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Biogeochemical processes in a clay formation in situ experiment: Part F –

Reactive transport modelling

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Abstract

Reactive transport modelling was used to simulate solute transport, thermodynamic reactions, ion exchange and biodegradation in the Porewater Chemistry (PC) experiment at the Mont Terri Rock Laboratory. Simulations show that the most important chemical processes controlling the fluid composition within the borehole and the surrounding formation during the experiment are ion exchange, biodegradation and dissolution/precipitation reactions involving pyrite and carbonate minerals. In contrast, thermodynamic mineral dissolution/precipitation reactions involving aluminosilicate minerals have little impact on the fluid composition on the time-scale of the experiment. With the accurate description of the initial chemical condition in the formation in combination with kinetic formulations describing the different stages of bacterial activities, we succeeded in reproducing the evolution of important system parameters, such as the pH, redox potential, total organic carbon, dissolved inorganic carbon and sulphate concentration. Leaching of glycerol from the pH-electrode may be the primary source of organic material that initiated bacterial growth, which caused the chemical perturbation in the borehole. Results from these simulations are consistent with data from the over-coring and demonstrate that the Opalinus Clay has a high buffering capacity in terms of chemical perturbations caused by bacterial activity. This buffering capacity can be attributed to the carbonate system as well as to the reactivity of clay surfaces.

1. Introduction

Over the past two decades, reactive transport models have evolved as valuable diagnostic and prognostic tools and have made a significant contribution to elucidating the inherently complex dynamics of natural and engineered environments (Appelo, 1994; Steefel et al., 2003; Steefel et al., 2005; Gaucher and Blanc, 2006; Appelo et al., 2008; Gaus et al., 2008; Han et al., 2010). These models provide the theoretical framework for simulating coupled thermal-hydraulic-chemical-biological processes within earth systems. As such, these models constitute a basis for testing concepts and hypotheses and for integrating new experimental, observational and theoretical knowledge about geochemical, biological and transport processes (e.g. Steefel and Lichtner, 1994; Lichtner et al., 1996; Appelo et al., 1998; Maher et al., 2009).

The Porewater Chemistry (PC) experiment in the Mont Terri Laboratory was designed to improve our understanding of the compositional characteristics and the buffering mechanisms of the porewater in the Opalinus Clay. For that purpose, a vertical borehole of 52 mm diameter was drilled to a depth of 10.10 m. The bedding dips at an angle of about 45° to the SE. The first 5 meters of the borehole were drilled with air. For the remaining 5.1 m, nitrogen was used in order to minimise ingress of molecular oxygen and hence oxidation of pyrite and organic matter around the borehole wall. Immediately after drilling, the borehole was filled with Ar. The downhole equipment including the 4.5 m long screen made of porous (40 µm mesh size) low pressure polyethylene with a porosity of 0.3 and a 0.33 m long hydraulic mechanical packer was emplaced into the borehole. The remaining part of the borehole was filled with epoxy resin (Sikadur 52).

The borehole was filled with synthetic porewater (2.8 L) which had been previously saturated with an Ar/CO₂ gas mixture corresponding to a pCO₂ of 10^{-3.5} bar, as in air. This synthetic porewater was traced to keep track of transport-controlled exchange of solutes between

the borehole and the surrounding formation. More details about the design and results of the experiment are summarized in Wersin et al. (This Issue-a). The original focus of this experiment was to obtain high-quality data on the porewater composition and thus to reduce uncertainties in pH/pCO₂ and Eh. However, unexpected microbial activity in the borehole observed after about nine months led to a revised research program with the following objectives:

- i. to identify biogeochemical processes occurring in the borehole and describe these quantitatively
- ii. to obtain diffusion parameters of injected conservative tracers
- iii. to identify the source of organic carbon for microbial degradation
- iv. to draw conclusions on the findings with regard to conditions of the clay host rock around a nuclear waste repository

To understand the complexity of processes and to identify and/or quantify crucial system parameters of the PC experiment, modelling efforts were initiated by different groups involved in the project. These efforts were only loosely coordinated and different groups were allowed to use a software package of their choice and were free to decide on how to approach the task. Consequently, it was never expected that the different groups would produce exactly the same results. A summary of these modelling efforts can therefore only touch on some of the aspects that had to be taken into account by the groups during the design of their model (e.g. model dimensions and geometry, initial and boundary conditions, choice of parameters, choice of relevance) and the reasons for differences in the model outputs.

The following section 2 aims at giving an overview of the reactive transport simulations performed over the course of the PC-experiment. This overview serves as an introduction to a model, discussed in detail in section 3 of the paper, that is almost fully capable of reproducing the evolution of the borehole fluid during the five years of the experiment, as well as the observations

made on the over-core samples. The geochemical and transport properties of the Opalinus clay formation are then discussed in the light of modelling results.

2. Overview of previous reactive transport simulations of the PC experiment

Over the course of the PC experiment, reactive transport models that couple diffusive transport with chemical reactions were designed and simulations were carried out in a collective effort by different groups involved in the PC experiment. The aim was to develop models that reproduce not only the time series of tracer concentrations but also time series of reactive species and the evolution of the redox state and the pH of the borehole fluid. A model that successfully represents the measured time series of borehole fluid compositions can then be used to identify critical processes and to quantify system parameters and properties within the borehole as well as in the surrounding rock. Furthermore, a working model can be used to make predictions about the system's behaviour in the future and/or to test what-if scenarios that assess the system's response to different physical or chemical conditions (ANDRA, 2005).

Common to all reactive transport models was the incorporation of the processes that were thought to control the chemical evolution of the system: diffusive transport, ion exchange, biodegradation and mineral precipitation/dissolution reactions. Even though these were considered the processes driving the chemical evolution of the system, relatively little was known about the relative importance of each of these processes and if and how these processes interact. One aim of coupled modelling was to elucidate some of these issues.

Integrating transport and chemistry into a model entails a much larger number of system parameters that need to be constrained than in a model that considers non-reactive transport alone. Because few constraints were available for conditions in the surrounding rock, values for

critical parameters regarding conditions outside the borehole could only be based on “educated guesses” and were therefore associated with a large degree of uncertainty (see discussion in Gaucher and Blanc, 2006). Owing to this uncertainty and other factors, which include among many others: 1) the use of different software packages and geochemical datasets, 2) the choice of parameters and the degree of detail, 3) the choice and the mathematical implementation of processes and the couplings between them, 4) the choice of initial and boundary conditions, 5) species dependent or independent diffusion, 6) uniform or species dependent accessible porosities, it was expected that the results from different modelling efforts could show substantial differences but should agree at least qualitatively and in some aspects quantitatively.

The earliest simulations that couple diffusive transport with chemical reactions were carried out by Arcos et al. (2003). Reactive transport was modelled in one dimension with the PHREEQC (Parkhurst and Appelo, 1999) code. These simulations already included the most important processes that were thought to control the chemistry of the porewater: the degradation of organic matter via sulphate reduction, ion exchange reactions and mineral precipitation/dissolution reactions. Of these processes, the degradation of organic matter was thought to be that which dominates the behaviour of the system in agreement with preliminary microbiological analyses (Stroes-Gascoyne et al., This Issue). Biodegradation was formulated as

and incorporated into the model via a Monod-type rate equation.

Overall, the model was able to reproduce on-line measurements of critical parameters such as the pH and Eh reasonably well and confirmed the significance of biodegradation as the most prominent process in controlling the redox evolution of the system. Discrepancies between

measured and modelled data, in particular those related to sulphate and inorganic carbon, were attributed to the over-simplification of the formulation for organic matter degradation, the selection of the type of dissolved organic matter and the choice of kinetic parameters used in the degradation reactions.

Tournassat and Gaucher (2004) used the PHAST code (Parkhurst et al., 2004) to simulate, in 1D, the evolution of the borehole fluid composition by using constraints from isotopic data (e.g. $\delta^{13}\text{C}$), dissolved methane, the SO_4^{-2} concentration, the pH and the alkalinity. They concluded that methanogenic and sulphate reducing bacteria in the borehole led to a redox zonation that causes methanogenesis and methane oxidation to occur simultaneously. The redox state of the system is controlled by the S(-2)/S(+6) couple, whereby the S(-2) and S(+6) activities are buffered by pyrite (FeS_2) and a Fe-carbonate-phase (FeCO_3). The authors suggested that the system is in a redox disequilibrium that is used by sulphate-reducing bacteria to produce methane, acetate and various organic acids.

Grandia et al. (2006) used PHREEQC to implement a kinetic formulation for the degradation of acetone through a carboxylation process:

and a Monod-type rate equation for the subsequent degradation of acetate to carbonate ions via sulphate reduction:

The production of HS^- leads to the precipitation of an amorphous FeS-phase, which controls the Fe concentration in the borehole. All rate parameters in the biodegradation process were adjusted to match the measured data from the PC experiment and the simulations were able to reproduce many aspects of the evolving system.

Alt-Epping et al. (2006) used FLOTRAN (Lichtner, 2007) to run simulations of a cylindrical model with radial coordinates, which accounted for the oblique angle between the borehole and the bedding. These simulations were fully coupled, which implies that these simulations also considered the feedback between porosity changes following mineral dissolution/precipitation reactions and diffusive transport. This study incorporated many parameters and built on results from previous studies: the formulation and selectivity coefficients for ion exchange were taken from Tournassat and Gaucher (2004) and biodegradation was formulated in an analogous manner to that of Grandia et al (2006). Simulations included a sensitivity analysis that compared different model outcomes as a function of the initial borehole fluid composition.

To elucidate the importance of individual reaction processes (ion exchange, biodegradation, mineral dissolution/precipitation), different model scenarios included a successive increase in model complexity, from the implementation of a single process only to the implementation of all reaction processes and a full coupling between them. The results from the simulations showed that the different initial compositions of the borehole fluid (scenarios 1-3) have relatively little impact on the evolution of the system. Without ion exchange or biodegradation, the reactivity of the system is low, which is consistent with very small volumes of calcite, dolomite and siderite precipitation (Figure 1). Species concentrations in the borehole either increase or decrease monotonously, which indicates that these changes are primarily controlled by diffusive exchange with the surrounding rock (Figure 2).

181 In contrast, after implementing biodegradation and ion exchange, the evolution of the
182 fluid composition in and around the borehole becomes more complex and the system has not
183 attained steady state after 1426 days. The system is more reactive, which is reflected in a larger
184 amount of precipitated carbonate minerals. The implementation of biodegradation reproduces one
185 of the key characteristics of the borehole fluid, which is the decrease in sulphur over time (Figure
186 2). In the borehole, organic matter reduces sulphate to sulphide, which subsequently diffuses
187 outward into the formation where it precipitates as pyrite (Figure 1). The uptake of sulphide into
188 pyrite outside the borehole steepens the total sulphur concentration profiles, thus enhancing
189 outward diffusion and causing a decrease in the total sulphur concentration in the borehole fluid
190 (Figure 2).

191 These results demonstrate the buffering capacity of the system, which is due primarily to
192 ion exchange and the buffering by carbonate phases. Biodegradation exerts the strongest impact
193 on the evolving fluid composition and causes the precipitation of pyrite. These simulations were
194 successful in describing qualitatively the processes occurring in the borehole and the surrounding
195 formation. The simulations also suggest that by selecting only those constituents and processes
196 that are relevant to the chemical evolution of the system, it is possible to design a “minimal”
197 model that is simple yet fully capable of reproducing quantitatively the evolution of the borehole
198 fluid during the five years of this experiment. This model is presented in the following sections.

200 **3. A simplified reactive transport model**

201 *3.1 Overview of the proposed reactive transport model*

202 As stated above, the aim of this modelling exercise was to develop a “minimal” model capable of
203 reproducing the chemical evolution of the PC experiment, i.e. the chemical evolution of
204 compounds that are coupled with each other through the simultaneous occurrence of biological

transformation of solute or solid compounds, in-diffusion and out-diffusion of solute species and precipitation/dissolution of minerals (in the borehole and in the formation).

This section aims at giving an overview of the concepts and parameters used in the model. Each of these parameters, including their calibration, are then discussed in the following section 4.

Mainly because biological activities are highly non linear, processes occurring in the experimental borehole could not be modelled using a purely mechanistic approach without fitting parameters. Thus, it is not within the scope of this paper to try to present a biological mechanistic model.

Different events during the course of the experiment (e.g. water sampling, leakage and others) caused changing boundary conditions. As discussed elsewhere in this series of papers, the major changes in the water chemistry during the PC experiment included decreasing concentrations of bromide, deuterium and sulphate and increases in the organic carbon and total dissolved carbonate contents. The changes in the bromide and deuterium contents were expected because the test water was spiked with both of them to act as tracers. The measured concentrations of these tracers in the borehole are shown in Part A, Figure 7. They differ considerably from those expected in that the concentrations in samples taken late in the experiment, instead of continuing to decreasing asymptotically to the low concentrations in the formation water, began to increase toward those of the initial test water. This behaviour could be linked to the experimental needs, where the chemical composition of the water in the borehole was changed through dilution of the borehole water with volumes of synthetic water (high concentration of bromide, but also zero concentration of sulphides, etc.) introduced into the system to compensate the losses due to sampling or leakages. As a second consequence, these events led also to changes in the concentration gradients between the borehole and the surrounding formation, hence having an effect on the solute diffusion in/from the formation. It

was then necessary to take these events into account in the reactive transport calculation to achieve good mass balance. This was achieved by building a model with several restarts after having changed the conditions in the borehole through mixing of the borehole water with synthetic porewater.

Changing boundary conditions as a function of time had to be considered also for bacterial activity. Biological analyses (Stroes-Gascoyne et al., This Issue) showed that different bacterial strains with different sources of energy (e.g. sulphate reduction vs. methanogenesis) were active in the borehole. Four different periods of bacterial activity can be discerned in Figure 3. Phase 1 is characterized by almost no release of organic matter into the system. As a consequence, a low bacterial activity is expected. A significant release of organic matter different from acetate is observed in phase 2, while in phase 3 there is a release of organic matter and a concomitant transformation into acetate. In phase 4, the organic matter concentration in the borehole decreases due to degradation into inorganic carbon and diffusion into the surrounding formation, providing that the organic matter release in the borehole stopped or decreased drastically. Figure 4 also shows that phase 4 must itself be subdivided into two periods for the description of a bloom of methanogenesis before it slows down. This event has been recorded in biological analysis through the presence of active methanogenic bacteria at the end of the experiment.

Figure 3 clearly shows that acetate was not the primary source of organic carbon in the system because acetate concentration is well below total or dissolved organic carbon concentration before phase 3. Acetate must therefore be considered as a secondary product of the bacterial activity. This secondary product can itself be degraded into inorganic carbon, as will be shown later. The nature of the primary source organic matter that was released into the borehole and then transformed into acetate was the subject of much controversy over the course of the

experiment: among the possible candidates, acetone ($\text{CH}_3\text{-CO-CH}_3$), which was used for cleaning the filters before the experiment, was long preferred until modern carbon measurements on dissolved organic carbon revealed that the carbon source was a modern one (De Cannière et al., This issue). After thoroughly scrutinizing the potential sources of modern carbon in the system, De Cannière et al. came to the conclusion that glycerol ($\text{C}_3\text{H}_8\text{O}_3$), originating from the gel pH-electrode, was the most probable candidate as the primary source of organic carbon in the system.

The two samples during phase 3 exhibited acetate concentration of the same level as total organic matter. Moreover, these concentrations increased during phase 3. This observation can only be explained by considering that the primary source of organic carbon, once released into the borehole water, is immediately converted into acetate. From a modelling conceptual point of view, this behaviour is equivalent to the presence of a “solid” source of carbon that is not released into solution but is directly degraded into acetate. If we consider that glycerol from the electrode is indeed the primary source of carbon, this could be explained by the presence of an intense bacterial activity in the vicinity of the electrode degrading glycerol into acetate. On the contrary, during phase 2, total organic carbon concentration is much higher than acetate concentration, evidencing a release from the electrode that is faster than the consumption by surrounding bacteria, possibly because the initial population of active bacteria was very small. As a consequence, organic matter releases in the system were modelled by three distinct kinetic rates accounting for these three situations: (i) a rate for glycerol (or another organic compound) release into solution, (ii) a rate for its degradation into acetate and (iii) a rate for direct release of acetate into solution accounting for the rapid conversion of glycerol (or another organic compound) into acetate at the source term.

These rates were arbitrarily changed as a function of time in order to accurately reproduce the data shown in Figure 3. This approach must be seen as a purely fitting approach that is

justified because the interest of the modelling was to understand the response of the system to the bacterial activity.

3.2. Numerical modelling methods

3.2.1 Geometry and transport

In the modelling approach that follows, the experimental borehole was considered to be a perfect cylinder. Diffusion taking place at the bottom and the top ends of the cylinder was neglected in comparison to radial diffusion owing to the low value of their surface area as compared to radial surfaces. Anisotropy of diffusion due to the bedding of the rock (Arcos et al., 2004; Van Loon et al., 2004a; Van Loon et al., 2004b) was not taken explicitly into account. With this approximation, the system turned into a 1D radial model. This type of geometry can be implemented in PHREEQC using the “-stagnant_cells” option. (Parkhurst and Appelo, 1999; Appelo, 2007; Appelo and Wersin, 2007). Transport by diffusion is solved at each time step by mixing iteratively adjacent cells (n and $n+1$) following the relationship:

$$mixf_{n,n+1} = \varepsilon \times D_p \times \Delta t \times \frac{A_{n,n+1}}{h_{n,n+1} \times V_n} \times f_{bc} \quad \text{Equation 1}$$

where $\varepsilon \times D_p$ is the harmonic mean of the effective diffusion coefficient, i.e.:

$$\varepsilon \times D_p = 2 \frac{\varepsilon_n \times D_{p,n} \times \varepsilon_{n+1} \times D_{p,n+1}}{\varepsilon_n \times D_{p,n} + \varepsilon_{n+1} \times D_{p,n+1}} \quad \text{Equation 2}$$

where Δt is the time step (s), $A_{n,n+1}$ is the shared surface area among cells n and $n+1$ (m²), $h_{n,n+1}$ is the distance between midpoints of the cells n and $n+1$ (m), V_n is the water volume in cell n for

which the concentration change is calculated (m^3), and f_{bc} is a correction factor that equals 2 for constant concentration (end cell of the system) and 1 otherwise (inner cell of the system with closed boundary). ε_n (-) is the porosity of cell n. $D_{p,n}$ is the pore diffusion coefficient of cell n ($\text{m}^2 \text{s}^{-1}$). If no surface diffusion (in the electrostatic double layer at charged mineral surfaces) is considered, the pore diffusion coefficient is related to the effective diffusion coefficient (D_e) by the relationship:

$$D_{e,n} = \varepsilon_n \times D_{p,n} \quad \text{Equation 3}$$

The borehole was modelled using only one numerical cell representative of the ring volume containing the test water (the inner part of the borehole was filled with instrumental devices). Surface to volume ratios between adjacent cells were calculated according to the diameter of the borehole (0.052 m) and the size of each numerical cell. The Opalinus Clay formation was represented by 33 cells extending 1.5 m into the clay formation. Grid size was refined when approaching the borehole/formation interface: cell sizes ranged from 0.002 m at the interface up to 0.2 m in the clay formation. Considering the total length of the borehole (4.63 m), this corresponds to a porous rock volume of 0.0016 m^3 for the cell at the interface and 8.3 m^3 for the last cell in the clay formation. Transport parameters were fitted according to the Br and deuterium diffusion profiles using the multicomponent diffusion option of PHREEQC (different D_p values can be attributed to different solutes in the system). All dilution events (sampling and leakages reported in Wersin et al., This issue-a) were taken into account.

3.2.2 Chemistry Database

The BRGM Thermoddem database (<http://thermoddem.brgm.fr/index.asp?langue=GB>) was used for chemical species and minerals solubility given the need for reliable thermodynamic data of clay minerals. Preliminary simulation runs made it possible to simplify calculations by removing unnecessary solute species. The database used for the simulation is given in Electronic Annex 1.

3.3. *Boundary conditions*

3.3.1 Anion concentration and accessible porosity

Because of the out-diffusion of chloride at the Lias and Dogger boundaries, porewaters of the Opalinus Clay at Mont Terri show a distinct diffusion profile through the formation (See Figure 2 in Wersin et al., This issue-a). The stability of the Cl + Br concentration profile due to diffusion of Br from the borehole in the formation and Cl from the formation in the borehole confirmed that porewater chloride concentration was about 0.3 mol/L (Figure 5). Sulphate concentration was adjusted to match the Cl/sulphate seawater ratio in agreement with porewater modelling results (Pearson et al., This issue).

Total water loss at 105°C ($7.42 - 8.4 \text{ kg}_{\text{water}} \text{ kg}_{\text{rock}}^{-1}$) together with rock bulk density determination ($2.38\text{-}2.4 \text{ kg dm}^{-3}$) enabled Koroleva et al. (This issue) to determine a mean total porosity of 0.19. This value is also in agreement with reported grain density of 2.7 kg dm^{-3} (Pearson et al., 2003, Table A9.12). This porosity value is high when compared to previously reported values measured with the same method (Pearson et al., 2003, Table A9.12). However, it is still in agreement with porosity values obtained from HTO diffusion experiments: for instance Van Loon et al. (2003) reported values up to 0.2. According to (i) this porosity value, (ii) the total chloride content that can be leached from the sample and (iii) the Cl concentration in the porewater (as given by the final concentration of the test water), Koroleva et al. (This issue) also calculated that anion accessible porosity represents ~75% of total porosity. This value is higher

than the usually reported mean value of ~50-60%, but still in reasonable agreement with the range of variation reported in the literature (40-70%, Van Loon et al., 2003; Van Loon et al., 2004a; Van Loon et al., 2007). As a consequence, it was decided to consider this measured value in the modelling exercise. In the following, an anion accessible porosity of 0.14 corresponding to 0.06 kg_w/kg_r will be used and the remaining 0.02 kg_w/kg_r must be considered as “surface water” (Appelo and Wersin, 2007; Appelo et al., 2008).

3.3.2. Major cations (Na, K, Ca, Mg, Sr) and cation exchange

A cation exchange reaction can be represented by the following reaction equation, in the case of a Na⁺/Me^{z+} binary system (Me = K, Ca, Mg or Sr):

where X⁻ represents a negatively charged surface site. The selectivity coefficient of this reaction is $K_{GT}^{Na/Me}$:

$$K_{GT}^{Na/Ca} = \frac{\{Na^+\}^z}{\{Me^{z+}\}} \times \frac{E_{Me}}{E_{Na}^z} \quad \text{Equation 4}$$

Where E values are charge fractions on the exchanger.

The over-coring analysis showed that cation exchanger composition is very constant as a function of borehole distance (Koroleva et al., This issue). In these conditions, Equation 4 implies that the

ratio of solute activity $\frac{\{Na^+\}^z}{\{Me^{z+}\}}$ is also constant. This can be verified in Figure 6.

The exchange selectivity coefficient of Na/Me exchange reactions can then be calculated from exchanger population analysis and borehole sample data (Table 1). These values can be compared to those predicted by the illite and smectite exchanger models given by Tournassat et al. (Tournassat et al., 2007; Tournassat et al., 2009). The present exchange selectivity coefficients can be explained by a combination of illite and smectite surfaces: modelled Na/K selectivity coefficients are lower than the measured selectivity coefficient for illite/smectite mixed layer minerals (I/S). This observation is in agreement with the recommendation of Tournassat et al. (2009) to increase the Na/K coefficient by 0.2 – 0.4 $\log_{10}$ unit for I/S surfaces. Exchange selectivity coefficients are also in agreement with those calculated at another location with the same chlorinity (BWS-A1), while they are slightly different for a location with lower chlorinity (BWS-A3) (Pearson et al., This issue).

In the following, the $\log_{10}K_{GT}$ value calculated from borehole and core samples (first column of Table 1) will be used to run the simulations.

3.3.3. Porewater chemistry

Initial porewater chemistry was calculated at 25°C with the model presented in Pearson et al. (This issue) and with the parameters given above. The minerals considered at equilibrium with the formation porewater were: quartz, calcite, siderite, chlorite (Chlorite-CCa-2), illite (Illite_IMt2) and pyrite. Chosen chlorite and illite data were originally obtained from calorimetric measurements (Gailhanou et al., 2007; Gailhanou et al., 2009). Porewater modelling results are given in Table 2

3.3.4 HDO and Br⁻ diffusion

Diffusion parallel to the bedding of Opalinus Clay from Mont Terri has already been studied at the laboratory scale (Van Loon et al., 2004a) as well as in in-situ experiments (Van Loon et al., 2004b). Van Loon et al., 2004b report a diffusion coefficient (D_p) of $1.1 \cdot 10^{-10}$ and $2.7 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for I^- and HTO respectively. Together with the measured accessible porosity (Koroleva et al., This issue), these values were used in our calculations and then slightly adjusted to better match the data. A good fit was obtained with D_p of $0.9 \cdot 10^{-10}$ and $2.4 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for Br^- and HDO respectively (Figure 7).

Koroleva et al. (This issue) report spatial profiles of Br and Cl concentrations in the immediate vicinity (first 17 centimetres) of the borehole. Even though the data, in particular the data for Cl^- , are associated with a relatively large degree of uncertainty, there appears to be a discrepancy between the computed (with diffusivities estimated from time-series of tracer concentrations in the borehole fluid) and measured spatial profiles (Figure 7, lower right panel). It is not easy to decide whether this shift is significant or not. If significant, this shift would suggest the presence of a disturbed zone surrounding the borehole having enhanced diffusion properties (Cartalade et al., 2007). Considering the overall good agreement of the model and the measured data and their associated uncertainty, the possibility of a disturbed zone is not further discussed.

In the following models, a porosity corresponding to the volume of 75% of the total water content (i.e. volumetric porosity = 0.14) was assumed for the entire rock formation. In the proposed reactive transport model, this porosity applies not only to anions but also to positively charged and neutral species for simplicity and calculation time saving reasons. By the way, considering the total porosity instead of the reduced porosity for HDO transport has little effect on the calculated HDO concentrations as a function of time in the borehole (Figure 7). It is possible to consider different D_p for different solute species using the multi-component diffusion

option of PHREEQC (Appelo and Wersin, 2007). Differences in D_p originate from differences in the diffusion coefficient in pure water (D_0) and tortuosity (τ) for different solute species. For each species i , the relationship $D_p = \tau D_0$ applies. In the present studies, D_0 values from the Phreeqd.dat database were considered together with a tortuosity factor calculated from experimental D_p for Br and HTO: we set the tortuosity (τ) for anions and neutral species as $\tau_{anions} = D_p(Br)/D_0(Br)$ and $\tau_{neutral} = D_p(HDO)/D_0(HDO)$. D_0 for OH^- and H^+ were set to the value of HDO for calculation time saving reasons. As a further simplification of the system, we considered that the same tortuosities τ_{anions} applied to all of the anions, independently of their charge and $\tau_{neutral}$ to both neutral species and cations. Cations are expected to have lower tortuosities than neutral species (Appelo and Wersin, 2007) but this effect was neglected.

3.4. Borehole conditions

3.4.1 Biological activity kinetic parameters

Once the solute species diffusion properties were fixed, six kinetic parameters for material degradation and bacterial activity could be fitted: three of them account for the release of the primary organic matter and its transformation into acetate (see section 2); two others are for sulphate reduction/acetate oxidation and the last one is for methanogenesis. Each of these parameters was constrained by measured data:

- The release rate of primary organic carbon source in solution can be computed through the difference between TOC (total organic carbon) and acetate concentrations.
- The degradation rate of this organic carbon together with the degradation rate of a “solid” carbon source into acetate was fitted with the acetate concentrations as a function of time.

- The sulphate reduction rate (through acetate oxidation) was constrained by sulphate concentration as a function of time.
- The rate of methane production from acetate degradation was given by the methane concentration profile as a function of time.

As stated in the introduction, it was not within the scope of this work to describe the system with all of the intermediate degradation products and no attempt has been made to find them in the literature. Measurable initial and final products solely were considered, as well as zero-order kinetic reactions. Bacteria are considered here only as catalysts for thermodynamically possible reactions.

Glycerol (described as $C_3H_8O_3$) transformation into acetate was described with:

Even though it is now clear that the source of carbon in the system was glycerol that leached from the electrode (De Cannière et al., This issue), the question regarding the nature of this source was also addressed through this reactive transport model exercise by considering two other potential sources of carbon. One of these potential sources was acetone that could have entered into the system after the filter cleaning procedure (De Cannière et al., This issue):

The other potential source was natural organic matter present in the formation, taken here as a generic CH₂O formula:

The sensitivity of the modelling result to the considered source of carbon could then be tested. Acetate degradation during sulphate reduction was described with

and methanogenesis with:

Table 1 in Electronic Annex 2 gives the fitted parameters for all of these reactions. Reaction 5 to Reaction 9 were normalized to ½ acetate (corresponding to 1 organic carbon atom). Changes in kinetic rates were defined at each experimental event.

Figure 8 shows the good agreement (because fitted) between modelled concentrations in the borehole as a function of time for organic compounds, sulphate and methane.

3.4.2 Mineral precipitation/dissolution

Due to the intense bacterial activity, a large amount of sulphide has been produced that has precipitated as FeS compounds and pyrite (Koroleva et al., This issue). According to speciation calculations using experimental data (pH, Fe(II) and sulphide concentration when available), pyrite was oversaturated. As a consequence, pyrite could not be considered at equilibrium in the simulation. According to the fast kinetic of precipitation for FeS in the experimental conditions (Rickard, 1995) with regards to the simulation time-step, we decided to consider equilibrium for a FeS compound:

The solubility K_{FeS} of the compound was fixed at the mackinawite solubility tabulated in the database ($\log_{10} K_{\text{FeS}} = -3.54$). Pyrite precipitation was considered as a kinetic process linked to the abundance of FeS (Rickard and Luther III, 2007). The rate of pyrite precipitation had little influence on the outcome of the simulation with regards to simulated Fe and sulphide concentrations in the borehole. The only effect is on the FeS/pyrite ratio of precipitated minerals. Unfortunately no quantitative data is available for this parameter.

Calcite was found to precipitate in the borehole as well (Koroleva et al., This issue), in agreement with its saturation index calculated from alkalinity, pH and Ca concentration (Figure 9). Calcite was oversaturated during the whole of the experiment due to (i) kinetic limitation for its precipitation and/or (ii) measurement uncertainties and/or (iii) uncertainties in the database with regards to the solute complex of Ca. We took these effects into account by considering that calcite precipitated in the borehole at thermodynamic equilibrium but with a saturation index of 0.2 instead of 0.

3.4.3 pH buffer effect of clay mineral surfaces

The pH buffer effect of clay minerals was taken into account by considering the clay 2-pK non electrostatic model of Bradbury and Baeyens (Bradbury and Baeyens, 1997). The amounts of sites were recalculated from the measured amount of illite + illite/smectite in the rock (~38%, Koroleva et al., This issue). We considered that illite and smectite sites have nearly the same buffer properties (Bradbury and Baeyens, 2009a; Bradbury and Baeyens, 2009b). In addition, we considered that H^+ could undergo cation exchange reaction with the same affinity for the surface as Na^+ (Laudelout et al., 1968; Ferrage et al., 2005). The effect of compaction on site accessibility in the intact rock material was not taken into account.

4. Results and discussion

4.1 Influence of the nature of the organic matter on modelling results

Once organic matter production and degradation rates have been determined, the effect of these reactions can be assessed on key parameters such as pH and alkalinity. However, these parameters are potentially highly buffered by the surrounding formation. In a first attempt, we considered the pH buffer of the clay surfaces as described above together with the equilibrium of the formation with its calcite and siderite constituents. No other mineral in the formation was introduced into the model. Figure 10 shows that the consideration of CH_2O , glycerol or acetone as the primary source of carbon has a significant effect on the result. Modelled alkalinity increases in the order acetone < glycerol < CH_2O . Conversely, pH decreases in the order acetone > glycerol > CH_2O . These relationships can be easily appreciated through the consideration of combinations of reactions 11 to 14 that all concern organic matter degradation via sulphate reduction:

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511 For each sulphate mole that is transformed into sulphide in these reactions, glycerol produces 1.7
 512 moles of bicarbonate, CH_2O , 2 moles and acetone, 1.5 moles. The evolution is similar for pH: the
 513 acetone case, with 0.5 H^+ produced per mole of sulphate, exhibits logically the highest pH while
 514 the CH_2O case led to the most acidic result with 1 H^+ per sulphate molecule. Glycerol produces
 515 0.7 H^+ per sulphate and leads to an intermediate result between CH_2O and acetone.

516 Whereas, in all cases, pH predicted by the simulation is in general agreement with
 517 measured pH, TIC and alkalinity are best reproduced with the glycerol model (Figure 10). This
 518 result is in agreement with the results of De Cannière et al. (This issue), who demonstrate that
 519 glycerol is the best candidate for organic source in the system.

520

521 4.2 Influence of the pH buffer from the formation

522 The test-case without clay surface pH buffering in the formation revealed that this buffer has an
 523 important effect on the outcome of the simulation: without this buffering effect, total inorganic
 524 carbon concentration increases too much while the pH is too low (Figure 11). The results remain

however in good agreement with the measurements. Increasing the buffering capacity by a factor of three has little effect on the results (Figure 11): as a consequence, the present experiment cannot be used to finely determine this buffering capacity although it confirms its existence. With regard to our boundary conditions, the pH of the porewater is a parameter whose uncertainty must be addressed: measured and modelled pH values up to 7.5 have been reported (Pearson et al., This issue). An additional simulation was run with an initial pH of 7.4 in the porewater of the formation. The alkalinity value was adjusted accordingly to achieve equilibrium with calcite without changing the calcium concentration. This change has a marked effect on the modelling result (Figure 11) with too low inorganic carbon concentration and too high pH: as a consequence, at the location of the experiment, the pH of the porewater is rather at a value of 7 than 7.5. The outcome of this sensitivity analysis is summarized in Table 3.

4.3 Iron and sulphide controls

Iron and sulphide concentrations are not well reproduced by the model as a function of time (Figure 12). It should be noted that the maximum concentration of sulphide at day 600 in the system is in agreement with the solubility of mackinawite representative here of an “amorphous” FeS compound (note that, at that time, the predicted iron concentration is not too much in error). It was however neither possible to reproduce the decrease in sulphides after day 600, nor the strong increase in iron concentration at day 1061. The iron and sulphide systems are highly oscillatory and it is thus difficult to describe them with an equilibrium approach. In particular, the peak of sulphide concentration is fully correlated with the peak in acetate concentration, although the precipitated FeS in the borehole should have buffered its concentration as shown by the model. Potential degassing (departure of H₂S) and introduction of atmospheric O₂ during the

leakage events were not taken into account in the simulations and could have played a role in the control of the sulphide concentration.

With regards to iron, the presence of organic chelates in solution, originating from bacterial activity, could be an explanation for its too high measured concentration as compared to the model.

4.4 Concentrations of major cations

Major cations (Na, Ca, Mg, K, Sr) are adequately described by the model (Figure 13). This result was fully expected since the porewater composition was calculated in agreement with their concentrations that remained almost constant in the borehole during the experiment. It may be noted that the modelled calcium concentration decreases with time in the borehole and with an evolution parallel to the measured concentration. A slight increase in the Ca concentration in the porewater (corresponding to a small decrease in the exchange selectivity coefficient for Ca) together with an increase in the saturation index of calcite would make it possible to reproduce almost perfectly the data (not shown).

4.5 Comparisons with over-coring data

Mineralogical and chemical data obtained from over-coring sampling did not show significant changes in the composition of the clayrock material directly surrounding the experiment in spite of the dramatic changes of concentration of some elements in the borehole (e.g. sulphate, sulphur, pH and total inorganic carbon). Conversely, the analysis of mineralogical phases having precipitated inside the borehole revealed the high reactivity of the system. This type of contrasting information between clay-rock and borehole is direct proof of the high

buffering capacity of the rock with regard to chemical perturbations and it can be further ascertained from the analysis of reactive transport modelling outcomes.

The precipitation of “amorphous” sulphide mineral in the borehole together with a kinetically controlled precipitation of pyrite was an input condition for the modelling. The important information obtained from the modelling work is that (i) sulphide minerals can effectively precipitate (from the thermodynamic and kinetic points of view) and (ii) that more than 99.9% of amorphous sulphide mineral precipitated at the interface. Figure 14 illustrates the presence of a zone enriched in precipitates at the borehole/clay formation interface (the y-axis is in log scale). Detachment of minerals from this zone due to water circulation causing erosion of the borehole wall could explain the massive presence of sulphide minerals at the bottom of the borehole and in the circulation tubes at the end of the experiment. This simulation result also explains why it was not possible to detect precipitation of such phases inside the clayrock formation.

While calcite precipitation has been observed in the borehole, it was not possible to detect any newly precipitated calcite in the first centimetres of the formation. The simulations are also in agreement with this observation, since only the borehole shows significant change in its calcite content (8.85 mmol L⁻¹ were precipitated in the borehole according to simulation results). The maximum relative increase in calcite content is at the interface and accounts only for 0.3% of the initial amount of calcite. Accordingly, the change of pH in the formation is rapidly buffered as shown in Figure 15.

5. Conclusions

Reactive transport modelling simulation of the porewater chemistry experiment at Mont Terri proved to be efficient in reproducing a complex set of chemical analyses as a function of time.

The good agreement between the model and the measurements performed in the borehole water and also in samples from over-coring enables the following conclusions to be drawn:

(i) The Opalinus Clay rock formation has a high buffering capacity with regard to chemical perturbation due to bacterial activity: sulphur production as well as pH decrease or alkalinity increase was buffered within a few centimetres around the borehole. This buffering capacity is attributed to the carbonate system as well as to the clay surfaces reactivity.

(ii) The chemical controls of pH and major cations and anions in Opalinus Clay porewater chemistry are now well constrained (Pearson et al., This issue), enabling realistic simulations of a perturbed system thanks to an accurate description of the initial unperturbed system.

(iii) Reactive transport models proved to be useful in discriminating between hypotheses with regard to different reactive pathways (e.g. different sources of organic carbon for bacteria in this experiment).

Of course, it is not possible to prove that the proposed model is the unique solution to the system with regards to the numerous parameters that are (or could be) included. The present work only shows that it is possible to reproduce all main outcomes of a chemical perturbation in a clay host-rock with a model that takes into account the state of the art on chemical controls in these rocks. Potential applications of this model are discussed in the next synthesis paper (Wersin et al., This issue-b).

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References

- Alt-Epping, P., Gimmi, T., and Waber, H. N., 2006. Porewater Chemistry (PC) Experiment at Mt. Terri, Switzerland: Reactive transport simulations. NAGRA Technical Note, TN 2006-66.
- ANDRA, 2005. Référentiel du comportement des radionucléides et des toxiques chimiques d'un stockage dans le Callovo-Oxfordien jusqu'à l'Homme. Dossier 2005 Argile. Agence Nationale pour la gestion des déchets radioactifs, Châtenay-Malabry, France.
- Appelo, C. A. J., 1994. Some Calculations on Multicomponent Transport with Cation-Exchange in Aquifers. *Ground Water* **32**, 968-975.
- Appelo, C. A. J., 2007. Multicomponent diffusion modeling in clay systems with application to the diffusion of tritium, iodide, and sodium in Opalinus clay. Supporting information.
- Appelo, C. A. J., Verweij, E., and Schäfer, H., 1998. A hydrogeochemical transport model for an oxidation experiment with pyrite/calcite/exchangers/organic matter containing sand. *Appl. Geochem.* **13**, 257-268.
- Appelo, C. A. J., Vinsot, A., Mettler, S., and Wechner, S., 2008. Obtaining the porewater composition of a clay rock by modeling the in- and out-diffusion of anions and cations from an in-situ experiment. *J. Contam. Hydrol.* **101**, 67-76.
- Appelo, C. A. J. and Wersin, P., 2007. Multicomponent diffusion modeling in clay systems with application to the diffusion of tritium, iodide, and sodium in Opalinus clay. *Environ. Sci. Technol.* **41**, 5002-5007.
- Arcos, D., 2003. Porewater chemistry (PC) experiment: Results of the geochemical modelling. Mont Terri Project TN 2003-18.
- Arcos, D., Gimmi, T., Duro, L., and Waber, H. N., 2004. Modelling of tracer behaviour and dominant reactions during the pore water chemistry (PC) experiment in the Opalinus Clay, Switzerland. *11th Water-Rock Interaction Congress*, Saratoga Springs.
- Bradbury, M. H. and Baeyens, B., 1997. A mechanistic description of Ni and Zn sorption on Na-montmorillonite. Part II: modeling. *J. Contam. Hydrol.* **27**, 223-248.
- Bradbury, M. H. and Baeyens, B., 2009a. Sorption modelling on illite Part I: Titration measurements and the sorption of Ni, Co, Eu and Sn. *Geochim. Cosmochim. Acta* **73**, 990-1003.
- Bradbury, M. H. and Baeyens, B., 2009b. Sorption modelling on illite. Part II: Actinide sorption and linear free energy relationships. *Geochim. Cosmochim. Acta* **73**, 1004-1013.
- Cartalade, A., Montarnal, P., Filippi, M., Mugler, C., Lamoureux, M., Martinez, J. M., Clement, F., Wileveau, Y., Coelho, D., and Tevissen, E., 2007. Application of inverse modeling methods to thermal and diffusion experiments at Mont Terri Rock laboratory. *Physics and Chemistry of the Earth* **32**, 491-506.
- Courdouan, A., Christl, I., Meylan, S., Wersin, P., and Kretzschmar, R., 2007. Characterization of dissolved organic matter in anoxic rock extracts and in situ pore water of the Opalinus Clay. *Appl. Geochem.* **22**, 2926-2939.
- De Cannière, P., Schwarzbauer, J., Höhener, P., Lorenz, G., Salah, S., Leupin, O. X., and P., W., This issue. Biogeochemical processes in a clay formation in-situ experiment: Part C -

- Organic contamination and leaching data in porewater chemistry experiment at Mont Terri Rock laboratory *Appl. Geochem.*
- Ferrage, E., Tournassat, C., Rinnert, E., and Lanson, B., 2005. Influence of pH on the interlayer cationic composition and hydration state of Ca-montmorillonite: Analytical chemistry, chemical modelling and XRD profile modelling study. *Geochim. Cosmochim. Acta* **69**, 2797-2812.
- Gailhanou, H., van Miltenburg, J. C., Rogez, J., Olives, J., Amouric, M., Gaucher, E. C., and Blanc, P., 2007. Thermodynamic properties of anhydrous smectite MX-80, illite IMt-2 and mixed-layer illite-smectite ISCz-1 as determined by calorimetric methods. Part I: Heat capacities, heat contents and entropies. *Geochim. Cosmochim. Acta* **71**, 5463-5473.
- Gailhanou, H., van Miltenburg, J. C., van Genderen, A., Rogez, J., Greneche, J. M., Gilles, C., Gaucher, E. C., and Blanc, P., 2009. Thermodynamic properties of ripidolite CCa-2. Part I. Heat capacities, heat contents and entropies. *Geochim. Cosmochim. Acta* **73**, 4738-4749.
- Gaucher, E. C. and Blanc, P., 2006. Cement/clay interactions - A review: Experiments, natural analogues, and modeling. *Waste Management* **26**, 776-788.
- Gaus, I., Audigane, P., Andre, L., Lions, J., Jacquemet, N., Dutst, P., Czernichowski-Lauriol, I., and Azaroual, M., 2008. Geochemical and solute transport modelling for CO₂ storage, what to expect from it? *International Journal of Greenhouse Gas Control* **2**, 605-625.
- Grandia, F., Domènech, C., and Arcos, D., 2006. Pore water chemistry (PC) experiment: Results of the geochemical modelling. ENVIROS report, R-2225.1.
- Han, W. S., McPherson, B. J., Lichtner, P. C., and Wang, F. P., 2010. Evaluation of trapping mechanisms in geologic CO₂ sequestration: case study of sacroc northern platform, a 35-Year Co₂ injection site. *Am. J. Sci.* **310**, 282-324.
- Koroleva, M., Lerouge, C., Mäder, U., Claret, F., and Gaucher, E. C., This issue. Biogeochemical processes in a clay formation in-situ experiment: Part B - Results from overcoring and evidence of strong buffering by the rock formation *Appl. Geochem.*
- Laudelout, H., Van Bladel, R., Bolt, G. H., and Page, A. L., 1968. Thermodynamics of heterovalent cation exchange reactions in a montmorillonite clay. *Transactions of the Faraday Society* **64**, 1477-1488.
- Lichtner, P. C., 2007. FLOTRAN Users Manual: Two-phase non-isothermal coupled thermal-hydrologic-chemical (THC) reactive flow and transport code, Version 2 Los Alamos National Laboratory, Los Alamos, New Mexico.
- Lichtner, P. C., Steefel, C. I., and Oelkers, E. H., 1996. *Reactive transport in porous media*. Mineralogical Society of America.
- Maher, K., Steefel, C. I., White, A. F., and Stonestrom, D. A., 2009. The role of reaction affinity and secondary minerals in regulating chemical weathering rates at the Santa Cruz Soil Chronosequence, California. *Geochim. Cosmochim. Acta* **73**, 2804-2831.
- Parkhurst, D. L. and Appelo, C. A. J., 1999. User's guide to PHREEQC (Version 2) - A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations *Water-resources investigations*.
- Parkhurst, D. L., Kipp, K. L., Engesgaard, P., and Charlton, S. R., 2004. PHAST- A program for simulating ground-water flow, solute transport, and multicomponent geochemical reactions *Techniques and Methods 6-A8*. U.S. Geological Survey.
- Pearson, F. J., Arcos, D., Boisson, J.-Y., Fernandez, A. M., Gäbler, H.-E., Gaucher, E., Gautschi, A., Griffault, L., Hernan, P., and Waber, H. N., 2003. Mont Terri project - Geochemistry

- of water in the Opalinus clay formation at the Mont Terri Rock Laboratory. *Geology Series No. 5 Swiss Federal Office for Water and Geology*. Bern.
- Pearson, F. J., Tournassat, C., and Gaucher, E. C., This issue. Equilibrium controls on chemistry of pore water from the Opalinus Clay, Mont Terri Underground Research Laboratory, Switzerland. *Appl. Geochem.*
- Rickard, D., 1995. Kinetics of FeS precipitation: Part 1. Competing reaction mechanisms. *Geochim. Cosmochim. Acta* **59**, 4367-4379.
- Rickard, D. and Luther III, G. W., 2007. Chemistry of iron sulfides. *Chemical Reviews* **107**, 514-562.
- Steeffel, C. I., Carroll, S., Zhao, P., and Roberts, S., 2003. Cesium migration in Hanford sediment: a multisite cation exchange model based on laboratory transport experiments. *J. Contam. Hydrol.* **67**, 219-246.
- Steeffel, C. I., DePaolo, D. J., and Lichtner, P. C., 2005. Reactive transport modeling: An essential tool and a new research approach for the Earth sciences. *Earth and Planetary Science Letters* **240**, 539-558.
- Steeffel, C. I. and Lichtner, P. C., 1994. Diffusion and reaction in rock matrix bordering a hyperalkaline fluid-filled fracture. *Geochim. Cosmochim. Acta* **58**, 3595-3612.
- Stroes-Gascoyne, S., Sergeant, C., Schippers, S., Hamon, C. V., Nèble, S., Vesvres, M.-H., Barsotti, V., Poulain, S., and Le Marrec, C., This Issue. Biogeochemical processes in a clay formation in-situ experiment: Part D - Microbial analyses - Synthesis of results. *Appl. Geochem.*
- Tournassat, C., Gailhanou, H., Crouzet, C., Braibant, G., Gautier, A., and Gaucher, E. C., 2009. Cation exchange selectivity coefficient values on smectite and mixed-layer illite/smectite minerals *Soil Sci. Soc. Am. J.* **73**, 928-942.
- Tournassat, C., Gailhanou, H., Crouzet, C., Braibant, G., Gautier, A., Lassin, A., Blanc, P., and Gaucher, E. C., 2007. Two cation exchange models for direct and inverse modelling of solution major cation composition in equilibrium with illite surfaces. *Geochim. Cosmochim. Acta* **71**, 1098-1114.
- Tournassat, C. and Gaucher, E., 2004. Progress in modelling PC-experiment results including thermodynamics, kinetics, micro-organism activity and isotopic fractionation considerations. BRGM/RP-53395-FR, NAGRA/TN 2004-72.
- Van Loon, L. R., Glaus, M. A., and Müller, W., 2007. Anion exclusion effects in compacted bentonites: Towards a better understanding of anion diffusion. *Appl. Geochem.* **22**, 2536-2552.
- Van Loon, L. R., Soler, J. M., Jakob, A., and Bradbury, M. H., 2003. Effect of confining pressure on the diffusion of HTO, $^{36}\text{Cl}^-$ and $^{125}\text{I}^-$ in a layered argillaceous rock (Opalinus Clay): diffusion perpendicular to the fabric. *Appl. Geochem.* **18**, 1653-1662.
- Van Loon, L. R., Soler, J. M., Muller, W., and Bradbury, M. H., 2004a. Anisotropic diffusion in layered argillaceous rocks: a case study with Opalinus Clay. *Environ. Sci. Technol.* **38**, 5721-5728.
- Van Loon, L. R., Wersin, P., Soler, J. M., Eikenberg, J., Gimmi, T., Hernan, P., Dewonck, S., and Savoye, S., 2004b. In-situ diffusion of HTO, $^{22}\text{Na}^+$, Cs^+ and I^- in Opalinus Clay at the Mont Terri underground rock laboratory. *Radiochim. Acta* **92**, 757-763.
- Wersin, P., Leupin, O. X., Mettler, S., Gaucher, E. C., Mäder, U., De Cannière, P., Vinsot, A., Gäbler, H. E., Kunimaro, T., Kiho, K., and Eichinger, L., This issue-a. Biogeochemical processes in a clay formation in-situ experiment: Part A - Overview, experimental design

756 and water data of an experiment in the Opalinus Clay at the Mont Terri Underground
757 Research Laboratory, Switzerland. *Appl. Geochem.*
758 Wersin, P., Stroes-Gascoyne, S., Pearson, F. J., Tournassat, C., Leupin, O. X., and Schwyn, B.,
759 This issue-b. Biogeochemical processes in a clay formation in-situ experiment: Part G -
760 Key interpretations and conclusions. Implications for repository safety. *Appl. Geochem.*
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763

764 Table 1. Calculated and predicted selectivity coefficient for Na/Me exchange on Opalinus Clay.

Exchange reaction	Calculated $\log_{10}K_{GT}$ from borehole and core sample analysis	Predicted $\log_{10}K_{GT}$ for illite surfaces (from a)	Predicted $\log_{10}K_{GT}$ for smectite surfaces (from b)	Calculated $\log_{10}K_{GT}$ for BWS-A1 samples water (from c)	Calculated $\log_{10}K_{GT}$ for BWS-A3 samples water (from c)
Na→K	1.40 ± 0.05	0.96	0.96	1.32	1.26
Na→Ca	0.78 ± 0.06	0.41	0.99	0.83	0.63
Na→Mg	0.62 ± 0.05	0.71	0.75	0.61	0.48
Na→Sr	1.14 ± 0.22	-	1.17	0.97	0.51

765 a. Tournassat et al., 2007

766 b. Tournassat et al., 2009, including effects of cation-chloride ion pairs

767 c. Pearson et al., this volume

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769

Table 2. Modelled initial porewater composition.

	Modelled initial porewater composition	Analysed test water composition (mean of initial and final)
pH	7.01	7.74
pe	-2.74	
Elements	Concentration (mmol/kg _w)	
Cl	300	262
Br ¹	0.6	29.0
S(6)	15.0	14.8
TIC	3.16	1.3
Na	257	256
K	1.96	1.45
Ca	16.7	15.8
Mg	19.9	18.0
Sr	0.43	0.33
Fe	0.14	
Si	0.18	
Al	21.4 10 ⁻⁶	
Acetic acid ²	0.2	
Methane ³	0.035	

770 ¹ From Pearson et al., 2003771 ² From Courdouan et al., 2007772 ³ Taken at the value of the first plateau of methane concentration from day 116 to day 529

773

774 Table 3. Outcome of sensitivity analysis on organic matter source and clay pH buffer effect.

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	Organic matter	Clay pH buffer	Comment
Simulation 1	CH ₂ O	Yes	High alkalinity, low pH
Simulation 2	Acetone	Yes	Low alkalinity, high pH
Simulation 3 = reference simulation	Glycerol	Yes	
Simulation 4	Glycerol	No	High alkalinity, low pH
Simulation 5	Glycerol	Yes × 3	Almost no effect
Simulation 6	Glycerol	Yes and initial pH = 7.4	Low alkalinity, high pH

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Figure captions

778 Figure 1. Profiles of mineral volume changes over a period of 1426 days, without (A) and with
779 ion exchange and biodegradation (B) from Alt-Epping et al. (2006). The vertical line represents
780 the borehole/rock interface. The precipitation of carbonate phases, calcite, dolomite and siderite
781 along with ion exchange with clay surfaces act as buffer for the fluid composition. Increasing
782 chemical complexity leads to a larger volume fraction of carbonate minerals. Sulphate reduction
783 through biodegradation causes pyrite to precipitate.

784 Figure 2. Spatial profiles of selected species concentrations at different times during the
785 simulation from Alt-Epping et al. (2006). The left and right panels are model scenarios without
786 and with ion exchange and biodegradation, respectively. The interface between borehole and
787 surrounding rock is marked by a vertical line. The profiles show that a greater complexity of
788 system processes entails a non-monotonous evolution of species concentration in the borehole.

789 Figure 3. Measurement of organic compounds as a function of time (TOC = total organic carbon,
790 DOC = dissolved organic carbon).

791 Figure 4. Measurements of methane concentrations as a function of time. a: bloom of
792 methanogenic activity. b: decrease in methanogenic activity.

793 Figure 5. Cl (open circles) and Br (closed circles) concentrations as a function of time.

794 Figure 6. $\frac{\{Na^+\}^z}{\{Me^{z+}\}}$ solute activity ratio as a function of time in the PC experiments (Me = K, Ca,

795 Mg and Sr).

Figure 7. Comparison between measurements (circles and red dashed line) and Br and HDO modelled diffusion profiles. Plain and dashed curves are representative of calculations using porosities of 75 or 100% of the measured total water content. Squares are representative of the sample taken at day twelve while refilling the borehole. The pore diffusion coefficient (D_p) remained unchanged at 0.9 and $2.4 \cdot 10^{-11} \text{ m}^2 \text{ s}^{-1}$ for anions and HDO respectively. Upper left figure: Br concentration in the borehole as a function of time. Upper right figure: focus on the initial stage of the experiment. Bottom left figure: HDO concentrations in the borehole as a function of time. Bottom right figure: Br concentration ratio profile in the rock at the end of the experiment. The distance is expressed in the bedding plane geometry (see Koroleva et al., this volume).

Figure 8. Comparison of experimental results and model using glycerol as the organic carbon source. Top left figure: organic matter. Plain line = acetate; dashed line = TOC (= acetate + solute organic source). Top right figure: sulphate concentration. Bottom left figure: methane concentration. Bottom right figure: evolution of kinetic rates as a function of time.

Figure 9. Saturation index of calcite as a function of time.

Figure 10. Left: total inorganic carbon (squares) and alkalinity (circles) as a function of time. Right: pH (solid black line) as a function of time. Lines are indicative of modelled total inorganic carbon and pH according to the following scenario (organic carbon release in solution / solid source of carbon): 1- $\text{CH}_2\text{O}/\text{CH}_2\text{O}$; 2- Acetone / Acetone; 3- Glycerol / glycerol.

Figure 11. Left: total inorganic carbon (squares) and alkalinity (circles) as a function of time. Right: pH (solid black line) as a function of time. Lines are indicative of modelled total inorganic carbon and pH according to the following scenario (organic carbon release in solution / solid

818 source of carbon): 4- Glycerol / Glycerol without pH buffer of clay surfaces; 5- buffering
819 capacity $\times 3$; 6- porewater pH at 7.4 instead of 7.

820 Figure 12. Left: sulphide concentration as a function of time. Right: iron concentration as a
821 function of time (note that the concentration is in log scale). Lines are indicative of modelled
822 concentrations (Scenario 3 with glycerol).

823 Figure 13. Concentrations of major cations as a function of time. Circles: measurements. Lines:
824 model (Scenario 3 with glycerol).

825 Figure 14. Modelled pyrite (red) and amorphous sulphide (blue) solid concentration profile (in
826 mmol L^{-1} porewater) after 1846 days of perturbation (Glycerol simulation case).

827 Figure 15. pH profile after 1846 days of perturbation (Glycerol simulation case).

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834 Figure 1. Profiles of mineral volume changes over a period of 1426 days, without (A) and with
 835 ion exchange and biodegradation (B) from Alt-Epping et al. (2006). The vertical line represents
 836 the borehole/rock interface. The precipitation of carbonate phases, calcite, dolomite and siderite
 837 along with ion exchange with clay surfaces act as buffer for the fluid composition. Increasing
 838 chemical complexity leads to a larger volume fraction of carbonate minerals. Sulphate reduction
 839 through biodegradation causes pyrite to precipitate.

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844 Figure 2. Spatial profiles of selected species concentrations at different times during the
 845 simulation from Alt-Epping et al. (2006). The left and right panels are model scenarios without
 846 and with ion exchange and biodegradation, respectively. The interface between borehole and
 847 surrounding rock is marked by a vertical line. The profiles show that a greater complexity of
 848 system processes entails a non-monotonous evolution of species concentration in the borehole.

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852 Figure 3. Measurement of organic compounds as a function of time in the borehole (TOC = total
853 organic carbon, DOC = dissolved organic carbon).

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Figure 4. Measurements of methane concentrations as a function of time. a: bloom of methanogenic activity. b: decrease in methanogenic activity.

Figure 5. Cl (open circles) and Br (closed circles) concentrations as a function of time.

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873 Figure 6. $\frac{\{Na^+\}^z}{\{Me^{z+}\}}$ solute activity ratio as a function of time in the PC experiments (Me = K, Ca,

874 Mg and Sr).

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882 Figure 7. Comparison between measurements (circles) and Br and HDO modelled diffusion
 883 profiles (obtained from calibration). Black plain and red dashed curves are representative of
 884 calculations using porosities of 75 or 100% of the measured total water content. Squares are
 885 representative of the sample taken at day twelve while refilling the borehole. The pore diffusion
 886 coefficient (D_p) remained unchanged at 0.9 and $2.4 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for anions and HDO respectively.
 887 A: Br concentration in the borehole as a function of time. B: focus on the initial stage of the
 888 experiment. C: HDO concentrations in the borehole as a function of time. D: Br concentration
 889 ratio profile in the rock at the end of the experiment. The distance is expressed in the bedding
 890 plane geometry (Koroleva et al., This issue).

Figure 8. Comparison of experimental results and model using glycerol as the organic carbon source. A: organic matter. Plain line = acetate; dashed line = TOC (= acetate + solute organic source). B: sulphate concentration. C: methane concentration. D: evolution of kinetic rates as a function of time.

Figure 9. Saturation index of calcite as a function of time.

Figure 10. Left: total inorganic carbon (squares) and alkalinity (circles) as a function of time. Right: pH (solid black line) as a function of time. Lines are indicative of modelled total inorganic carbon and pH according to the following scenario (organic carbon release in solution / solid source of carbon): 1- CH₂O/CH₂O; 2- Acetone / Acetone; 3- Glycerol / glycerol.

Figure 11. Left: total inorganic carbon (squares) and alkalinity (circles) as a function of time. Right: pH (solid black line) as a function of time. Lines are indicative of modelled total inorganic carbon and pH according to the following scenario (organic carbon release in solution / solid source of carbon): 4- Glycerol / Glycerol without pH buffer of clay surfaces; 5- buffering capacity $\times 3$; 6- porewater pH at 7.4 instead of 7.

Figure 12. Left: sulphide concentration as a function of time. Right: iron concentration as a function of time (note that the concentration is in log scale). Lines are indicative of modelled concentrations (Scenario 3 with glycerol).

Figure 13. Concentrations of major cations as a function of time. Circles: measurements. Lines: model (Scenario 3 with glycerol).

Figure 14. Modelled pyrite (red) and amorphous sulphide (blue) solid concentration profile (in mmol L^{-1} porewater) after 1846 days of perturbation (Glycerol simulation case).

Figure 15. pH profile after 1846 days of perturbation (Glycerol simulation case).