could have been strongly influenced by hydrothermal plumes. Shirodkar et al. (2006), on the other hand, reported $^{37}\text{Cl}$ values for surface (uppermost 1 m) ocean waters from 51 worldwide locations between -0.76 ‰ and +0.74 ‰ (mean ± SD of 0.039 ± 0.04 ‰). Based on a multivariate statistical analysis, they could link the variation to local air-sea flux variables, such as wind speed and water temperature.

The variation of $\delta^{37}\text{Cl}$ of sea water in the past is not well known. Eastoe et al. (2001) conclude from the chlorine isotope content of Jurassic salt that Jurassic sea water had a $\delta^{37}\text{Cl}$ value of 0 ‰, that is, the same value as modern sea water.

Slightly varying values for $R_{\text{SMOC}}$ can be found in the literature. Coplen et al. (2002) give molar fractions in SMOC of 0.75779 for $^{35}\text{Cl}$ and of 0.24221 for $^{37}\text{Cl}$ (the amount of $^{36}\text{Cl}$ is negligible). From these values, a $R_{\text{SMOC}}$ value of 0.31963 can be calculated. Groen et al. (2000) used a value of 0.31978, citing Eggenkamp (1994). Clark & Fritz (1997) give $R_{\text{SMOC}} = 0.324$, but this value is inconsistent with the abundances given in the same text. From the latter, a value of $R_{\text{SMOC}} = 0.3198$ is calculated. We consider the value of 0.31963 from Coplen et al. (2002) as the most reliable and based all our simulations of $\delta^{37}\text{Cl}$ values on this number. We checked the sensitivity of the results on the used value of $R_{\text{SMOC}}$ (see Figure A4.4-1). Luckily, using a slightly different value for $R_{\text{SMOC}}$ has a negligible effect on the simulation results (fifth or sixth significant digit of delta value).

Fractionation of Cl isotopes

Cl isotopes are fractionated within the solution by molecular diffusion (e.g. Desaulniers et al. 1986, Kaufmann et al. 1993, Eggenkamp et al. 1994), which appears to be the most important process.
for Cl in ground and pore waters at shallow depths and/or low temperatures. A fractionation by ultrafiltration during advective flow has been postulated by Phillips & Bentley (1987) but has never been experimentally confirmed. Precipitation of chloride minerals is another fractionation mechanism at low temperatures (Coplen et al. 2002). Eggenkamp et al. (1995), investigating the isotope fractionation in evaporites, showed that the total fractionation between NaCl, KCl, or MgCl₂·6H₂O and the corresponding solutions is small but significant. From these data they calculated δ³⁷Cl values of brines (typically depleted with respect to δ³⁷Cl) and precipitates (typically enriched) and isotope fractionation factors during the formation of evaporites. Schauble et al. (2003) calculated the equilibrium fractionation for various compounds based on published vibrational spectra and molecular modelling results and came to similar conclusions, that is, an enrichment of the solids in ³⁷Cl, for silicates containing Cl. According to Hesse et al. (2006), Eggenkamp et al. (1999) found ³⁷Cl-enriched clays in Jurassic sediments. Equilibrium isotope exchange between different phases may occur in hydrothermal fluids. Finally, biochemical reactions that involve – mostly anthropogenic – chlorinated organic compounds can also lead to a fractionation of chlorine isotopes.

Range of observed δ³⁷Cl values

According to Coplen et al. (2002), the range of δ³⁷Cl values for naturally occurring samples is about 16 ‰, from about -8 ‰ to +8 ‰. Positive values were found in rock and sediment samples (range of about 0 to +8 ‰), in qualitative agreement with the discussion above, whereas ground, surface, pore, and oil formation waters range between about -8 ‰ and +3 ‰. The largest value for a sample of terrestrial origin of +7.5 ‰ was reported for Cl in a smectite from the Costa Rica rift system. The enrichment was attributed to a stronger bonding of ³⁷Cl in the solid phase as compared to the solution. The lowest value of -7.7 ‰ for a natural terrestrial material was reported for pore water from the Nankai subduction zone, and is similarly attributed to a preferred incorporation of ³⁷Cl in clays and the corresponding depletion of ³⁷Cl in the pore water.

Figure A4.4-1: Influence of value used for RSMOC and of the way the chloride concentrations were calculated on simulated δ³⁷Cl profiles (Benken example)

Curves for evolution times of 0.5 and 1 Ma are shown. Virtually no differences are visible for the different simulations.
A4.4.2 Modelling the spatial $\delta^{37}\text{Cl}$ distribution in pore water

Processes considered and modelling approaches

As mentioned, molecular diffusion is considered to be the most important fractionation mechanism for Cl isotopes in ground and pore waters at low temperatures. Therefore, our modelling of $\delta^{37}\text{Cl}$ only considered this process. The $\delta^{37}\text{Cl}$ values used to represent the isotope contents in pore waters can be considered as non-linearly scaled and shifted concentrations of $^{37}\text{Cl}$. The non-linearity of this scaling originates from the fact that not only $^{37}\text{Cl}$, but also the lighter reference isotope $^{35}\text{Cl}$ typically varies considerably as a function of time and space. As a consequence, it is not possible to apply the transport equations of Section 4.2 directly to the $\delta^{37}\text{Cl}$ values. Instead, two independent simulations for each isotope, $^{35}\text{Cl}$ and $^{37}\text{Cl}$, have to be performed that use the individual transport coefficients. Advection velocity and hydrodynamic dispersion are considered to be equal for both isotopes, but their diffusion coefficients differ (see below). Only in cases where the background concentration of Cl is approximately constant, the scaling introduced by the $\delta$ values is about linear and the $\delta^{37}\text{Cl}$ values can be modelled directly.

Ratio of pore diffusion coefficients $D_p$ of $^{35}\text{Cl}$ and $^{37}\text{Cl}$

The fractionation factor for diffusive transport of two isotopes is given as the ratio of the corresponding diffusion coefficients of the isotopes. According to Graham’s law, which was empirically found for the ‘effusion’ (diffusion of a single component) of a gas and theoretically confirmed for dilute gases by kinetic theory, diffusion coefficients are inversely proportional to the square root of the mass $m$ of the diffusing molecule. For diffusion of one gas in another gas, the effect of collisions between the different molecules can be considered by relating the diffusion coefficient to the reduced mass $\mu = m/(m + M)$ instead of the molecular mass $m$, with $M$ being the molecular mass of the second gas (Craig & Gordon 1965, cited in Richter et al. 2006). The corresponding relations have also been used to estimate diffusion coefficients of solutes in water. However, the applicability of both laws to solutes is uncertain because, depending on the solute, collisions with solvent molecules and intermolecular forces between solutes and solvents are important. Jähne et al. (1987) found experimentally that diffusion coefficients of dissolved noble gases depend regularly (according to Graham’s law) on the molecular masses, whereas those of dissolved $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ deviate. Richter et al. (2006) mention that the radius of a molecule in solution is very likely more relevant than its mass. Diffusion coefficients may then be estimated from the Stokes-Einstein relation, which seems to be adequate as long as the radius of the diffusing species is clearly larger than that of water (see, e.g., Flury & Gimmi 2002).

Anions and cations in solution are generally hydrated. Accordingly, it is often assumed that the hydrated radius or the hydrated mass should be used when estimating the diffusion coefficients. For chlorine, a fractionation factor $D_p(^{35}\text{Cl})/D_p(^{37}\text{Cl})$ of 1.0093 is calculated when assuming a hydration with four water molecules (Desaulniers et al. 1986), or of 1.0080 or 1.0070 with five or six water molecules (Eggenkamp et al. 1994). However, experimentally determined values are always lower. Desaulniers et al. (1986), Eggenkamp et al. (1994) and Groen et al. (2000) report values between 1.0009 and 1.0030 obtained from mobility measurements. From modelling $\delta^{37}\text{Cl}$ profiles in low-permeability Quaternary glacial till deposits in Ontario, Desaulniers et al. (1986) found a value of 1.0012. For other sediments, Eggenkamp et al. (1994) derived a value of 1.0023, and Groen et al. (2000) a value of 1.0027. Richter et al. (2006) measured fractionation factors of Cl in the laboratory; they obtained a value of 1.00143±0.00080.
For the present study, we use 1.002 as a reference value, but also made some simulations using other fractionation factors. The choice of the fractionation factor strongly affects the results of transport models considering diffusion, and this adds to the uncertainty related to the interpretation of natural $\delta^{37}\text{Cl}$ profiles.

**Boundary and initial conditions**

Because two simulations, one for $^{35}\text{Cl}$ and one for $^{37}\text{Cl}$, have to be performed to model $\delta^{37}\text{Cl}$ values, a total of six boundary and initial conditions is required for a finite domain, and not just three as in case of total chloride. In addition to the three conditions for $\text{Cl}^-$, another three are needed for the delta values. Unfortunately, it is even more difficult to constrain the evolution of $\delta^{37}\text{Cl}$ from palaeohydrogeological arguments than of total $\text{Cl}^-$ because the possible fractionation mechanisms during diagenesis or compaction, for instance, are not yet well understood. Accordingly, the simulation of $\delta^{37}\text{Cl}$ values may help to constrain possible scenarios and to interpret other results, but it also introduces new uncertainties.

Chloride concentrations at boundaries or time = 0 within a domain are typically given in mass of chloride per volume of water (e.g. g/L), whereas $\delta^{37}\text{Cl}$ values are based on mole fractions. In order to derive the boundary conditions for $^{35}\text{Cl}$ and $^{37}\text{Cl}$ correctly, the mass concentrations of Cl have to be first transformed to molar concentrations and then split into the two isotope concentrations according to the $\delta^{37}\text{Cl}$ value. For the first step, we considered the corresponding $\delta^{37}\text{Cl}$ values to calculate the local average molecular weight of Cl, instead of just using the global average molecular weight of Cl given in periodic tables. The local average molecular weight was calculated as

$$MW_{l,\text{Cl}} = \frac{^{35}\text{Cl}}{\text{Cl}} MW_{^{35}\text{Cl}} + \frac{^{37}\text{Cl}}{\text{Cl}} MW_{^{37}\text{Cl}},$$

where $MW_{^{35}\text{Cl}} = 35$ g/mol and $MW_{^{37}\text{Cl}} = 37$ g/mol. The mole fractions $^{35}\text{Cl}/\text{Cl}$ and $^{37}\text{Cl}/\text{Cl}$ were calculated from the local $\delta$ values as

$$\frac{^{35}\text{Cl}}{\text{Cl}} = \frac{1}{1 + \left(\frac{\delta^{37}\text{Cl}}{1000} + 1\right) R_{\text{SMOC}}}$$

and

$$\frac{^{37}\text{Cl}}{\text{Cl}} = 1 - \frac{^{35}\text{Cl}}{\text{Cl}}.$$

The molar Cl concentration was then obtained as

$$\text{Cl}[\text{mol/L}] = \frac{\text{Cl}[\text{g/L}]}{MW_{l,\text{Cl}}[\text{g/mol}]},$$

and the molar isotope concentrations could be calculated with this value from the corresponding mole fractions.
Applying the δ values to the mass instead of the molar concentrations, or using the global instead of the local molecular weight for Cl has, fortunately, only a very small effect on the simulated results (fifth or sixth significant digit for delta values), as shown in Figure A4.4-1.

**Numerical precision of simulations**

Numerical solutions of partial differential equations are only approximations of the true solutions. For simulations of Cl, this is usually not of a big concern. However, when calculating δ^{37}Cl values from ratios of Cl concentrations, relatively small numerical errors in Cl concentrations may amplify, especially because δ^{37}Cl values are typically in the order of per mills only. Thus, care has to be taken that the achieved numerical precision is high enough in order not to introduce any artefacts. For the simulation code FLOTRAN, the desired numerical precision can be set by a number of parameters, notably the keywords `tol` and `dcmx`. According to our experience, these parameters should be set such that in the end a relative tolerance of 1E-5 or better is achieved with respect to the Cl concentrations (unless these concentrations are close to zero). In any case, convergence of the obtained δ^{37}Cl values for decreasing values of the relative concentration tolerance `dcmx` should be checked. Figure A4.4-2 illustrates the effect of accepting a too large tolerance in the numerical solution.

![Figure A4.4-2: Effect of numerical precision on simulations of δ^{37}Cl transport with FLOTRAN (Benken example)](image)

Curves indicate evolution times of 1, 1.4, 2 and 3 Ma. The precision was varied by changing the parameter `dcmx` (relative tolerance). The simulations converge and become identical to the results obtained with a code based on a Laplace-transformed solution for `dcmx` lower than 1E-5.
A5.1 Overview of FLOTRAN and the FLOW and TRANS modules

The simulations presented in this report were carried out with the computer code FLOTRAN, written by Peter Lichtner (Lichtner 2004). FLOTRAN can simulate time-dependent, coupled thermal-hydrologic-chemical processes in variably saturated, non-isothermal porous media in up to three spatial dimensions. FLOTRAN calculates multi-component reactive transport involving aqueous, mineral or gaseous species. It can also be used for systems involving two-phase flow, that is systems containing a liquid and a gaseous phase, such as in the unsaturated zone above the water table, and for systems consisting of fractured porous media. Both Cartesian and cylindrical model geometries can be used.

FLOTRAN incorporates a wide range of features and is one of the most powerful and complex reactive transport codes available today. Even though only a fraction of the features of FLOTRAN are used in the simulations described in this report, a brief overview of the capabilities of the code is given below, in order to outline the possibilities for implementing additional processes to the scenarios discussed here at later stages.

FLOTRAN consists of two distinct modules: The first module (FLOW) solves the flow equation for water and (optionally) air, and the heat transport equation. The second module (TRANS) solves the mass conservation (i.e. transport) equations for a multi-component geochemical system. This module is the chemistry solver which is used for calculating the speciation in the aqueous phase in local chemical equilibrium, kinetic mineral dissolution/precipitation reactions, gaseous speciation, redox reactions as well as ion exchange, surface complexation and sorption reactions. Both modules can operate in stand-alone mode or can be coupled to assess the interaction between fluid flow, temperature distribution, solute transport and fluid/rock interaction. The coupling between the TRANS and the FLOW modules is either loose – i.e. transient flow and temperature fields are sequentially passed from FLOW to TRANS – or full – i.e. changes in porosity and permeability from mineral precipitation/dissolution reactions are passed from TRANS to FLOW.

FLOTRAN is continuously being developed further. We decided to use FLOTRAN at the University of Bern because of its wide range of capabilities and because the source code was made available to us. This allowed us to carry out modifications, testing and corrections of the code if necessary. We can customise the code to solve a specific problem of interest. For major changes of the code, the author Peter Lichtner has been very supportive and helpful.

A5.1.1 The TRANS module

In stand-alone mode, the TRANS module incorporates advective/dispersive and diffusive transport in the liquid or both gaseous and liquid phase. TRANS may use a constant flow velocity read
from an input file or may read an externally calculated steady-state flow field. The former option is useful for simulating 1D scenarios where fluid flow is simulated along a flow line of the fluid, whereas the latter allows for simulations in up to three spatial dimensions.

The diffusion coefficient is temperature dependent and optionally species dependent. The tortuosity is allowed to vary in space and to be isotropic or anisotropic. Consequently, the pore diffusion coefficient $D_p$ can be spatially heterogeneous or can vary in the principal coordinate directions. This makes it possible, for instance, to account for anisotropic diffusion coefficients in a bedded sedimentary rock.

Homogeneous aqueous reactions by default are assumed to be sufficiently fast to be in local equilibrium, but a kinetic formulation for aqueous reactions is also available. A kinetic formulation is used for describing mineral dissolution/precipitation reactions. A kinetic formulation is a more general approach to modelling fluid/rock interaction because fast reactions rates can be used to approximate local equilibrium. The disadvantage of a kinetic formulation is that a reaction rate needs to be calculated for each mineral in the system. The reaction rate is a function of the saturation state of the mineral with respect to the fluid composition, the reactive surface area of the mineral, the temperature, the fluid composition (including the pH) and a rate constant at standard conditions. Whereas the saturation state and temperature are calculated during the simulation, the rate constant and the initial reactive surface area have to be input explicitly before starting a simulation. In contrast to thermodynamic properties, which are available for a wide range of minerals, kinetic properties such as the rate constant have only been measured for the most common minerals (e.g. quartz, feldspars). Other parameters, such as the reactive surface area of a mineral, tend to be site specific and vary with the type and properties of rock. However, they are virtually never measured in the field. It is the user’s task to calibrate mineral reaction rates such that the results are reasonable and/or agree with observations. One alternative is to use the local equilibrium assumption for fluid/rock reactions by considering fast reaction rates for all minerals. Some reactive transport codes and most speciation codes such as PHREEQC use an equilibrium formulation for mineral dissolution/precipitation reactions. However, it is well known that mineral dissolution/precipitation rates vary significantly, so that the equilibrium assumption can be a limitation, and the results of the calculations may be far more unrealistic than the kinetic formulation using uncertain reaction rates. In addition to the kinetic formulation of mineral dissolution/precipitation reactions, the code includes other rate laws that can be used for Monod kinetics, kinetic sorption and decay. TRANS can also be used for chemically heterogeneous media. This means that the mineralogical composition of the rock, mineral properties, porosity and the initial fluid composition are allowed to vary in space.

TRANS uses a range of solution algorithms based on the finite difference method. In this method, the model domain (i.e. the spatial representation of the natural system to be modelled) is discretised or divided into a grid of rectangular blocks. These blocks represent volumes over which material and system properties, such as pore-water composition, mineralogy, porosity, permeability, temperature, pressure etc. are assumed to be uniform. These blocks are also called representative elementary volumes (REVs). Properties are assigned to and solved at nodes that are centred in each of these blocks. Properties between neighbouring nodes are assumed to vary linearly. Because reactive transport is time-dependent by default, in addition to the spatial discretisation, time has to be discretised as well. There are several time-stepping algorithms available in TRANS. These include implicit and explicit methods and the operator splitting method, which solves transport and chemistry sequentially, that is it splits each time step into a transport time step and a reaction time step. Each approach has certain advantages and disadvantages, and the choice of time-stepping depends on the problem to be solved. Generally, the implicit time stepping is fast and not restricted by the Courant condition (meaning that a solute particle is not allowed to be transported beyond the length of a grid block during any single time step), which limits the time step in the explicit and operator-splitting
method. This means that implicit methods are well suited for simulating problems over geological
time scales. On the other hand, the computational requirements can be enormous in the global implicit
approach because the transport and reaction steps are solved simultaneously, and the system of
equations is stored in a single matrix equation. This is becoming less of an issue, however, as
computational memory and power are constantly increasing. The explicit scheme has the Leonard
Total Variation Diminishing (TVD) algorithm built in, which makes it suitable for high Peclet number
(i.e. advection dominated) systems. Because the size (i.e. the number of nodal points used to discretise
the model domain) of the problems solved in this report is small (generally <1 000), the implicit time-
stepping was used in all simulations presented here.

The solution of boundary-value problems requires the input of boundary conditions. Two types of
boundary conditions are available in the stand-alone TRANS module, a Dirichlet type (constant
concentration) or a zero flux type boundary condition. When the Dirichlet boundary condition is used,
the user fixes the concentrations of primary species in „ghost cells“ outside the model domain. When
diffusion is the only transport mechanism in the system, diffusive mass transfer can occur across the
boundary and depends on the concentration gradient across the boundary. If advection occurs into the
system at this boundary, the fluid entering the system has the composition specified by that boundary
condition. In contrast, if a zero-flux condition is specified, the concentration gradient across that
boundary is zero and the boundary is closed with respect to mass transport.

The user can also specify sources and sinks for mass and heat anywhere within the model
domain. The source/sink term is also time-dependent, which means temporal variations of mass/heat
input or extraction can be incorporated. This option is particularly useful for simulating the production
and accumulation of He from the radioactive decay of the U and Th decay chains in the rock. Details
of this option with respect to the accumulation of He are discussed below.

The solution of homogeneous aqueous reactions and heterogeneous mineral
precipitation/dissolution and gaseous speciation reactions require thermodynamic and molar properties
for each complex, mineral and gas in the system. These properties are read from an external database
that contains the molar volume and molar mass, the formulation of the dissociation or association
reactions and the log K (log of the equilibrium constant) at different temperature points for each
complex, mineral and gas. The chemical system is defined by a set of primary species spanning the
space in which chemical reactions occur. This means that primary species represent the basic building
blocks of all species, minerals and gases in the system. The primary species are also the primary
unknowns, and a reactive transport simulation requires that the concentration of each primary species
be either input explicitly or implicitly, such as through an equilibrium constraint by a particular
mineral. The chemical composition of a fluid can be fully described by the total concentration of each
primary species, so that only these need to be transported in any single transport step.

If all aqueous reactions are assumed to be in local equilibrium, the system of equations to be
solved consists of mass balance equations and thermodynamic relationships between the primary
species and aqueous complexes. These thermodynamic relationships are the laws of mass action for
which the equilibrium constant from the external database is needed. Similarly, the calculation of the
saturation state of a mineral, which constitutes a term in the rate equation, and the dissolution of a gas
phase into the solution require an equilibrium constant to be read from the database.

Because the equilibrium constant is temperature dependent, the database contains log K values at
different temperature points. For intermediate temperatures, FLOTRAN interpolates between the log
K values from the database. The equilibrium constant is also slightly pressure dependent, but most
chemistry simulation packages assume this dependence to be negligible and use log K values at a
pressure of 1 bar and along the steam saturation curve for temperatures above 100 ºC. In general, a
A thermodynamic database for FLOTTRAN can be constructed for any temperature range and pressure condition. Databases are also provided for implementation of the Pitzer equation for the correction of activity coefficients for high ionic strength solutions. Non-isothermal problems require the calculation of the fluid density as a function of temperature. TRANS uses the equation of state for pure water by Haar et al. (1980).

A5.1.2 The FLOW module

Even though not used in the simulations presented here, a short summary of the capabilities of the FLOW module is also included here. Some of the scenarios presented in this report included an advective component but it was assumed to be constant and spatially uniform, which means that the flow equation did not need to be solved, and so, even for these cases, there was no need to apply FLOW.

For transient and/or heterogeneous hydrological systems in which advection plays a role, the user needs to solve for the flow field explicitly and to feed it into TRANS. The module FLOW solves the flow equation for liquid and gas and the energy balance equation for non-isothermal systems. Heat transport is either convective or conductive, and the equation of state for pure water implemented in FLOW allows for temperature ranges of 1 to 1200 °C and pressures below 165 bars. In addition to pure liquid systems, FLOW also has the capability of simulating two-phase and even single-phase gas flow. This allows the user to account for processes in the unsaturated zone above the water table. FLOW incorporates several options for representing fractured porous media. One option is the representation of the fracture and matrix continua as an equivalent single continuum. This implies that the capillary pressure of the matrix equals that of fractures within an REV. Two forms of dual continuum models are implemented each representing a distinct formulation of the connectivity of the matrix.

The calculation of mass transport in the liquid phase is based on Darcy’s law, which includes capillary, gravity and viscous forces. Heterogeneous media can be defined through the permeability and porosity distribution. The permeability can also be anisotropic. Similarly, the thermal properties of the medium (e.g. thermal conductivity) can vary in space. Boundary conditions include Dirichlet (constant properties) and Neumann (constant flux) types and are allowed to change in time. Sources and sinks for mass and/or heat can be included at specified nodes in the domain. The source/sink term is also optionally time dependent.

Because FLOW is designed to be coupled with the TRANS module, the discretisation schemes are identical. Care has to be taken when FLOW is to be run in coupled mode because the dimension and discretisation of the model domain, the extent and type of boundary condition and certain properties, such as the porosity of the rock, have to be consistent with the input to the TRANS module, otherwise the simulation will not converge.

A5.2 Code modifications carried out at the University of Bern

The range of features that have been added to the code at the University of Bern in the context of the CLAYTRAC project include the following:

- **Heterogeneous tortuosity**: Because of the linear relationship between tortuosity and the diffusion coefficient, we can now account for heterogeneous diffusion coefficients throughout the model domain by specifying a heterogeneous distribution of the tortuosity. Tortuosity in our simulations has effectively been turned into a factor of proportionality that incorporates spatial changes of the diffusion coefficient D0 (i.e. the diffusion coefficient in
free water). For the calculation of the effective diffusion coefficient, $D_0$ and the porosity remain independent parameters. The anisotropy of the tortuosity had been implemented by Peter Lichtner upon our request prior to these modifications.

- **Time-dependent boundary conditions:** We can change boundary properties (e.g. concentrations along boundaries for Dirichlet conditions) and the type of boundary condition (e.g. change from a Dirichlet to a zero-flux type or vice versa) through time in the TRANS module. The changes take effect either explicitly at specified times or through a linear function. This gives us greater flexibility and accuracy for incorporating the (hydro)geochemical history of a system into our calculations.

- **Simple node-by-node input of He accumulation rates:** Because of the spatial variability of the U and Th contents of the rock, the in-situ He accumulation rate shows the same degree of heterogeneity. The resolution of the model grid has to take the spatial variability into account. Thus, the input of He accumulation rates can be extremely tedious, considering the number of grid blocks within a model domain. For that reason, a pre-processing routine was written that reads in U and Th contents of the rock from a file and converts them into He accumulation rates in a format that can be pasted directly into FLOTRAN input files.

- **Python wrapping of FLOTRAN output:** The results from FLOTRAN can be extracted during the simulation with a Python wrapper. Python is a high-level programming language which, because of the modular structure of Python programs, is well suited for coupling different software packages. During the simulation FLOTRAN writes results to a temporary dump file. The Python program runs in parallel to the FLOTRAN simulations and checks in regular intervals whether this dump file has been updated. If it has, the results are read into the Python wrapper and processed. Data processing in the Python wrapper is particularly useful for visualisation purposes. The calculations in FLOTRAN can be visualised in real time either as spatial plots or time series by using the plotting packages Gnuplot or MayaVi. The images can be printed to image files in various formats immediately during the simulation, and these image files can be automatically encoded into movies after the simulation.

These modifications were incorporated into FLOTRAN as additional subroutines, which have been passed on to Peter Lichtner for inclusion into future versions of the FLOTRAN code.

### A5.3 Comparing results from FLOTRAN simulations with published analyses

Because FLOTRAN (note we use the term FLOTRAN here even though we are using the TRANS module only) is not yet widely used in the reactive transport community, an additional effort was required to assure that our calculations are correct.

#### A5.3.1 Benchmarking FLOTRAN with results from the Dogger and Lias at Benken

Given the availability of a comprehensive tracer-data set and of extensive modelling efforts (Gimmi & Waber 2004, Gimmi *et al.* 2007), the Benken case study was selected to test the accuracy of FLOTRAN. Only $^{18}$O will be considered here because we can expect that other conservative tracers will behave in the same manner.

We first attempt to reproduce the simple base-case scenario for diffusive $^{18}$O transport described in Gimmi & Waber (2004). The profile through the low-permeability sequence (see Section 2.3) extends over a vertical distance of 312 m (397 – 709 m depth). The boundaries between the over- and underlying units are assumed to be open for diffusive exchange (*i.e.* a fixed concentration boundary
condition is applied). The initial concentration profile is uniform throughout the sequence. The value for the initial concentration corresponds to the maximum measured value at Benken. At the boundaries, $\delta^{18}$O values remain fixed during the simulations and correspond to the measured present-day values at the Keuper and Malm boundaries of the low-permeability sequence. Diffusion times of 0.25, 0.5 and 1 Ma are considered. The porosity of the low-permeability sequence is 0.12 and the temperature-corrected pore-diffusion coefficient ($D_p$) is $1.0E-10 \text{ m}^2/\text{s}$. These parameter choices correspond to the base-case scenario as presented in Gimmi and Waber (2004). The result from the numerical simulation with FLOTRAN is shown in Figure A5.3-1. There is virtually no difference between our numerical results and the analytical calculations by Gimmi & Waber (2004). This confirms that the calculation of diffusive transport in FLOTRAN is correct and accurate.

Gimmi & Waber (2004) also assessed the effect of an advective component to the total flux on the shape of the tracer profiles for a range of flow velocities and flow directions. We only reproduce one scenario here, assuming an advective downward flow velocity $v_a$ of $2E-12 \text{ m/s}$. The result for a diffusion/advection time of 0.5 Ma is shown in Figure A5.3-2. Again, the agreement between the numerical calculation using FLOTRAN and the analytical solution (in Laplace space) of Gimmi & Waber (2004) is excellent.

Figure A5.3-1: Benchmarking FLOTRAN: Evolution of $\delta^{18}$O profiles for the base case scenario at Benken

Numerical simulations with FLOTRAN shown by solid lines, pre-existing results from Gimmi & Waber (2004) by crossmarks. Dots indicate measured data
A5.3.2 Benchmarking FLOTRAN with a study on the Opalinus Clay at Mont Terri

Introduction

In a second benchmarking exercise, we reproduce the results from the study by Rübel et al. (2002) on the Opalinus Clay at Mont Terri, Switzerland. In this study, pore-water profiles of δD and δ18O and dissolved He were used to gain insight into the pore-water evolution and solute transport properties of Opalinus Clay. The most important result of the study was the determination of the apparent in-situ, large-scale diffusion coefficient Da(He) = (3.5±1.3)E-11 m²/s in Opalinus Clay. Helium concentrations in the pore water reflect the balance between in-situ accumulation due to the decay of uranium and thorium in the rock and the diffusive loss across the boundaries. Whereas other tracer profiles, such as those for stable water isotopes, evolve due to diffusion only and the steady-state profile will always be a straight line connecting the boundary concentrations at both ends, the He profile will most often show some degree of curvature, unless the diffusion rate completely overprints the accumulation rate. Figure A5.3-3 shows the He data points measured at Mont Terri and the associated model curve calculated by Rübel et al. (2002).

Recalculation of input data

Some parameters, such as porosity of the rock, can be input directly into the FLOTRAN input file, while others, such as the He concentrations and accumulation rates, need to be converted into

24 Production rate is expressed in units of cm³ STP/grock/a, whereas accumulation rate relates to cm³ STP/gwater/a, i.e. to He concentrations in pore water. In accordance with Rübel et al. (2002), it is assumed that the release efficiency is 1, i.e. all He produced in the rock is released to the pore water.

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FLOTRAN readable units. The standard unit for dissolved He concentration is cm$^3$ STP/g$_{\text{water}}$, but FLOTRAN reads concentrations in moles/kg$_{\text{water}}$ or moles/L$_{\text{water}}$. Similarly, FLOTRAN’s source term reads accumulation rates in kg$_{\text{solution}}$/s per grid block, which means that units have to be converted accordingly. Note that the code handles sources and sinks of solution (e.g. water with dissolved species) but not of the species themselves. This means that He accumulation is simulated considering a source of water with dissolved He.

**Figure A5.3-3:** Measured He concentrations in pore waters at Mont Terri and model calculations from Rübel et al. (2002)

Rübel et al. (2002) assume a uniform He accumulation rate of 1.1E-11 cm$^3$ STP/g$_{\text{water}}$/a in pore water throughout the Opalinus Clay. As mentioned above, the conversion and formatting of accumulation rates into FLOTRAN readable text has been automated by means of a pre-processing routine. The conversion can be summarised as follows:

The ideal gas law is

$$n = \frac{VP}{RT},$$

where $n$ is the number of moles, $V$ the volume of the gas phase (in litres), $P$ is standard pressure (1.0 atm), $R$ is the gas constant (0.0821 L atm/(K mol)) and $T$ is the standard temperature (298.15 K). Ignoring the time-dependence, 1.1E-11 cm$^3$ STP/g$_{\text{water}}$ of dissolved He corresponds to 4.5E-13 moles/kg$_{\text{water}}$. With a cell volume of 0.63 m$^3$ and a porosity of 0.16, the amount of dissolved He per cell is 4.53E-11 moles. Now, including the time dependence, the accumulation rate is 4.53E-11 moles/a, corresponding to 1.44E-18 moles/s per cell. Assuming a source term consisting of
an aqueous solution with a 1 molal He concentration, the accumulation rate per grid block amounts to
1.436E-18 kg\text{solution}/s.

\textit{Calculations performed by Rübel et al. (2002)}

The He contents of the adjacent formations are used as boundary conditions for the simulation. Rübel et al. (2002) used a value of 5.5E-8 cm\textsuperscript{3} STP/g\text{water} He in the upper and lower formations. Converting this into FLOTTRAN readable units, we obtain 2.45E-9 moles/kg\text{water}. Rübel et al. (2002) assumed steady-state conditions (i.e. He production from radioactive decay equals the loss by diffusion, leading to a time-invariant He profile), under which the He profile can be described by the differential equation (Boudreau 1997):

\[ D \frac{\partial^2 C}{\partial x^2} = -A, \]

where A is the \textit{in-situ} accumulation rate. Assuming a fixed concentration of He on the one side (i.e. the boundary to the embedding aquifer) and zero flux on the other side (i.e. at mid point of the Opalinus Clay profile), integration yields the parabolic profile:

\[ C(x) = -\frac{A \cdot x^2}{2D} + \frac{A \cdot L \cdot x}{D} + C_0, \]

where L is the half-length of the profile (=133.6 m orthogonal distance). A polynomial regression was carried out on the measured He data and fitted to the calculated parabolic profile, and this yielded a value for Da of (3.5±1.3)E-11 m\textsuperscript{2}/s (Figure A5.3-3).

\textit{Calculations using FLOTTRAN}

The same formation thickness and boundary concentrations were applied as in Rübel et al. (2002), and their Da of 3.5E-11 m\textsuperscript{2}/s was used as input to the calculation. The initial He concentration across the low-permeability sequence was assumed to be 0, even though this parameter is not relevant if evolution times long enough to attain steady state are chosen. A very long run time of 50 Ma was used (snapshots at shorter evolution times show that steady state is already reached after about 20 Ma). Results from the numerical simulation with FLOTTRAN, considering both He accumulation and diffusion, are shown in Figure A5.3-4. The agreement between the regression curve of Rübel et al. (2002) and our simulated curve is excellent. The maximum He concentration is 9E-5 cm\textsuperscript{3} STP/g\text{water}, which is consistent with the value derived by Rübel et al. (2002) (see Figure A5.3-3). This means that our calculations yield the same results as the analytical solution of Rübel et al. (2002), provided the same input parameters (diffusion coefficient, length of profile) are used. This consistency shows that the data pre-processing routine written to recalculate He concentrations and He accumulation rates works correctly.

\textit{A5.3.3 Conclusions}

We have demonstrated that we can reproduce published analyses of diffusive transport, diffusive plus advective transport and of diffusive transport plus \textit{in-situ} accumulation accurately with the reactive transport code FLOTTRAN. The scenarios discussed throughout this report are modifications of the same type of calculations, and we can be confident that the results presented are accurate as well.
The calculation starts at time \( t = 0 \) and builds up until reaching steady state at times > \( \text{ca.} 20 \text{ Ma} \).

With FLOTRAN, we have a powerful numerical tool available to us. Carrying out benchmarking and code testing tasks is a normal procedure during code development and is required only when new features are to be incorporated into the simulations. The numerical simulations described above are obviously not a rigorous code validation and testing exercise. Nevertheless, the benchmarking exercise demonstrates that our decision to use FLOTRAN as the main numerical tool for simulating (reactive) transport was reasonable.
Natural Tracer Profiles Across Argillaceous Formations: The CLAYTRAC Project

Disposal of high-level radioactive waste and spent nuclear fuel in engineered facilities, or repositories, located deep underground in suitable geological formations is being developed worldwide as the reference solution to protect humans and the environment both now and in the future. An important aspect of assessing the long-term safety of deep geological disposal is developing a comprehensive understanding of the geological environment in order to define the initial conditions for the disposal system as well as to provide a sound scientific basis for projecting its future evolution. The transport pathways and mechanisms by which contaminants could migrate in the surrounding host rock are key elements in any safety case. Relevant experiments in laboratories or underground test facilities can provide important information, but the challenge remains in being able to extrapolate the results to the spatial and temporal scales required for performance assessment, which are typically tens to hundreds of metres and from thousands to beyond a million years into the future. Profiles of natural tracers dissolved in pore water of argillaceous rock formations can be considered as large-scale and long-term natural experiments which enable the transport properties to be characterised.

The CLAYTRAC Project on Natural Tracer Profiles Across Argillaceous Formations was established by the NEA Clay Club to evaluate the relevance of natural tracer data in understanding past geological evolution and in confirming dominant transport processes. Data were analysed for nine sites to support scientific understanding and development of geological disposal. The outcomes of the project show that, for the sites and clay-rich formations that were studied, there is strong evidence that solute transport is controlled mainly by diffusion. The results can improve site understanding and performance assessment in the context of deep geological disposal and have the potential to be applied to other sites and contexts.