



**HAL**  
open science

## Bayesian inversion of a chloride profile obtained in the hydraulically undisturbed Opalinus Clay: mass transport and paleo-hydrological implications.

Catherine Yu, Julio Goncalves, Jean-Michel Matray

### ► To cite this version:

Catherine Yu, Julio Goncalves, Jean-Michel Matray. Bayesian inversion of a chloride profile obtained in the hydraulically undisturbed Opalinus Clay: mass transport and paleo-hydrological implications.. Applied Geochemistry, 2018, 93, pp.178-189. 10.1016/j.apgeochem.2017.11.004 . hal-01771469

**HAL Id: hal-01771469**

**<https://hal.science/hal-01771469v1>**

Submitted on 27 Jan 2020

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial - NoDerivatives 4.0 International License

Manuscript Number:

Title: Bayesian inversion of a chloride profile obtained in the hydraulically undisturbed Opalinus Clay: mass transport and paleo-hydrological implications

Article Type: Research Paper

Keywords: Mont Terri rock laboratory, Opalinus Clay, natural tracer profile, chloride, Markov Chain Monte Carlo, leaching, diffusion

Corresponding Author: Mrs. Catherine Yu,

Corresponding Author's Institution: IRSN

First Author: Catherine Yu

Order of Authors: Catherine Yu; Julio Gonçalvès, Pr.; Jean-Michel Matray, Dr.

Abstract: The BDB-1 deep-inclined borehole was drilled at the Mont Terri rock laboratory (Switzerland) and enabled to acquire relevant data on porewater composition through the Opalinus Clay (OPA) and its bounding formations. Petrophysical measurements were carried out and included water content, water accessible porosity and grain density determination. Mobile anion profiles were obtained by aqueous leaching and out diffusion experiments performed on drillcore samples, and revealed to be consistent with previous studies carried out at the rock laboratory level. Diffusive properties were also investigated using three experimental setups: parallelepiped out diffusion, radial diffusion and through diffusion. These transport parameters were used as a priori values in a Monte Carlo Markov Chain inversion modelling approach to interpret the chloride profile in the Opalinus Clay. Based on a Peclet number analysis, a purely diffusive scenario enabled specifying the paleohydrogeological evolution of the Mont Terri site from the folding of the Jura Mountains and transport parameters.

Suggested Reviewers: Claude Degueldre Pr.  
Professor of Nuclear Engineering, Engineering, Lancaster University  
c.degueldre@lancaster.ac.uk

Margarita Koroleva Dr.  
Geol.-Pal. Institute, Universität Hamburg  
margarita.koroleva@uni-hamburg.de

Ana Maria Fernandez Dr.  
Departamento de Medio Ambiente , CIEMAT  
anamaria.fernandez@ciemat.es

Andreas Gautschi  
Chief Geoscientific Advisor, Advisory Team Science & Technology, NAGRA  
Andreas.Gautschi@nagra.ch

Paul Wersin Dr.  
Institut für Geologie, University of Bern  
paul.wersin@geo.unibe.ch

**Title of the submitted manuscript:**

Bayesian inversion of a chloride profile obtained in the hydraulically undisturbed Opalinus Clay: mass transport and paleo-hydrological implications

**List of all authors' names and affiliations:**

Catherine Yu<sup>1) 2)</sup>, Julio Gonçalvès<sup>2)</sup>, Jean-Michel Matray<sup>1)</sup>

- 1) Institut de Radioprotection et de Sûreté Nucléaire, 31 Allée du Général Leclerc, F92260 Fontenay-aux-Roses, France
- 2) Aix Marseille Univ., CNRS, IRD, Coll. De France, CEREGE, Aix-en-Provence, France

**Short statement of the precise problem or objective addressed in the paper: (<50 words)**

Understanding the salinity profile and its transient geological evolution across the Opalinus Clay at Mont Terri as a prerequisite for further transient interpretation of pressure profile.

**Brief description of the essence of the approach :(<100 words)**

The paper presents an exhaustive and self-consistent acquisition of transport parameters and natural tracer profiles in the hydraulically undisturbed zone crossed by the BDB-1 borehole, which is the first deep borehole drilled at the Mont Terri rock laboratory. The obtained chloride profile was interpreted by means of a purely diffusive 1D numerical model, based on a statistical approach enabling to obtain fitted parameters and associated confidence intervals.

**List of the specific major novel contributions reported here :up to 3**

- Consistency between data acquired at the Mont Terri tunnel level and in the hydraulically undisturbed zone crossed by the BDB-1 deep borehole.
- Confirmation of the paleohydrogeological evolution of the Mont Terri site from the folding of the Jura Mountains.

**List of other journal or conference papers published or submitted that have a significant overlap with the contribution submitted here accompanied by a brief explanation of the nature of this overlap pointing out clearly which novel ideas submitted here have not been discussed in these prior publications:**

- Acquisition of anion profiles and diffusion coefficients in the Opalinus Clay at the Mont Terri rock laboratory (Switzerland), Yu, C., Matray, J.M., 2017, Procedia Earth and Planetary Science, Vol. 17, Pages 57-60. Published
- Characterisation of anions and stable water isotopes diffusive properties in the Opalinus Clay by three experimental setups applied on BDB-1 borehole samples, C. Yu, C., Matray, J.-M., Bagagnan, S., Wittebroodt, C., Michelot, J.-L., 2017. 7<sup>th</sup> International Conference on Clays in Natural and Engineered Barriers for Radioactive Waste Confinement. Submitted and accepted for poster presentation.

These papers focused essentially on the experimental part of our work and did not detail our transport modelling at geological formation scale.

**A reference to the closest prior article (by others) upon which your contributions improve:**

Mazurek, M., Alt-Epping, P., Bath, A., Gimmi, T., Waber, H.N., Buschaert, S., De Cannière, P., De Craen, M., Gautschi, A., Savoye, S., Vinsot, A., Wemaere, I., Wouters, L., 2011. Natural tracer profiles across argillaceous formations. Appl. Geochem., 26, 1035-1064

**Names, emails, and homepage URLs of four experts covering these areas and fields:**

- Claude Degueldre, [c.degueldre@lancaster.ac.uk](mailto:c.degueldre@lancaster.ac.uk),  
<http://www.lancaster.ac.uk/engineering/about-us/people/claude-degueldre>
- Margarita Koroleva, [margarita.koroleva@uni-hamburg.de](mailto:margarita.koroleva@uni-hamburg.de),  
[http://4dweb.proclim.ch/4dcgi/polar/en/Detail\\_Person?korolevam.bern](http://4dweb.proclim.ch/4dcgi/polar/en/Detail_Person?korolevam.bern)
- Jim Hendry, [jim.hendry@usask.ca](mailto:jim.hendry@usask.ca),  
<http://artsandscience.usask.ca/profile/MHendry#/profile>
- Martin Mazurek, [martin.mazurek@geo.unibe.ch](mailto:martin.mazurek@geo.unibe.ch),  
[http://4dweb.proclim.ch/4dcgi/geosciences/en/Detail\\_Person?mazurekm.bern](http://4dweb.proclim.ch/4dcgi/geosciences/en/Detail_Person?mazurekm.bern)

**Names of the two GMOD associate editors who we believed are the most qualified to handle our paper:**

Philippe Negrel and Elisa Sacchi

**Technical areas and fields of expertise necessary to fully understand our contribution and to evaluate its potential and novelty:**

Hydrogeology, transport modelling

1 **Bayesian inversion of a chloride profile obtained in the hydraulically undisturbed**

2 **Opalinus Clay: mass transport and paleo-hydrological implications**

3 Catherine Yu<sup>1)2)</sup>, Julio Gonçalves<sup>2)</sup>, Jean-Michel Matray<sup>1)</sup>

4 1) Institut de Radioprotection et de Sûreté Nucléaire, 31 Allée du Général Leclerc,  
5 F92260 Fontenay-aux-Roses, France

6 2) Aix Marseille Univ., CNRS, IRD, Coll. De France, CEREGE, Aix-en-Provence,  
7 France

8 Corresponding author: Catherine Yu. E-mail: [catherine.jiyu@irsn.fr](mailto:catherine.jiyu@irsn.fr)

9 **Keywords:** Mont Terri rock laboratory, Opalinus Clay, natural tracer profile, chloride,  
10 Markov Chain Monte Carlo, leaching, diffusion

11

12 **Abstract**

1  
2  
3 13 The BDB-1 deep-inclined borehole was drilled at the Mont Terri rock laboratory  
4  
5 14 (Switzerland) and enabled to acquire relevant data on porewater composition through the  
6  
7 15 Opalinus Clay (OPA) and its bounding formations. Petrophysical measurements were carried  
8  
9  
10 16 out and included water content, water accessible porosity and grain density determination.  
11  
12 17 Mobile anion profiles were obtained by aqueous leaching and out diffusion experiments  
13  
14  
15 18 performed on drillcore samples, and revealed to be consistent with previous studies carried  
16  
17 19 out at the rock laboratory level. Diffusive properties were also investigated using three  
18  
19  
20 20 experimental setups: parallelepiped out diffusion, radial diffusion and through diffusion.  
21  
22 21 These transport parameters were used as *a priori* values in a Monte Carlo Markov Chain  
23  
24  
25 22 inversion modelling approach to interpret the chloride profile in the Opalinus Clay. Based on  
26  
27 23 a Peclet number analysis, a purely diffusive scenario enabled specifying the  
28  
29  
30 24 paleohydrogeological evolution of the Mont Terri site from the folding of the Jura Mountains  
31  
32 25 and transport parameters.  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65

## 26 **1 Introduction**

27 The Swiss National Co-operative for the Disposal of Radioactive Waste (Nagra) selected the  
28 Opalinus Clay (OPA) as a potential host rock suitable for deep geological repository of high-  
29 level radioactive waste and long-lived-intermediate-level waste. The evaluation of the  
30 confinement properties of this formation has been ongoing since 1996 in the Mont Terri rock  
31 laboratory, which is located in the Jura Mountains in north-western Switzerland. An overview  
32 of the safety aspects covered by this international research program and its contribution to the  
33 understanding of argillaceous formation behaviour was given by Bossart et al. (2017).

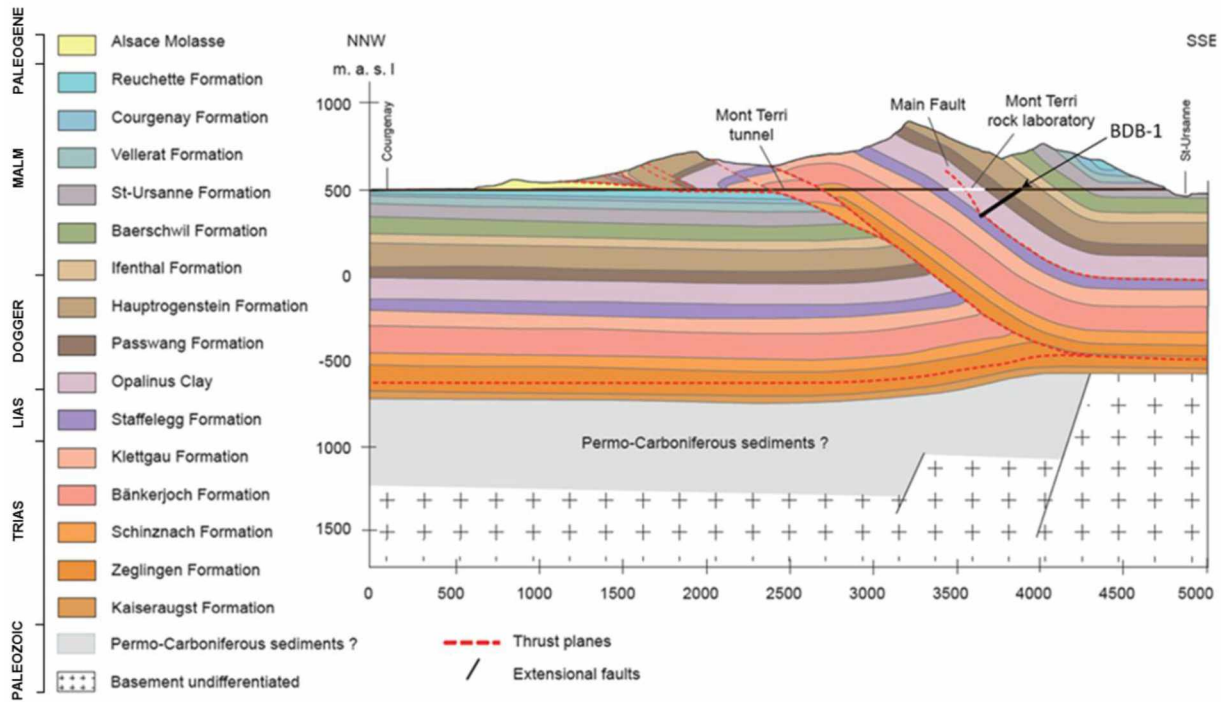
34 Solute transport is considered to be dominated by diffusion in compacted claystones due to  
35 their low permeability (Patriarche et al., 2004b; Sellin and Leupin, 2014). Limited water flow  
36 in these formations make standard sampling of porewater non applicable. Unconventional  
37 extraction processes based on physical or chemical extraction were developed and include  
38 centrifugation, squeezing, leaching, advective displacement and diffusive equilibration (Sachi  
39 et al., 2001). Natural tracer profiles across argillaceous formations give information on fluid  
40 flow and transport properties, as they result from a long-term exchange between the aquitard  
41 and the bounding aquifers porewaters (Mazurek et al., 2011; Bensenouci et al., 2013). The  
42 example of the Opalinus Clay was studied through the interpretation of several natural tracers  
43 ( $\text{Cl}^-$ ,  $\delta^2\text{H}$  and He) profiles by Mazurek et al. (2011). This study concluded that a purely  
44 diffusive transport model could explain the present profiles and proposed values for activation  
45 times of the Opalinus Clay bounding aquifers and initial chlorinity. However, the mainly  
46 diffusive mass transport behavior was tested by means of a sensitivity test on advection using  
47 plausible but not based on global driving forces (pressure, temperature, salinity gradients)  
48 Darcy's velocity values and no corresponding Peclet number calculation were made. In  
49 addition, only a single value of the diffusion coefficient was applied to the stratigraphic  
50 column and no uncertainties were associated with the fitting parameters.



1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51 At the end of 2014 and in the framework of the Deep Borehole experiment (DB), a 247.5 m  
52 long 45° downward inclined borehole named BDB-1 was drilled through the Opalinus Clay  
53 and the bounding formations. The aim of the experiment is to develop and validate a  
54 methodology for assessing the confinement properties of a thick argillaceous unit using the  
55 Opalinus Clay as an example. In this framework, mobile anion profiles were acquired by  
56 leaching and out diffusion experiments and diffusive transport parameters (effective diffusion  
57 coefficients and accessible porosities) were also identified by radial and through diffusion  
58 experimental setups.

59 This paper presents an exhaustive and self-consistent acquisition of transport parameters and  
60 natural tracer profiles in the hydraulically undisturbed zone crossed by the BDB-1 borehole.  
61 The chloride profile was interpreted by means of a purely diffusive 1D numerical model. The  
62 assumption of purely diffusive mass transport phenomena was verified by estimating the  
63 Peclet number including osmotic processes in the advection term. A bayesian inversion based  
64 on effective diffusion coefficients, initial value of the chloride concentration and two  
65 exhumation and thus hydraulic activation times for the two bounding aquifers (10 parameters)  
66 allowed to evaluate the best fit parameter sets and their uncertainties not evaluated so far.  
67 Obtaining a relevant interpretation of the chloride profile is crucial for water flow and flow  
68 characterisation. Hence, overpressures (pore pressure exceeding the hydrostatic or  
69 surrounding aquifer ones) were recognised in the Opalinus Clay and assumed so far to be  
70 remnant from its burial history (Mazurek et al., 2002). The influence of osmotic phenomena  
71 (water flow due to salinity or temperature gradients) on this pressure anomaly has not been  
72 investigated yet and depends strongly on the porewater composition. Therefore,  
73 understanding the salinity profile and its transient geological evolution across the formation is  
74 a necessary prerequisite for further transient interpretation of pressure profile (Gonçalvès et  
75 al., 2004).

76 **2 Geological setting**



77

78 Figure 1: Geological cross-section of the Mont Terri anticline. Location of the rock laboratory  
 79 is indicated by a white line. The BDB-1 deep borehole, represented by a thick black line,  
 80 crosses the lower part of the Dogger aquifer, the entire Opalinus Clay formation and the upper  
 81 part of the Liassic marls (adapted from Nussbaum et al., 2017).

82 The Opalinus Clay at the Mont Terri site is an overconsolidated claystone of Aalenian-  
 83 Toarcian age, overlain by 800 m of Middle to Late Jurassic limestones, marls and shales, and  
 84 underlain by 400 m of Early Jurassic to Triassic marls and limestones, dolomites and  
 85 anhydrites (Figure 1). The thickness of the Opalinus Clay in the Mont Terri anticline varies  
 86 between 130 m in the BDB-1 borehole and 160 m at rock laboratory level, depending on the  
 87 tectonic contribution. This corresponds to a sedimentary thickness of about 120 m, when  
 88 corrected for tectonic overthrusting. The Opalinus Clay reached a burial depth of 1350 m  
 89 about 120 Ma ago during early Cretaceous, which resulted in a maximum temperature of 80-  
 90 90°C (Mazurek et al. 2006).

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
91 A period of marine regression occurred between 100 and 40 Ma, leading to a subaerial  
92 exposure of the top of the Malm limestone. Starting about 40 Ma, the rifting of the Rhine  
93 Graben affected Northern Switzerland, resulting in considerable subsidence of the area in the  
94 mid-Tertiary, which brought the Opalinus Clay sequence back to about 500 m depth.  
95 According to Clauer et al. (2017), two sea invasions into the Mont Terri area took place  
96 during Priabonian (37 to 34 Ma) and during the Rupelian (34 to 28 Ma). Mazurek et al.  
97 (2017) proposed that the Malm limestones, represented by the Baershwil Formation, acted as  
98 a fresh-water boundary that induced a decrease of the Opalinus Clay porewater salinity to half  
99 the original value at the end of the Paleogene (23 Ma). Partial evaporation potentially  
100 occurred in the Chattian/Aquitanian and afterwards, brines would have diffused in the  
101 underlying formation, resulting in a salinity increase in the Opalinus Clay before Late Alpine  
102 folding during the late Miocene to Pliocene (about 12 to 3 Ma) that formed the Folded Jura.  
103 Erosion exposed the core of the Mont Terri anticline between 6 and 2.5 Ma, and activated the  
104 Middle Jurassic limestones aquifer (overlying the Opalinus Clay), causing a porewater  
105 flushing. Similarly, infiltration to the Early Jurassic limestones would have started in the  
106 Quaternary, between 0.5 and 0.2 Ma ago (Pearson et al., 2003, Mazurek et al., 2011).

39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65  
107 Three main facies were identified within the Opalinus Clay (Blaesi et al., 1991): a shaly facies  
108 in the lower part of the sequence, a thin carbonate-rich sandy facies in the middle part of the  
109 formation, and a sandy facies interstratified with shaly facies in the upper sequence. The shaly  
110 facies mineral composition includes 27-78% of clay minerals (illite, chlorite, kaolinite and  
111 illite-smectite mixed layers), 4-29% of carbonates, 10-32% of quartz, and accessory feldspars,  
112 pyrite and organic matter (Bossart and Thury, 2008).

113 Several minor tectonic faults and a larger fault zone called “Main Fault” can be observed in  
114 the Opalinus Clay (Nussbaum et al., 2011). Nagra’s investigations in deep boreholes at  
115 Riniken, Weiach, Schafisheim and Benken revealed that the tectonically disturbed zones are

116 hydraulically similar to the undeformed matrix (Johns et al. 1994; Gautschi 2001a). This  
117 conclusion was also confirmed by hydraulic investigation in the BDB-1 borehole at Mont  
118 Terri (Yu et al., 2017).

### 119 **3 Material and methods**

#### 120 **3.1 Sampling**

121 The stratigraphic sequence crossed by the BDB-1 borehole is presented in Figure 2 and is  
122 described in detail in Hostettler et al. (2017). The Opalinus Clay section was drilled with air  
123 as drilling fluid. Drilling was immediately followed by the installation of a multipacker  
124 system (Fierz and Rösli, 2014) with pressure and temperature sensors. The borehole was  
125 entirely cored for lithostratigraphic, petrophysical, mineralogical and geochemical studies.  
126 Cores sent for analysis were sampled every 10 m along the borehole. Their preservation was  
127 ensured by nitrogen flushing and sealing after vacuum with plastic foil in aluminum coated  
128 plastic bags, in order to avoid further evaporation and contact with the atmosphere.

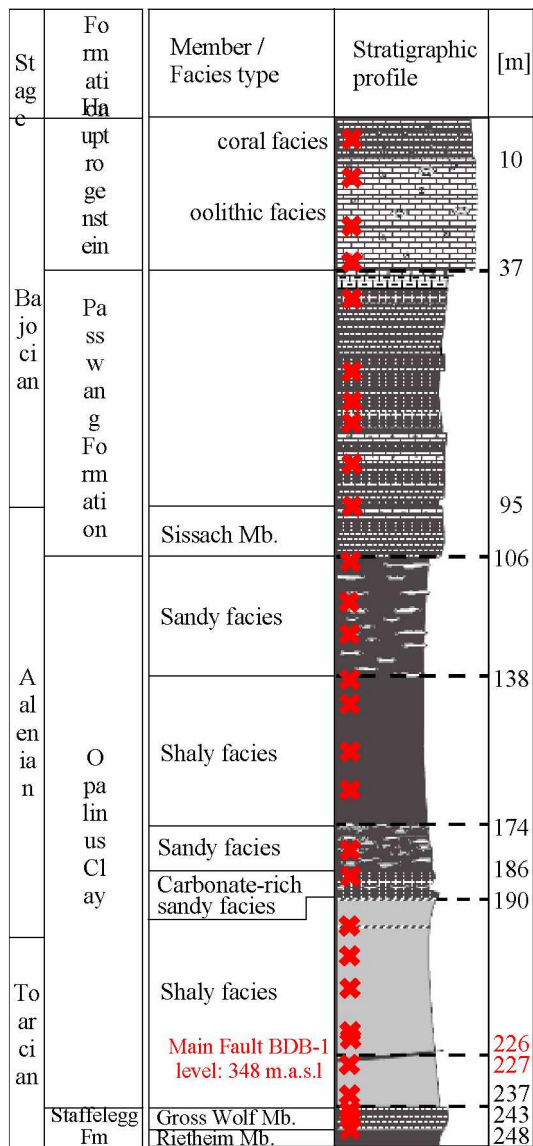


Figure 2: Lithostratigraphy of the formations crossed by BDB-1 borehole (adapted from Hostettler et al., 2017) and approximative location of the studied samples represented by red crosses.

### 3.2 Petrophysical characterisation

Determination of petrophysical parameters (water contents, porosity, apparent density, degree of saturation etc.) were performed in laboratory on representative elementary volume samples taken from the central part of the cores. Water contents were determined by weighing before and after oven-drying at 105 °C until mass stabilization. Density and degree of saturation were calculated based on Archimede's principle after sample immersion into kerdane (de-

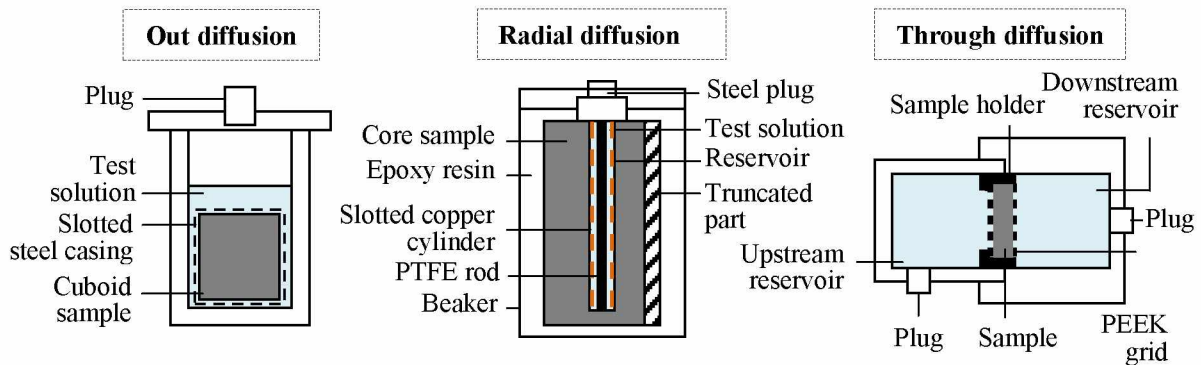
139 aromatized hydrocarbide), following the experimental protocol first proposed by Monnier et  
 140 al. (1973) and adapted to Tournemire and Mont Terri argillites (Matray et al., 2007; Matray  
 141 and Möri, 2010). Grain density was evaluated using a helium pycnometer (Micromeritics  
 142 Accupyc II 1340) on oven-dried samples.

### 143 3.3 Aqueous leaching

144 Leaching consists in diluting pore water solutes contained in a powdered rock sample into a  
 145 leaching solution (Sachi et al. 2001, Koroleva et al. 2011). Samples were crushed, sieved (<  
 146 100  $\mu\text{m}$ ) and placed together with deionised water at solid/liquid ratio of 1:2 in centrifuge  
 147 vessels. The procedure took place under controlled atmospheric condition in a glove box ( $\text{N}_2$   
 148 atmosphere). Centrifuge tubes were placed in a hermetic glass jar and stirred out of the glove  
 149 box using an end-over-end agitator during 2 hours. Then, samples were centrifuged at 10,000  
 150 rpm for 15 minutes and placed again inside the glovebox to be filtered with 0.22  $\mu\text{m}$  syringe  
 151 filter. Leachates were analysed by liquid ion chromatography using a Metrohm 861 Advanced  
 152 Compact IC with an accuracy of 10%.

### 153 3.4 Diffusion experiments

154 Schematic views of the alternative experimental setups used to characterise the Opalinus Clay  
 155 are shown in Figure 3.



157 Figure 3: Schematic views of the diffusion cells used in this study to characterise the Opalinus  
158 Clay diffusive properties.

### 159 3.4.1 In and out-diffusion

160 In parallelepiped configuration, an out diffusion experiment consists in immersing a cubic-  
161 shaped sample into a synthetic solution and sampling the solution until reaching diffusive  
162 equilibrium. The method has been employed on argillite from Tournemire rock laboratory  
163 (France) by Patriarche (2004a) and enables the estimation of halide concentrations in  
164 porewater, as well as pore diffusion coefficient of the tested samples. Eighteen samples  
165 measuring about 5 cm wide were prepared with a diamond wire saw. They were constrained  
166 by placing a metallic grid, after being coated with epoxy resin on four faces to impose a single  
167 diffusion direction (perpendicular or parallel to the bedding). Test solutions were prepared to  
168 present a similar ionic strength to the porewater one, based on chloride contents obtained by  
169 leaching experiments.

170 A radial diffusion experiment consists in diffusive equilibrium between pore water contained  
171 in a drillcore and a test solution with known composition placed in an axial drilled reservoir  
172 (Van der Kamp et al. 1996, Savoye et al. 2006a and 2006b). A total of ten samples were  
173 prepared, each consisting of a core portion cut with a circular saw with a diameter of 10.2 cm  
174 or 8.5 cm and a length between 6.7 and 10 cm. A 24 mm diameter reservoir was drilled with a  
175 drill press in each sample, in which was inserted a 22 mm outer diameter copper tube with  
176 horizontal slots in order to prevent sample swelling. A 18 mm diameter  
177 polytetrafluoroethylene (PTFE) rod was also placed in the reservoir to minimise the solution  
178 volume used for the experiment and the time required to reach diffusive equilibrium.  
179 Solutions were analysed for anions ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{Br}^-$ ) by ionic chromatography using a  
180 DIONEX ICS-1000, and for stable isotopes ( $^{18}\text{O}$  and  $^2\text{H}$ ) using a Las Gatos Research LWIA-

181 24IEP. The analytical uncertainties of these analysis are  $\pm 5-10 \%$  for anions,  $\pm 1 \text{ ‰}$  for  $^2\text{H}$   
182 and  $\pm 0.6 \text{ ‰}$  for  $^{18}\text{O}$ .

### 183 3.4.2 Through diffusion

184 Through diffusion cells consisted of a polypropylene sample holder, two polypropylene  
185 reservoirs for liquid phase (upstream and downstream, with respective capacities of 180 mL  
186 and 90 mL), two supporting grids and two sampling openings. Six cylindrical samples of  
187 approximately 10 mm thickness and 30 mm diameter were prepared from core samples by  
188 sawing with a diamond wire saw. These samples were confined between porous polyether  
189 ether ketone (PEEK) grids in order to control clay mineral swelling and the assembly was  
190 fixed to the sample holder using Sikadur<sup>®</sup> epoxy adhesive. After a resaturation phase with  
191 synthetic porewater, the solutions were replaced with fresh ones and the upstream reservoir  
192 added with conservative radioactive tracers (HTO and  $^{36}\text{Cl}$ ). The flux of radioactive species  
193 between the reservoirs was monitored as a function of time by liquid scintillation using a  
194 Packard Tri-carb 3100 TR counter. The accuracy of activity measurement is estimated at  
195 6.4% for HTO and 3.5% for  $^{36}\text{Cl}^-$ .

### 196 3.4.3 Modelling of the diffusion experiments

197 Parallelepiped out diffusion and through diffusion experiments were modelled numerically  
198 using the chemistry-transport coupled model code HYTEC (Van der Lee et al. 2003), which is  
199 based on finite volumes method. In purely diffusive system and for mobile components, the  
200 transport equation writes:

$$\omega \frac{\partial c_i}{\partial t} = \text{div} (D_e \nabla c_i) \quad (1)$$

201 where  $c_i$  is the total concentration of component  $i$ ,  $\omega [-]$  is the diffusion accessible porosity for  
202 mobile components, and  $D_e [\text{m}^2 \text{ s}^{-1}]$  is the effective diffusion coefficient with  $D_e = \omega D_p$ ,  
203 where  $D_p$  is the pore diffusion coefficient accounting for the tortuosity of the porous media.



204 For radial diffusion experiments, a numerical inversion of the semi-analytical solution given  
205 by Novakowski and Van der Kamp (1996) and Savoye et al. (2006b) was applied using  
206 Mathematica 5.2<sup>©</sup>.

### 207 3.5 Markov Chain Monte Carlo inversion approach

208 The chloride profile acquired on samples from the BDB-1 borehole was interpreted using a  
209 finite difference numerical resolution of the transport equation (1). This numerical treatment,  
210 which includes a statistical inversion process using a Markov Chain Monte Carlo (MCMC)  
211 algorithm (Metropolis), was implemented using Python<sup>©</sup>. MCMC methods are probabilistic  
212 sampling techniques for Bayesian parameter estimation and uncertainty quantification. The  
213 basic principle consists in an oriented random walk exploration of the parameter space in  
214 order to avoid large time-consuming and even unrealistic systematic (using regular steps)  
215 sampling of parameters sets that allow reproducing the chloride profile. Each selected  
216 parameters set throughout the random walk is introduced in direct transport simulations.  
217 Therefore, these algorithms generate a sequence of model parameter sets and compare the  
218 model-based predictions to a given set of observed measurements (Tarantola, 2005; Gallagher  
219 et al. 2009; Petersen et al. 2014). The model parameters are constrained to minimise the misfit  
220 between simulated ( $sim_i$ ) and measured values ( $obs_i$ ), represented here by the mean squared  
221 error function  $S(\mathbf{m})$ :

$$S(\mathbf{m}) = \frac{1}{n} \sum_i (obs_i - sim_i)^2 \quad (2)$$

222 where  $n$  is the number of measurements and  $\mathbf{m}(m_1 \dots m_n)$  is the vector of model parameters.

223 The random walk is based on sorted values in the *a priori* probability density function (pdf)  
224  $\rho(\mathbf{m})$  of each parameter while the forward modelling identifies a set of parameters allowing a  
225 good agreement between simulated and observed chloride values. This set of successful

226 parameters samples the *a posteriori* joint pdf  $\sigma(\mathbf{m})$  which describes the updated parameters  
 1  
 2 227 distribution (after forward modelling and data comparison) yielding the best simulations.  
 3  
 4  
 5 228 Then, marginal pdfs have to be identified for each parameter to estimate e.g., its mean value  
 6  
 7 229 and associated uncertainty. A complex mathematical treatment is required to assess rigorously  
 8  
 9  
 10 230 the marginal pdf of each parameter. Alternatively, the marginal distributions can be simply  
 11  
 12 231 identified by a statistical treatment of all the parameters samples that satisfy an acceptance  
 13  
 14 232 criterion (fraction of best simulations, misfit threshold). For the sake of simplicity, the  
 15  
 16  
 17 233 marginal pdf were identified using the second alternative approach.

20 234 Let's now consider a current step of the MCMC algorithm characterised by a position  $\mathbf{m}_i$  of  
 21  
 22 235 the random walk in the parameter space, and a potentially new position  $\mathbf{m}_j$  created by means  
 23  
 24  
 25 236 of a random perturbation of  $\mathbf{m}_i$ . The acceptance of the displacement from a former parameter  
 26  
 27 237 set  $\mathbf{m}_i$  to the posterior one  $\mathbf{m}_j$  follows the probabilistic rule (probability of acceptance  $P$ ):

$$P \begin{cases} 1 & \text{if } S(\mathbf{m}_i) > S(\mathbf{m}_j) \\ \frac{L(\mathbf{m}_j)}{L(\mathbf{m}_i)} = \exp\left(-\frac{\Delta S}{\alpha}\right) & \text{if } S(\mathbf{m}_i) < S(\mathbf{m}_j) \end{cases} \quad (3)$$

36 238 where  $L(\mathbf{m})$  is the likelihood function defined by :

$$L(\mathbf{m}) = k \times e^{-\frac{S(\mathbf{m})}{\alpha}} \quad (4)$$

43 239 where  $k$  is a normative constant that ensures that the integral of  $\sigma(\mathbf{m})$  over the parameter space  
 44  
 45 240 equals 1,  $\alpha$  is a convergence parameter to be set here by trial and error, and  $\exp(-\Delta S/\alpha) =$   
 46  
 47  
 48 241  $\exp(-(S(\mathbf{m}_j)-S(\mathbf{m}_i))/\alpha)$ .

51 242 The first option in equation (3) just states that if the displacement yields a lower error between  
 52  
 53 243 the direct model results and the observations, the displacement is accepted. The second one  
 54  
 55  
 56 244 states that an unfavourable displacement can be accepted in order to leave local minimum  
 57  
 58 245 values of the objective function and to explore other regions of the parameter space. This

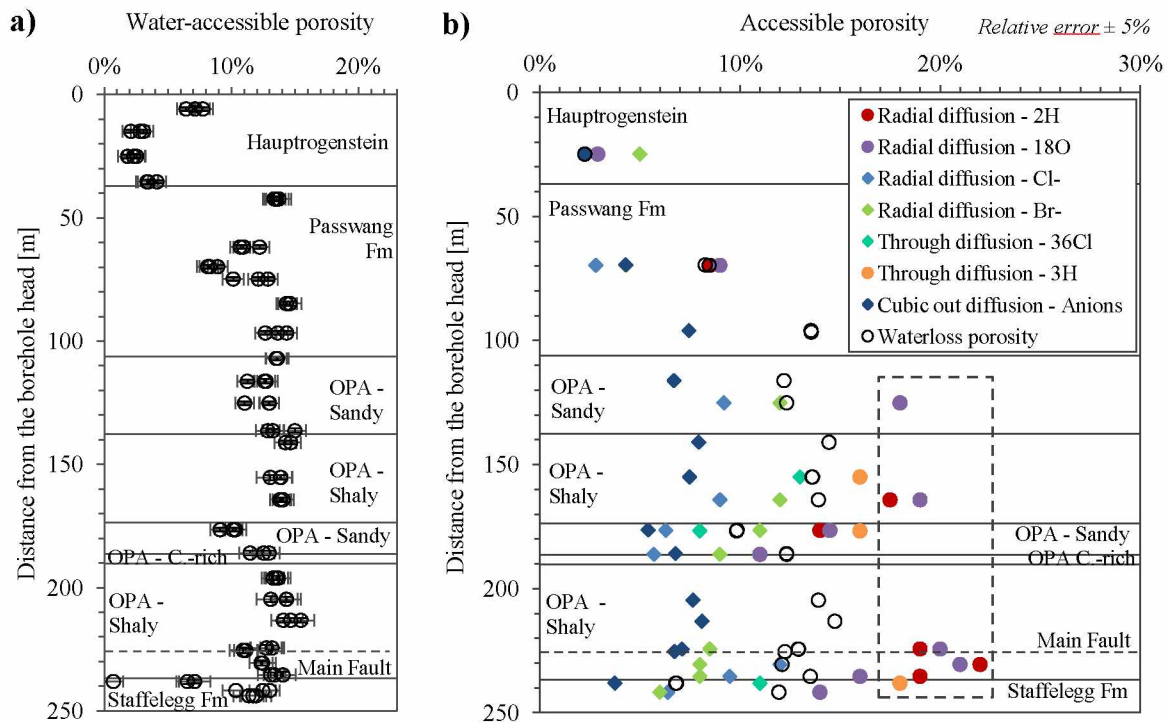
246 second option is practically treated by sorting a value in an uniform distribution between 0  
 1  
 2 247 and 1: if it is lower than  $\exp(-\Delta S/\alpha)$ , which occurs with a probability  $\exp(-\Delta S/\alpha)$ , then the  
 3  
 4  
 5 248 unfavourable displacement is accepted and the algorithm (Eq. 3) is satisfied. This algorithm  
 6  
 7 249 globally favours the displacements within the parameter space in the direction of decreasing  
 8  
 9  
 10 250 misfits. After a first convergence stage of the method, which consists in reaching the regions  
 11  
 12 251 of the parameter space where the error is minimum, the MCMC algorithm provides a set of  
 13  
 14  
 15 252 accepted parameters which allow the best simulations.

## 253 4 Results and discussion

### 254 4.1 Transport parameters

#### 255 4.1.1 Porosities

256 Porosity values obtained from petrophysical analysis and diffusion experiments are reported  
 27  
 28  
 29 257 in Figure 4.



258  
 259 Figure 4: a) Water accessible porosity acquired by oven-drying at 105°C of BDB-1 borehole  
 260 260 samples and b) accessible porosity to anions ( $\text{Cl}^-$ ,  $\text{Br}^-$ ), radioactive tracers ( $\text{HTO}$ ,  $^{36}\text{Cl}^-$ ) and

261 stable water isotopes ( $^3\text{H}$ ,  $^{18}\text{O}$ ) determined by laboratory-scale diffusion experiments. Values  
262 framed by a dashed line are probably overestimated due to swelling or microcracks.

263 The mean water accessible porosity determined by density measurements is 13.0% in the  
264 Opalinus Clay, with a lower average porosity of 12.0% in the sandy facies compared to the  
265 shaly facies, which shows a mean porosity of 13.5%. These values are lower than the mean  
266 value of 18% suggested by previous studies performed at the Mont Terri tunnel level (Bossart  
267 et al. 2017). The Passwang Formation presents slightly lower porosity values ranging between  
268 8.1% and 14.6% with a mean value of 12.2%. The Hauptrogenstein is characterised by the  
269 lowest porosity with a mean value of 3.9%.

270 Except for the carbonate-rich sandy facies, porosity values obtained by radial diffusion for  
271 stable water isotopes in the Opalinus Clay (up to 22 %) are higher than the values obtained by  
272 density measurements (maximum value of 15 %). Sample preparation steps, such as drilling,  
273 may have brought additional porosity by creating microcracks. Values obtained for  $^2\text{H}$  and  
274  $^{18}\text{O}$  are globally comparable and the anion exclusion (ratio of anion to water accessible  
275 porosities) is in the range of 51 % to 55 % in the OPA shaly facies and between 45 % and  
276 51 % in the sandy facies. These results are consistent with the ratio of 55%, which was chosen  
277 in out diffusion experiments to calculate anion contents in porewater and based on literature  
278 data (Pearson et al. 2003). Chloride and bromide diffusion accessible porosities are also  
279 comparable with values ranging between 6 % and 12 % and a best estimate at 8%.

#### 280 4.1.2 Diffusion coefficients

281 Deduced from radial diffusion experiments, chloride and bromide effective diffusion  
282 coefficient parallel to the bedding are in the order of  $4.0 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$  in the Opalinus Clay,  
283 which is in good agreement with the range of  $1.7 \times 10^{-11}$  to  $4.5 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$  for bromide and  
284  $1.8 \times 10^{-11}$  to  $6.8 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$  for chloride reported in previous studies (Bossart et al. 2011).  
285 Reasonable values from  $3.0 \times 10^{-11}$  to  $1.1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  are obtained for stable water isotopes.

286 Values obtained by through diffusion experiments are also in good agreement with literature  
 1  
 2 287 data. In the Opalinus Clay shaly facies, values of  $9.6 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$  for tritium and  $1.4 \times 10^{-11}$   
 3  
 4 288  $\text{m}^2 \text{ s}^{-1}$  for  $^{36}\text{Cl}$  are obtained parallel to the bedding. In the sandy facies, simulations give  $1.9 \times$   
 5  
 6  
 7 289  $10^{-11} \text{ m}^2 \text{ s}^{-1}$  for tritium and  $5.1 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$  for  $^{36}\text{Cl}$  perpendicular to the bedding (Figure 5).  
 8  
 9  
 10 290 Due to experimental artefacts linked to sample preparation, only three out of the six through  
 11  
 12 291 diffusion cells provided relevant data.

15 292 Alternative formula for the anion exclusion ratio is given by Jacquier et al. (2013) and writes:

$$P_a = \frac{D_e[\text{HTO}]/D_e[^{36}\text{Cl}^-]}{D_0[\text{HTO}]/D_0[^{36}\text{Cl}^-]} \quad (5)$$

22 293 where  $D_e [\text{m}^2 \text{ s}^{-1}]$  is the effective diffusion coefficient and  $D_0 [\text{m}^2 \text{ s}^{-1}]$  is the diffusion  
 23  
 24 294 coefficient in free water, equal to  $2.008 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  for HTO and  $1.771 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  for  $\text{Cl}^-$  at  
 25  
 26  
 27 295  $25^\circ\text{C}$  (Mills and Lobo, 1989).

30 296 Using equation (5), the diffusion anion exclusion deduced from through diffusion experiment  
 31  
 32 297 is equal to 5.9 in the Opalinus Clay shaly facies, and 3.2 in the sandy facies.

35 298 The diffusion anisotropy ratio is the ratio between the effective diffusion coefficients parallel  
 36  
 37  
 38 299 and perpendicular to the bedding. Based on out diffusion experiments, a low anisotropy ratio  
 39  
 40 300 of 2.4 was estimated for chloride effective diffusion coefficient in the Opalinus Clay sandy  
 41  
 42  
 43 301 facies, which is lower than the value of 4 reported by Van Loon et al. (2004) on a shaly facies  
 44  
 45 302 sample. Anisotropy of diffusive parameters could not be determined in the shaly facies due to  
 46  
 47 303 sample cracking and other unloading artefacts.

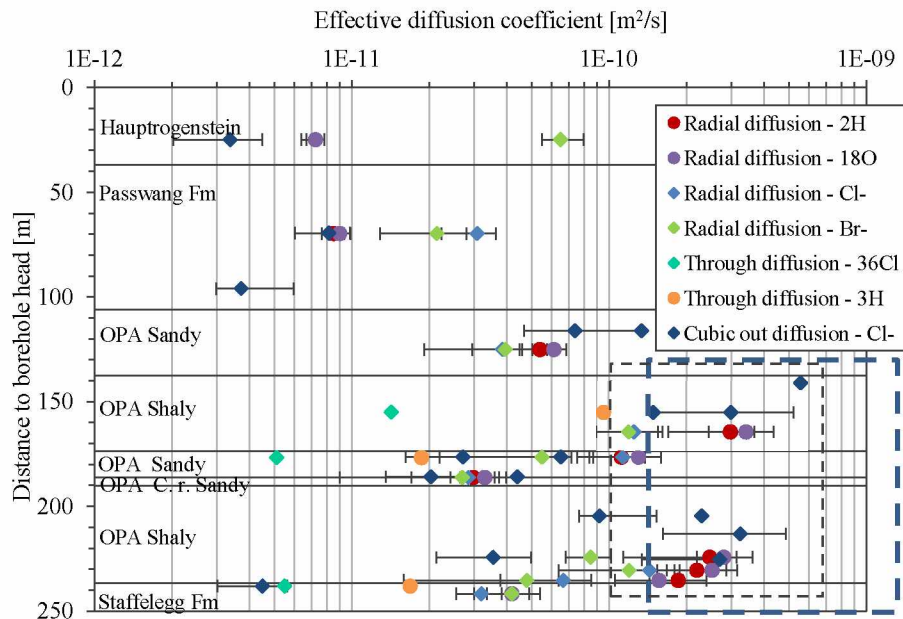
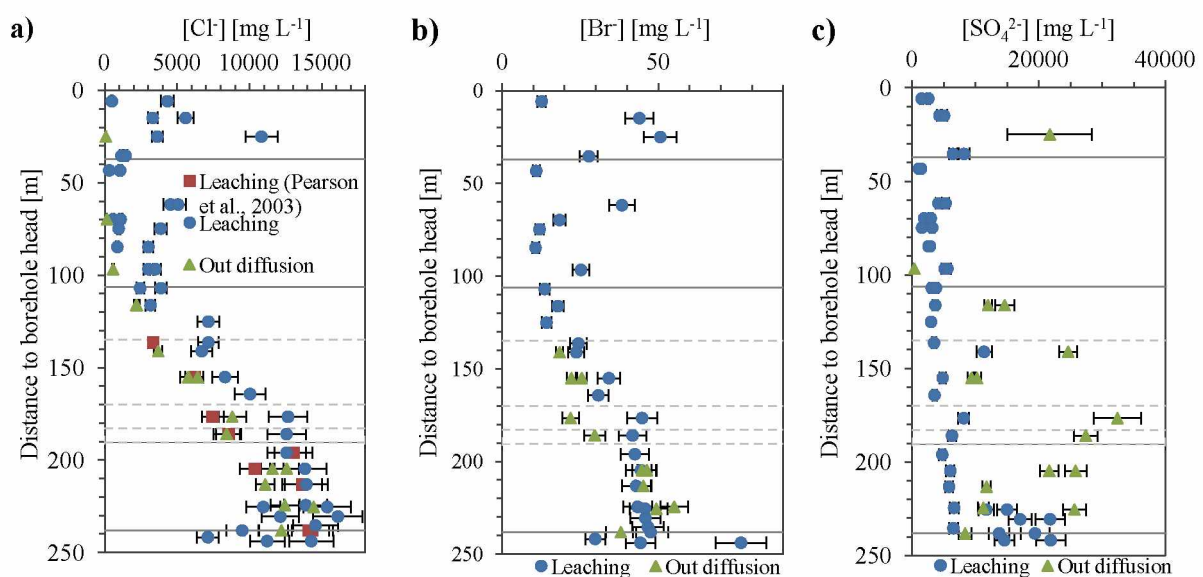


Figure 5: Effective diffusion coefficients acquired on BDB-1 borehole samples. Values framed by a dashed line are probably overestimated due to swelling or microcracks.

#### 4.2 Anion profiles

Chloride, bromide and sulphate profiles acquired by leaching and out diffusion experiments on BDB-1 samples are presented in Figure 6 and confirm the vertical variability of porewater composition along the stratigraphic column.



313 Figure 6: Chloride, bromide and sulphate profiles acquired along BDB-1 borehole by leaching  
1  
2 314 experiments and out diffusion tests.  
3  
4

5 315 Chloride and bromide values obtained by aqueous leaching are systematically higher  
6  
7 316 compared to out diffusion results. Higher values of halides given by aqueous leaching  
8  
9  
10 317 compared to out diffusion are likely due to mineral dissolution or release of elements initially  
11  
12 318 contained in inaccessible porosity. However, the two methods reveal similar curved profiles  
13  
14  
15 319 with increasing chlorinity towards the basal part of the Opalinus Clay (up to  $16.1 \text{ g L}^{-1}$  from  
16  
17 320 leaching experiments). Out diffusion experiments give a range between  $2.1 \pm 0.3 \text{ g L}^{-1}$  and  
18  
19  
20 321  $14.4 \pm 1.0 \text{ g L}^{-1}$  for chloride contents with maximum concentrations found in the basal shaly  
21  
22 322 facies of the Opalinus Clay. The sulphate profile along BDB-1 borehole also shows an  
23  
24  
25 323 increasing trend with depth, but even when extraction was performed under anoxic conditions,  
26  
27 324 oxidation had a major effect on measured concentrations. Artificial increase of sulphate  
28  
29  
30 325 contents can be induced by artefacts linked to experimental procedures: pyrite oxidation  
31  
32 326 during the sample preparation or equilibration process, and dissolution of sulphate-bearing  
33  
34  
35 327 minerals such as gypsum or celestite (Pearson et al., 2003; Wersin et al., 2013). Previous  
36  
37 328 studies conducted at the tunnel level also concluded to a maximum value ranging from 13.6 to  
38  
39 329  $14.4 \text{ g L}^{-1}$  for chloride content, found at the limit between the Opalinus Clay and the  
40  
41  
42 330 Staffelegg Formation (Pearson et al. 2003). The halide concentration ratios are consistent with  
43  
44 331 a marine origin of the Opalinus Clay porewater.  
45  
46

#### 47 332 4.3 Chloride profile modelling 48 49 50

##### 51 333 4.3.1 Modelling assumptions and scenario 52 53

54 334 Although the predominant character of diffusion among other transport processes in low  
55  
56 335 permeability formations is generally claimed, such assumption, which greatly simplifies  
57  
58  
59 336 transport numerical calculations, must be verified using the Peclet number (Soler, 2001):  
60  
61  
62  
63  
64  
65

$$Pe = \frac{qL}{D_e} \quad (6)$$

where  $q$  [ $\text{m s}^{-1}$ ] is the specific discharge (Darcy's velocity),  $L$  [m] is a characteristic distance for transport, here taken to be the formation half thickness, and  $D_e$  [ $\text{m}^2 \text{s}^{-1}$ ] is the effective diffusion coefficient. It is classically stated that for  $Pe < 1$ , diffusion dominates over advection and advection is dominant over chemical diffusion if  $Pe > 1$ . However, in their discussion of transport phenomena in low permeability environments, Huysmans and Dassargues (2005) show that for Peclet numbers (Eq. 6) as high as 10, numerically simulated salinity profiles considering advection and diffusion or diffusion alone only differed by 10% pointing to a negligible advective contribution. Consequently, one can consider that below a value of 10 for  $Pe$ , diffusion models are sufficiently accurate for salinity profile interpretations.

The Opalinus Clay formation is characterized by maximum pressures (or hydraulic head  $h$ ) and chlorinity values within the formation yielding corresponding differences with the surrounding aquifers of at least 5 bars ( $\Delta h = 50$  m) and  $\Delta c = 0.42 \text{ mol L}^{-1}$  respectively. A monotonic cross-formational temperature difference of  $8^\circ\text{C}$  per 100 m is also observed.

Considering that osmotic processes are at work in the Opalinus Clay, the 1D Darcy's velocity accounting for osmotic terms can be expressed as (Gonçalvès et al., 2015):

$$q = -K \frac{\partial h}{\partial z} + \frac{\nu RT \varepsilon_c K}{\rho g} \frac{\partial c}{\partial z} - \frac{\varepsilon_T}{\rho g} K \frac{\partial T}{\partial z} \quad (7)$$

where  $K$  [ $\text{m s}^{-1}$ ] is the cross-formational hydraulic conductivity,  $z$  is the axis perpendicular to the bedding,  $h$  [m] is the hydraulic head,  $\rho$  is the porewater density [ $\text{kg m}^{-3}$ ],  $g$  [ $9.81 \text{ m s}^{-2}$ ] is the gravitational acceleration,  $\varepsilon_c$  [-] and  $\varepsilon_T$  [ $\text{Pa K}^{-1}$ ] are respectively the chemical osmotic efficiency and the thermo-osmotic coefficient,  $\nu$  is the number of dissociated species for a salt (e.g. 2 for NaCl),  $R$  [ $8.32 \text{ m}^3 \text{ Pa K}^{-1} \text{ mol}^{-1}$ ] is the gas constant,  $T$  [K] is the temperature, and  $c$



357 [mol m<sup>-3</sup>] is the chloride concentration. Note that for this first-order calculation, no gravity  
1  
2 358 effect due to salinity is considered enabling the use of the hydraulic head  $h$ .  
3  
4

5 359 The first term in the right-hand side of Equation (7) is related to purely darcian fluid flow, the  
6  
7 360 second and third terms to the chemical and thermal osmosis, i.e. fluid flow driven by salinity  
8  
9  
10 361 and temperature gradients. The petrophysical parameters of the Opalinus clay together with  
11  
12 362 the thermo-osmotic model by Gonçalves et al. (2015) points to a negligible thermo-osmotic  
13  
14  
15 363 term here. For the two remaining terms, simple gradients given by  $\Delta h/L$  and  $\Delta c/L$  can be  
16  
17 364 introduced in Eqs (6) and (7). Peclet calculations require equivalent transport parameters  
18  
19  
20 365 (harmonic means across the formation, perpendicular to the bedding). Using the data of this  
21  
22 366 study and of Yu et al. (2017), a harmonic mean of  $10^{-11}$  m<sup>2</sup> s<sup>-1</sup> and  $1.85 \times 10^{-13}$  m s<sup>-1</sup> is found  
23  
24  
25 367 for  $D_e$  and  $K$ . Using these values for an equivalent NaCl ( $\nu = 2$ ) system and  $\epsilon_c$  between 0.036  
26  
27 368 and 0.081 (Noy et al., 2004) yields a Peclet number of between 0.6 and 0.8. It can thus be  
28  
29  
30 369 concluded that transport is likely dominated by diffusion for the Opalinus Clay. Therefore,  
31  
32 370 mass transport calculations can be made by solving Equation (1) using a simple and robust  
33  
34  
35 371 finite difference numerical scheme.  
36  
37

38 372 The paleohydrogeological evolution was chosen accordingly to the conclusions of Bossart  
39  
40 373 and Wermeille (2003), who constrained the erosion and thus the exhumation of the Dogger  
41  
42  
43 374 limestone overlying the Opalinus Clay between 10.5 and 1.2 Ma (time  $t_0$  hereafter). At that  
44  
45 375 time, the subsequent rapid flushing of the Dogger limestone pore water by meteoritic water  
46  
47  
48 376 brought the salinity to zero which constitutes a boundary condition for the transport model.  
49  
50 377 The activation of the Liassic limestone aquifer underlying the Opalinus Clay occurred  
51  
52 378 between 0.5 and 0.2 Ma (time  $t_I$ ). A plausible range between 14 and 23 g L<sup>-1</sup> was chosen for  
53  
54  
55 379 the initial chlorinity  $C_0$  prior to the Jura Mountains folding (Mazurek et al., 2011). Cross-  
56  
57  
58 380 formational diffusive transport parameters, namely effective diffusion coefficient and  
59  
60 381 diffusion accessible porosity, were deduced from laboratory experiments carried out on BDB-  
61  
62  
63  
64  
65

1 382 1 samples and described in section 5.1. Exhumation times  $t_0$  and  $t_1$  together with the initial  
2 383 chlorinity are used for boundary and initial conditions definition of the 1D diffusion model.  
3  
4 384 At initial time  $t_0$ , the chlorinity is set to  $C_0$  within the Opalinus clay, the upper and lower  
5  
6  
7 385 concentration boundary conditions are 0 and  $C_0$ , respectively. Then, when the simulation time  
8  
9  
10 386 reaches  $t_1$ , the lower boundary condition is set to zero. These boundary conditions allow  
11  
12 387 simulating diverging diffusive mass transport from the Opalinus Clay towards first the upper  
13  
14 388 aquifer alone then towards both aquifers. The model takes into accounts 7 formations showing  
15  
16  
17 389 different properties listed in Table 1.

#### 20 390 4.3.2 Modelling results

23 391 The parameters to be calibrated must be chosen carefully since for more than 10 parameters,  
24  
25 392 implementing MCMC methods becomes hazardous (large time- and cpu-consuming,  
26  
27 393 convergence issues). However, under the assumption of purely diffusive mass transport, since  
28  
29  
30 394 the porosity intrinsically appears ( $D_e = \omega D_p$ ) in both sides of Equation (1), this parameter  
31  
32  
33 395 does not impact calculated chlorinity profiles which are only controlled by the pore diffusion  
34  
35 396 coefficient. Therefore, porosity was not considered in our inverse modelling and was kept  
36  
37  
38 397 constant for each formation. From a practical standpoint, the calibrated parameters were the  
39  
40 398 cross-formational effective diffusion coefficient for each of the 7 formations  $D_e$  (in fact  $D_p$   
41  
42 399 since  $\omega$  is fixed, see above),  $t_0$ ,  $t_1$  and  $C_0$  which are all considered uncertain. Uniform *a priori*  
43  
44  
45 400 distributions were considered for these 10 parameters using lower and upper boundaries  
46  
47 401 described in Section 4.3.1 for  $t_0$ ,  $t_1$  and  $C_0$ , and boundaries encompassing the measurements  
48  
49  
50 402 for the 7 formation  $D_e$  values (see Table 1)

53 403 In the course of the MCMC inversion process involving 10 parameters (a priori values in  
54  
55  
56 404 Table 1), the misfit function reached a plateau after about 2000 iterations for 100000  
57  
58 405 performed iterations (Figure A.1, Appendix A). Only about 800 random moves were accepted,

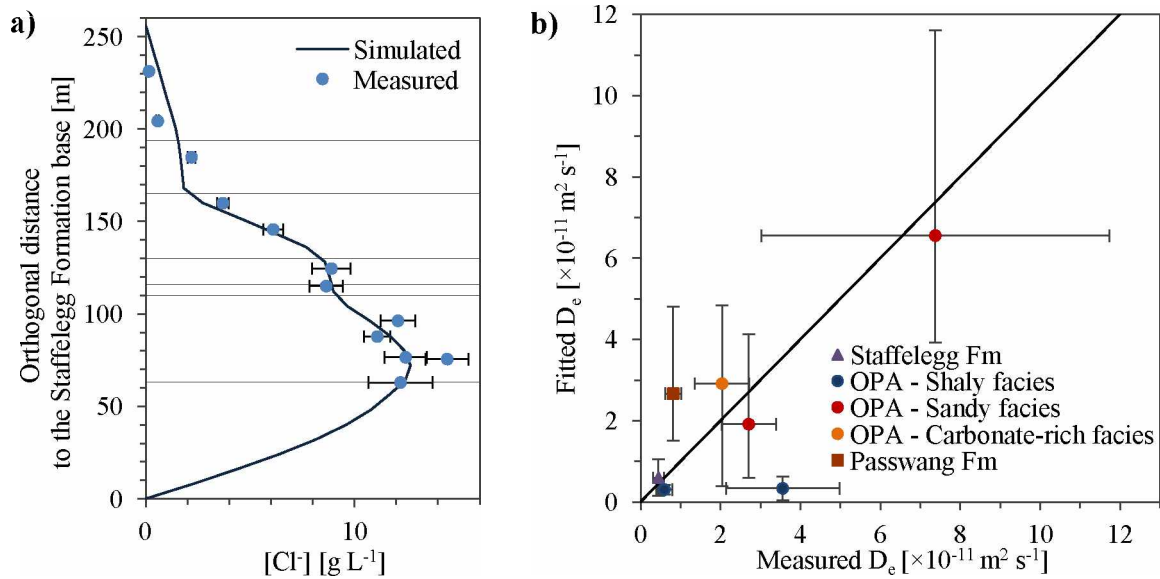
406 indicating a relatively low number of parameter sets that fit the experimental data. The sets of  
 407 parameters leading to the 5% lower misfit values were used to establish the *a posteriori*  
 408 marginal distributions of the ten parameters shown in Fig 2.A of Appendix A. Both  
 409 multimodal and unimodal distributions are obtained. Multimodal distributions were fitted by  
 410 gaussian mixture distributions, all unimodal variables were fitted by a gaussian model except  
 411 for  $C_0$  that is described by a log normal distribution (see Appendix A). Mean values and 95%  
 412 confidence intervals for each parameters were calculated using the fitted distributions (see  
 413 Table 1). For multimodal distributions, the weights and means of each fitted normal  
 414 distribution component are used to calculate an "overall mean" for a given parameter as the  
 415 weighted average of the mean values (see Appendix A). Therefore, the relative importance of  
 416 each gaussian distribution within the gaussian mixture is respected. Note that the low number  
 417 of sampled values in the parameter space is likely a limitation for the *a posteriori* marginal  
 418 pdfs identification method described in Section 3.5. However, taking more samples (40% of  
 419 accepted displacements) yields the same type of marginal distributions but with slightly  
 420 different statistical parameters and a larger misfit when the mean parameters values are used  
 421 in a direct simulation.

422 Table 1: Input parameters and associated uncertainties involved in the MCMC inversion  
 423 process. Accessible porosities and formation thicknesses were kept constant. CI stands for  
 424 Confidence Interval.

Formation	Thickness [m]	$\omega$ [vol.%]	De [m <sup>2</sup> /s] ( $\times 10^{-11}$ )		
			Measurements	<i>A priori</i>	<i>A posteriori</i> Mean and 95% CI
Passwang Formation	69	7.5	$D_e^7: 0.817 \pm 0.2$	[10 <sup>-1</sup> -20]	2.66 [1.51; 4.81]
OPA – Sandy facies	29	6.9	$D_e^6: 7.38 \pm 4.36$	[10 <sup>-1</sup> -20]	6.55 [3.92; 11.61]
OPA – Shaly facies	35	7.6	$D_e^5: 0.597 \pm 0.2$	[10 <sup>-1</sup> -20]	0.30 [0.18; 0.41]
OPA –	14	5.4	$D_e^4: 2.71$	[10 <sup>-1</sup> -20]	1.91

Sandy facies			$\pm 1.9$		[0.59; 4.12]
OPA – Carbonate-rich Sandy facies	6	6.8	$D_e^3: 2.04$ $\pm 0.68$	[10 <sup>-1</sup> -20]	2.91 [0.39; 4.84]
OPA – Shaly facies	47	7.7	$D_e^2: 3.56$ $\pm 1.42$	[10 <sup>-1</sup> -20]	0.33 [0.04; 0.62]
Staffelegg Formation	63	4.5	$D_e^1: 0.451$ $\pm 0.132$	[10 <sup>-1</sup> -20]	0.59 [0.15; 1.04]
Parameter	Value	Range			
			<i>A priori</i>		<i>A posteriori</i>
Activation time [Ma]					
Dogger aquifer (upper boundary)	-5	[-10.5; -1.2]			-4.54 [-6.77; 1.7]
Lias aquifer (lower boundary)	-0.25	[-0.5;-0.2]			-0.24 [-0.3; -0.2]
Initial chlorinity [g L <sup>-1</sup> ]	19	[14;23]			19 [17.3; 22]

As shown in Figure 7a, the simulation of diffusion for chloride matches fairly well the experimental data considering the mean a posteriori values for the parameters (Table 1). Except for two diffusion coefficients values (Passwang Formation and Opalinus Clay basal shaly facies), the fitted parameters are highly consistent with the measurements and exhumation time expectations (Figure 7b). The misfit for diffusion coefficients can be due to an imperfect mechanical confining of the Opalinus Clay sample leading to an overestimation of the measured  $D_e$  for the Opalinus Clay shaly facies. On the other hand, the Passwang Formation is more heterogeneous compared to the different facies of the Opalinus Clay. Lithostratigraphic investigation carried out by Hostettler et al. (2017) on BDB-1 drillcores showed that this formation exhibits variable lithology (silty to fine sandy marls, quartz sand and biotrital sandy limestones, ferruginous limestones, iron oolitic marls and limestones). The number of samples investigated in laboratory-scale diffusion experiments was likely insufficient to reflect this variability in the present study.



438  
439 Figure 7: Comparison between a) experimental and simulated chloride profile obtained with  
440 the mean *a posteriori* values for the parameters and b) experimental and fitted diffusion  
441 coefficients, error bars represent 95% confidence interval.

442 The modelling results are globally consistent with previous studies carried out at the Mont  
443 Terri rock laboratory. A lower equivalent effective diffusion coefficient for anions of  $4.6 \times$   
444  $10^{-12} \text{ m}^2 \text{ s}^{-1}$  was used in Mazurek et al. (2011) for the Opalinus Clay and the directly adjacent  
445 formations, whereas different diffusion coefficient values were considered for each unit along  
446 the rock sequence in the present study. A higher cross-formational equivalent diffusion  
447 coefficient of  $6.3 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$  for the Opalinus Clay explains the shorter time obtained for  
448 the adjacent aquifers activation in comparison with the study of Mazurek et al.(2011): 4.5 Ma  
449 compared to 6 Ma for the upper aquifer and 0.246 Ma compared to 0.5 Ma for the lower  
450 aquifer. However, the activation age at -4.54 Ma proposed here is close to one of the major  
451 morpho-tectonic event proposed by Kuhlemann and Rahn (2013) at -4.2 Ma.

## 54 452 5 Conclusions

55  
56 453 An integrated study from BDB-1 borehole samples characterisation on the Opalinus Clay  
57 454 transport capabilities and transport modelling was performed. Petrophysical analysis enabled

1  
2 455 the acquisition of water accessible porosity, grain density and water contents along the rock  
3  
4 456 sequence. Out diffusion and aqueous leaching techniques were used to obtain chloride  
5  
6 457 concentrations of porewater in the Opalinus Clay and its bounding formations. Effective  
7  
8 458 diffusion coefficients and diffusion accessible porosities were also investigated by radial  
9  
10 459 diffusion and through diffusion experiments.

11  
12 460 The measured chloride contents are in good agreement with previous investigation performed  
13  
14 461 at the Mont Terri tunnel level, and show an asymmetric bell-shaped trend increasing to a high  
15  
16 462 chloride concentration of  $14.4 \text{ g L}^{-1}$  towards the bottom of the Opalinus Clay. Moreover,  
17  
18 463 chloride to bromide ratios reflect a marine signature in the clay rock. The chloride profile  
19  
20 464 suggests a diffusive exchange between the argillaceous formation and the adjacent aquifers,  
21  
22 465 with deferred activation times of the fresh-water sources linked to the surface erosion of the  
23  
24 466 geological formations. This scenario was implemented in a Monte Carlo Markov Chain  
25  
26 467 algorithm, which enabled to assess the best fitting set of parameters (initial chloride content,  
27  
28 468 aquifer activation times and diffusion coefficients) and associated confidence intervals  
29  
30 469 explaining the present-day chloride profile. Experimental and simulated data are comparable  
31  
32 470 for respective diffusion times of 4.54 Ma and 0.246 Ma between the Opalinus Clay and the  
33  
34 471 Dogger (overlying) and Liassic (underlying) limestones.

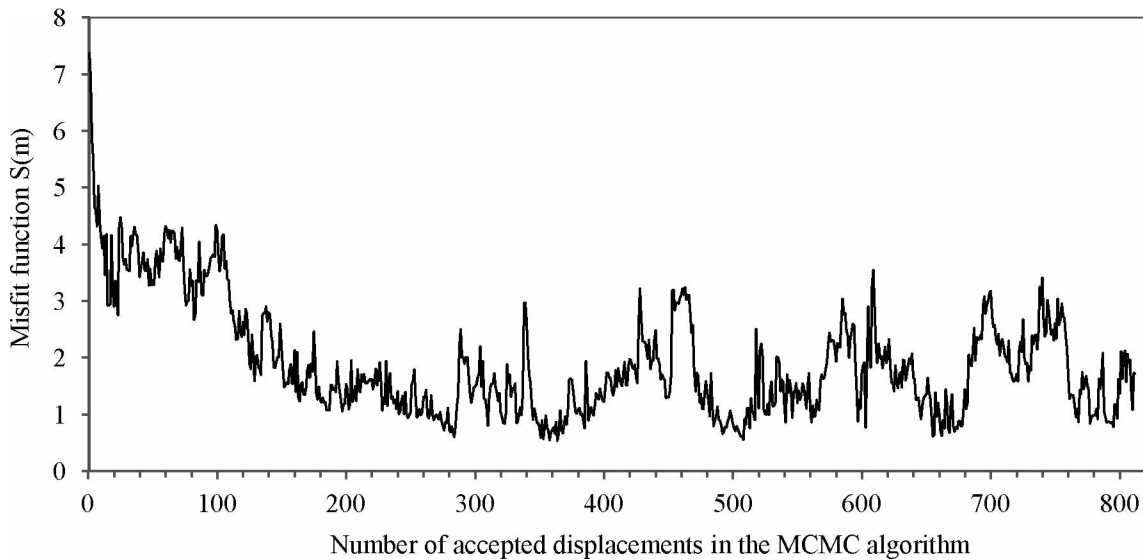
35  
36 472 The present study confirms the paleohydrogeological evolution of the Mont Terri site from  
37  
38 473 the folding of the Jura Mountains. This scenario is fundamental to constrain our future  
39  
40 474 transient modelling of the overpressure regime observed in the Opalinus Clay to fully  
41  
42 475 characterise transport processes in this formation.

476 **Acknowledgments**

1  
2  
3 477 This study was performed in the framework of the Deep Borehole experiment, financed by six  
4  
5 478 partners of the International Mont Terri Consortium (Swisstopo, NAGRA, BGR, GRS,  
6  
7 479 NWMO, IRSN).

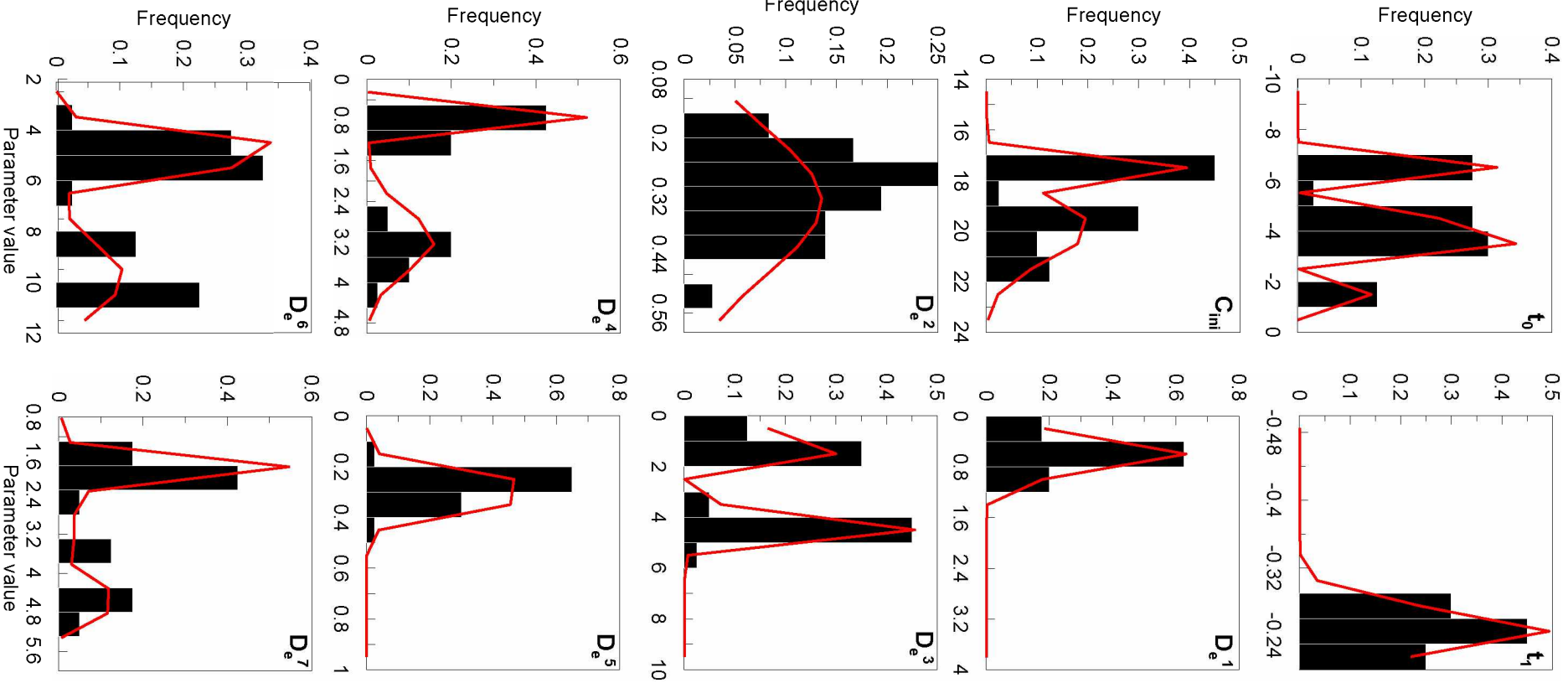
10 480 **Appendix A**

11  
12  
13 481 The convergence of the MCMC approach is characterised by a sharp decrease of the misfit  
14  
15 482 function value from almost 7 to 1.5 on average after 2000 iterations (almost 200 accepted  
16  
17 483 movements) of the random walk as shown in Figure A.1.



38  
39 484  
40  
41  
42 485 Figure A.1: Misfit function as a function of the number of accepted displacements in the  
43  
44 486 MCMC algorithm.

45  
46  
47 487 The sets of parameters leading to the 5% lower misfit values (errors lower than 0.7) were used  
48  
49 488 to establish the *a posteriori* marginal distributions (Figure A.2).



1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65

489



490 Figure A.2: *A posteriori* distributions (pdfs) for each parameter of the diffusion model.  
 1  
 2 491 Parameters values in [ $\times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ ] for  $D_e$ , [ $\text{g L}^{-1}$ ] for  $C_0$ , and [Ma] for  $t_0$  and  $t_l$ . The  
 3  
 4 492 histograms results from the MCMC approach (Section 3.5). In red, the fitted theoretical  
 5  
 6  
 7 493 distributions (Gaussian mixtures:  $t_0$ ,  $C_0$ ,  $D_e^3$ ,  $D_e^4$ ,  $D_e^6$ , and  $D_e^7$ , Gaussian:  $D_e^1$ ,  $D_e^2$ , and  $D_e^5$ ,  
 8  
 9 494 and Lognormal:  $t_l$ )

12 495 Multimodal distributions were fitted by gaussian mixture distributions:

$$\alpha G(\mu_1, \sigma_1) + \beta G(\mu_2, \sigma_2) + \gamma G(\mu_3, \sigma_3) \quad (\text{A.1})$$

18 496 where  $G(\mu_i, \sigma_i)_{i=\{1,2,3\}}$  are Gaussian distributions and  $\alpha$ ,  $\beta$ , and  $\gamma$  are the respective weights. The  
 19  
 20 497 fitted distribution parameters are listed in Table A.1.

23 498 Table A.1: Parameters of fitted pdf with effective diffusion coefficients  $D_e$  [ $\times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ ],  
 24  
 25 499 activation times  $t_0$  and  $t_l$  [Ma], and initial chloride concentration  $C_0$  [ $\text{g L}^{-1}$ ].

Variable	$\alpha$	$\beta$	$\gamma$	$\mu_1$	$\sigma_1$	$\mu_2$	$\sigma_2$	$\mu_3$	$\sigma_3$
$t_0$	0.32	0.56	0.12	-6.45	-3.95	-1.78	0.19	0.22	0.10
Log( $-t_l$ )	1	0	0	-0.61	0.04	-	-	-	-
$C_0$	0.37	0.63	0	17.48	19.87	1.22	0.09	-	-
$D_e^1$	1	0	0	0.60	0.22	-	-	-	-
$D_e^2$	1	0	0	0.33	0.14	-	-	-	-
$D_e^3$	0.16	0.3	0.54	0.48	1.74	4.33	0.08	0.08	0.3
$D_e^4$	0.53	0.47	0	0.75	3.18	0.57	0.10	-	-
$D_e^5$	1	0	0	0.3	0.06	-	-	-	-
$D_e^6$	0.67	0.33	0	4.91	9.83	1.24	0.55	-	-
$D_e^7$	0.58	0.22	0.2	1.86	3.08	4.58	0.14	1.19	0.14

44 500

501 **References**

- 1  
2  
3 502 Bensenouci, F., 2010. Apport des traceurs naturels à la compréhension des transferts au sein  
4  
5 503 des formations argileuses compactées. Thesis, Université Paris-Sud XI, Orsay, France, 194 pp.  
6  
7  
8 504 Bensenouci, F., Michelot, J.L., Matray, J.M., Savoye, S., Tremosa, J., Gaboreau, S., 2013.  
9  
10 505 Profiles of chloride and stable isotopes in pore-water obtained from a 2000 m-deep borehole  
11  
12 506 through the Mesozoic sedimentary series in the eastern Paris Basin. *Phys. and Chem. of the*  
13  
14 507 *Earth*, 65, 1-10.  
15  
16  
17  
18 508 Blaesi, H.-R., Peters, T. J., Mazurek, M., 1991. Der Opalinus-Ton des Mt. Terri (Kanton  
19  
20 509 Jura): Lithologie, Mineralogie und physiko-chemische Gesteinsparameter. *Nagra Interner*  
21  
22 510 *Bericht, 90-60*. Nagra, Wettingen, Switzerland. <[www.nagra.ch](http://www.nagra.ch)>  
23  
24  
25  
26 511 Bossart, P., Wermeille, S., 2003. Paleohydrological study of the Mont Terri rock laboratory.  
27  
28 512 In: Heitmann, P., Tripet, J.P. (Eds.), Mont Terri Project-Geology, paleohydrogeology and  
29  
30 513 stress field of the Mont Terri region. Federal Office for Water and Geology Rep. 4, Bern,  
31  
32 514 Switzerland, 45-64. <[www.swisstopo.admin.ch](http://www.swisstopo.admin.ch)>  
33  
34  
35  
36 515 Bossart, P., Thury, M., 2008. Mont Terri Rock Laboratory. Project, Programme 1996 to 2007  
37  
38 516 and Results. *Reports of the Swiss Geological Survey, No. 3*, 445 pp. Federal Office of  
39  
40 517 Topography (swisstopo), Wabern, Switzerland. <[www.mont-terri.ch](http://www.mont-terri.ch)>  
41  
42  
43  
44 518 Bossart, P., Bernier, F., Birkholzer, J., Bruggeman, C., Connolly, P., Dewonck, S., Fukaya,  
45  
46 519 M., Herfort, M., Jensen, M., Matray, J.-M., Mayor, J.C., Moeri, A., Oyama, T., Schuster, K.,  
47  
48 520 Shigeta, N., Vietor, T., Wiczorek, K., 2017. Mont Terri rock laboratory, 20 years of  
49  
50 521 research: introduction, site characteristics and overview of experiments. *Swiss J. of Geosci.*,  
51  
52 522 *110*, doi:10.1007/s00015-016-0236-1  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65

523 Clauer, N., Techer, I., Nussbaum, C., Laurich, B., 2017. Geochemical signatures of  
1  
2 524 paleofluids in microstructures from Main Fault of the Opalinus Clay, Mont Terri rock  
3  
4  
5 525 laboratory, (Switzerland). *Swiss J. of Geosci.*, 110, doi:10.1007/s00015-016-0253-0  
6  
7  
8 526 Fierz, T., Rösli, U., 2014. Mont Terri DB Experiment: Installation of a 7-interval multi-packer  
9  
10 527 system into borehole BDB-1. Instrumentation Report. *Mont Terri Technical Note*, TN 20414-  
11  
12 528 23. 37 pp. Federal Office of Topography (swisstopo), Wabern, Switzerland. <[www.mont-  
16  
17  
18 530 terri.ch](http://www.mont-<br/>13<br/>14<br/>15 529 terri.ch)>  
19  
20 531 Gallagher, K., Charvin, K., Nielsen, S., Sambridge, M., Stephensen, J., 2009. Markov chain  
21  
22 532 Monte Carlo (MCMC) sampling methods to determine optimal models, model resolution and  
23  
24  
25 533 model choice for Earth Science problems. *Mar. and Pet. Geol.*, 26, 525-535.  
26  
27  
28 534 Gautschi, A., 2001a. Hydrogeology of a fractured shale (Opalinus Clay): Implications for the  
29  
30  
31 535 deep disposal of radioactive wastes. *Hydrogeol. J.*, 9, 97-107.  
32  
33  
34 536 Gonçalvès, J., Violette, S., Wendling, J., 2004. Analytical and numerical solutions for  
35  
36 537 alternative overpressuring processes: applications of the Callovo-Oxfordian argillite in the  
37  
38  
39 538 Paris Basin, France. *J. of Geophys. Res.*, 109(B2), DOI: 10.1029/2002JB002278  
40  
41  
42 539 Gonçalvès, J., Adler, P.M., Cosenza, P., Pazdniakou, A., de Marsily, G., 2015. Semi-  
43  
44 540 permeable membrane properties and chemo-mechanical coupling in clay barriers. *Nat. and  
45  
46  
47 541 Eng. Clay Barriers*, pp. 269-327.  
48  
49  
50 542 Burkhardt, S., Waltschew, A., Dietze, V., Menkveld-Gfeller, U., 2017. Litho- and  
51  
52 543 biostratigraphy of the Opalinus Clay and bounding formations in the Mont Terri rock  
53  
54 544 laboratory (Switzerland). *Swiss J. of Geosci.*, 110, doi:10.1007/s00015-016-0250-3  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65

- 1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65
- 545 Huysmans, M., Dassargues, A., 2005. Review of the use of Péclet numbers to determine the  
546 relative importance of advection and diffusion in low permeability environments. *Hydrogeol.*  
547 *J.*, 13 (5–6), 895–904.
- 548 Jacquier, P., Hainos, D., Robinet, J.C., Herbette, M., Grenut, B., Bouchet, A., Ferry, C., 2013.  
549 The influence of mineral variability of Callovo-Oxfordian clay rocks on radionuclide transfer  
550 properties. *Appl. Clay Sci.* 83-84, 129-136.
- 551 Johns, R. T., Vomvoris, S. G., Löw, S., 1995. Review of hydraulic field tests in the Opalinus  
552 Clay of Northern Switzerland. *Hydraul. and hydrochem. Charact. of argillaceous rocks*. NEA.
- 553 Koroleva, M., Lerouge, C., Mäder, U., Claret, F., Gaucher, E.C., 2011. Biogeochemical  
554 processes in a clay formation in situ experiment: Part B - Results from overcoring and  
555 evidence of strong buffering by the rock formation. *Appl. Geochem.*, 26 (6), 954-966.
- 556 Kuhlemann, J., Rahn, M., 2013. Plio-Pleistocene landscape evolution in Northern Switzerland.  
557 *Swiss. J. Geosci.*, 106, 451-467.
- 558 Mazurek, M., Elie, M., Hurford, A., Leu, W., Gautschi, A., 2002. Burial history of Opalinus  
559 Clay. *Clays In Nat. And Eng. Barriers For Radioact. Waste Confinement*, December 9-12,  
560 Reims, France.
- 561 Mazurek, M., Hurford, A., Leu, W., 2006. Unravelling the multi-stage burial history of the  
562 Swiss Molasse Basin: intergration of apatite fission track, vitrinite reflectance and biomarker  
563 isomerisation analysis. *Basin Res.*, 18, 27-50.
- 564 Mazurek, M., Alt-Epping, P., Bath, A., Gimmi, T., Waber, H.N., Buschaert, S., De Cannière,  
565 P., De Craen, M., Gautschi, A., Savoye, S., Vinsot, A., Wemaere, I., Wouters, L., 2011.  
566 Natural tracer profiles across argillaceous formations. *Appl. Geochem.*, 26, 1035-1064

1 567 Mazurek, M., de Haller, A., 2017. Pore-water evolution and solute-transport mechanisms in  
2 568 Opalinus Clay at Mont Terri and Mont Russelin (Canton Jura, Switzerland). *Swiss J. of*  
3  
4  
5 569 *Geosci.*, 110, doi:10.1007/s00015-016-0249-9.  
6  
7 570 Mills, R.L., and Lobo, V.M.M., 1989. Self-diffusion in Electrolyte Solutions - A Critical  
8  
9  
10 571 Examination of Data Compiled from the Literature. Elsevier.  
11  
12  
13 572 Novakowski, K.S., Van der Kamp, G., 1996. The radial diffusion method 2. A Semianalytical  
14  
15 573 model for the determination of effective diffusion coefficients, porosity and adsorption. *Water*  
16  
17  
18 574 *Resour. Res.*, 32, No. 6, 1823-1830.  
19  
20  
21 575 Noy, D., Horseman, S., Harrington, J., Bossart, P., Fisch, H., 2004. An Experimental and  
22  
23 576 modelling study of chemico-osmotic effects in the Opalinus Clay of Switzerland. In:  
24  
25 577 Heitzmann, P. ed. (2004) Mont Terri Project - Hydrogeological Synthesis, Osmotic Flow. *Rep.*  
26  
27  
28 578 *of the Fed. Off. for Water and Geol. (FOWG)*, Geology Series (6), 95–126.  
29  
30  
31 579 Nussbaum, C., Bossart, P., Amann, F., Aubourg, C., 2011. Analysis of tectonic structures and  
32  
33 580 excavation induced fractures in the Opalinus Clay, Mont Terri underground rock laboratory  
34  
35  
36 581 (Switzerland). *Swiss J. of Geosci.*, 104, 187-210.  
37  
38  
39 582 Nussbaum, C., Kloppenburg, A., Caer, T., Bossart, P., 2017. Tectonic evolution of the Mont  
40  
41 583 Terri anticline based on forward modelling. *Swiss J. of Geosci.*, 110, doi:10.1007/s00015-  
42  
43 584 016-0248-x  
44  
45  
46 585 Patriarche, D., Michelot, J.L., Ledoux, E., Savoye, S., 2004a. Diffusion as the main process  
47  
48  
49 586 for mass transport in very low water content argillites: 1. Chloride as a natural tracer for mass  
50  
51 587 transport – Diffusion coefficient and concentration measurements in interstitial water. *Water*  
52  
53  
54 588 *Resour. Res.*, 40, W01516, doi:10.1029/2003WR002700.  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65

589 Patriarche, D., Michelot, J.L., Ledoux, E., Savoye, S., 2004b. Diffusion as the main process  
1  
2 590 for mass transport in very low water content argillites: 2. Fluid flow and mass transport  
3  
4  
5 591 modeling. *Water Resour. Res.*, 40, W01517, doi:10.1029/2003WR002700.  
6  
7  
8 592 Pearson, F. J., Arcos, D., Boisson, J-Y., Fernández, A. M., Gäbler, H.E., Gaucher, E.,  
9  
10 593 Gautschi, A., Griffault, L., Hernán, P., Waber, N., 2003. Mont Terri Project - Geochemistry  
11  
12 594 of water in the Opalinus Clay Formation at the Mont Terri Rock Laboratory. *Rep. of the Swiss*  
13  
14  
15 595 *Geol. Survey, No. 5*, 143 pp. Federal Office of Topography (swisstopo), Wabern, Switzerland.  
16  
17 596 <[www.mont-terri.ch](http://www.mont-terri.ch)>  
18  
19  
20 597 Petersen, J.O, Deschamps, P., Gonçalvès, J., Hamelin, B., Michelot, J.L., Guendouz, A.,  
21  
22  
23 598 Zouari, K., 2014. Quantifying paleorecharge in the Continental Intercalaire (CI) aquifer by a  
24  
25 599 Monte-Carlo inversion approach of  $^{36}\text{Cl}/\text{Cl}$  data. *Appl.Geochem*, 50, 209-221  
26  
27  
28 600 Sacchi, E., Michelot J-L., Pitsch, H., Lalieux, P., Aranyossy, J-F., 2001. Extraction of water  
29  
30 601 and solutes from argillaceous rocks for geochemical characterisation: Methods, processes, and  
31  
32  
33 602 current understanding, *Hydrogeol. J.*, 9, 17-33.  
34  
35  
36 603 Sellin, P., Leupin, O.X., 2014. The use of clay as an engineered barrier in radioactive waste  
37  
38 604 management – a review. *Clays and Clay Miner.*, 61, 477–498.  
39  
40  
41 605 Soler, J.M., 2001. The effect of coupled transport phenomena in the Opalinus Clay and  
42  
43  
44 606 implications for radionuclide transport. *J. of Contam. Hydrol.*, 53, 63–84  
45  
46  
47 607 Tarantola, A., 2005. Monte Carlo Methods. Chapter 2 in *Inverse Problem Theory and*  
48  
49 608 *Methods for Model Parameter Estimation. Soc. for Ind. and Appl. Math.*, 41-56.  
50  
51  
52 609 Van der Kamp, G., Van Stempvoort, D.R., Wassenaar, L.I., 1996. The radial diffusion  
53  
54  
55 610 method 1. Using intact cores to determine isotopic composition, chemistry, and effective  
56  
57 611 porosities for groundwater in aquitards. *Water Resour. Res.*, 32, No. 6, 1815-1822.  
58  
59  
60  
61  
62  
63  
64  
65

- 1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65
- 612 Van der Lee, J., De Windt, L., Lagneau V., Goblet, P., 2003. Module-oriented modeling of  
613 reactive transport with HYTEC. *Comput. & Geosci.*, 29-3, 265-275.
- 614 Van Loon, L.R., Soler, J., Müller, W. and Bradbury, M. H., 2004. Anisotropic diffusion in  
615 layered Argillaceous Rocks: a case study with Opalinus clay. *Environ. Sci. Technol.*, 38,  
616 5721–5728.
- 617 Wersin, P., Waber, H.N., Mazurek, M., Mäder, U.K., Gimmi, T., Rufer, D., Traber, D., 2013.  
618 Resolving Cl and SO<sub>4</sub> profiles in a clay-rich rock sequence. *Procedia Earth and Planet. Sci.*,  
619 7, 892-895.
- 620 Yu, C., Matray, J.M., Gonçalvès, J., Jaeggi, D., Gräsle, W., Wieczorek, K., Vogt, T., Sykes,  
621 E., 2017. Comparative study of methods to estimate hydraulic parameters in the hydraulically  
622 undisturbed Opalinus Clay (Switzerland). *Swiss J. of Geosci.*, 110, doi: 10.1007/s00015-016-  
623 0257-9h)