



## Effects of a thermal perturbation on mineralogy and pore water composition in a clay-rock: An experimental and modeling study

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Received 8 June 2016; revised 7 October 2016; accepted in revised form 13 October 2016; available online 19 October 2016

### Abstract

The physical and chemical properties of clay-rocks are, at least partly, controlled by the chemical composition of their pore water. In evaluating the concept of disposing of radioactive waste in clay-rock formations, determining pore water composition is an important step in predicting how a clay-rock will behave over time and as a function of external forces, such as chemical and thermal perturbations. This study aimed to assess experimental and modeling methodology to calculate pore water composition in a clay-rock as a function of temperature (up to 80 °C). Hydrothermal alteration experiments were carried out on clay-rock samples. We conducted comprehensive chemical and mineralogical characterization of the material before and after reaction, and monitored how the chemical parameters in the liquid and gas phases changed. We compared the experimental results with the *a priori* predictions made by various models that differed in their hypotheses on the reactivity of the minerals present in the system. Thermodynamic equilibrium could not be assessed unequivocally in these experiments and most of the predicted mineralogy changes were too subtle to be tracked quantitatively. However, from observing the neo-formation of minerals such as goethite we were able to assess the prominent role of Fe-bearing phases in the outcome of the experiments, especially for the measured pH and  $p_{\text{CO}_2}$  values. After calibrating the amount of reacting Fe-bearing phases with our data, we proposed a thermodynamic model that was capable of predicting the chemical evolution of the systems under investigation as well as the evolution of other systems already published in the literature, with the same clay-rock material but with significant differences in experimental conditions.

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**Keywords:** Clay; Radioactive waste storage; Pore water; Modeling; Thermodynamics; Hydrothermal alteration

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## 1. INTRODUCTION

The effectiveness of radioactive waste disposal in clay-rock formations relies in large part on how the host-rocks restrict radionuclide mass transport diffusion processes, on how they reduce dissolved radionuclide concentrations in the pore water by adsorption and precipitation phenomena, and on how favorable their mechanical properties are, for instance whether they allow fracture self-sealing in zones damaged by excavation procedures (Landais, 2006; Delay et al., 2007; Neuzil, 2013; Bianchi et al., 2014). The physical and chemical properties of clay-rocks are, at least partly, controlled by the chemical composition of their pore water, so assessing the stability of the physical and chemical properties of the host-rocks over geological time periods is of paramount importance. Determining pore water composition is an important step in predicting how a clay-rock will behave over time as a function of external forcing (Rosenqvist, 1984; Moore, 1991; Savage et al., 2002; Gaucher and Blanc, 2006; Altmann, 2008; Marty et al., 2009, 2014; Gaboreau et al., 2012; Zachara et al., 2016). Pore waters are however notoriously difficult to sample directly from clay-rocks, and sampling methods can result in many artifacts that impact the measured concentrations (Fernández et al., 2014; Mazurek et al., 2015). To circumvent this problem, a range of experimental and modeling methods have been developed or improved in the last two decades to characterize the chemical composition of pristine pore water. A comprehensive review of these methods and their associated commonly encountered errors and difficulties can be found in Tournassat et al. (2015). The overall consistency between measured chemical compositions, compositions that can be predicted from thermodynamic models, and information obtained from the solid (at least cation exchange composition, mineralogical composition and isotopic composition), is commonly taken as the basis for how much confidence we can put in the pore water composition determination.

Among the range of perturbations that are foreseen in a radioactive waste repository, thermal perturbations cannot be avoided because of the heat generated by the radioactive decay of the radioelements in the waste canisters. In the near-field of high-level radioactive waste storage, a temperature increase of up to 80–120 °C is expected, depending on the storage concept and size (Andra, 2005). So understanding and predicting the effect of the thermal perturbation on pore water composition is a key aspect of modeling the long-term evolution of radioactive waste disposals. For systems under perturbation, the question of the reliability of pore water composition determination is even more problematic than for pristine systems. In most cases, samples that are fully representative of the conditions of interest and from which pore water could be extracted and analyzed are missing. The time that would be necessary to achieve full equilibrium between the solid phases and the pore water, and the absence of clear criteria that could be used to state that full equilibrium has been achieved, could be a problem that is difficult to overcome. Consequently,

determining the composition of perturbed pore water inevitably relies for a large part on predictive modeling efforts. In undisturbed systems, pore water models are based on the Gibbs' phase rule that takes advantage of the hypothesis of local equilibrium between the pore water composition and surrounding reacting mineral phases (Bradbury and Baeyens, 1998; Beaucaire et al., 2000, 2008, 2012; Motellier et al., 2003; Pearson et al., 2003, 2011; Gaucher et al., 2006, 2009; Tremosa et al., 2012; Tournassat et al., 2015). The underlying justifications of this strong hypothesis are (i) that diffusion processes drive exchanges between the pore water in clay-rocks and the surrounding environment, (ii) that the mineral grains in clay-rocks are usually small, so they have a high specific surface area (SSA) that increases dissolution/precipitation kinetics, and (iii) that the interaction time has been long enough to establish equilibrium conditions between the pore water and a pool of minerals that includes minerals with low kinetic rates of dissolution or precipitation. In systems under perturbation, the third point is far from being certain, depending on the duration of the perturbation. In addition, while it is quite straightforward to choose the nature of the phases that must be considered in the Gibbs' phase rule for a pristine system – it must be the phases that are observed in the sample and that show some indications of having reached equilibrium (Gaucher et al., 2006; Lerouge et al., 2011; Kars et al., 2015) – choosing is far more problematic for a system under perturbation, for which, if a sample is made available, it is more difficult to assess equilibrium criteria. Most often, the pore water composition prediction depends on (i) guesses by modelers for the choice of phases that may or may not, or are likely or unlikely to appear during the perturbation, (ii) the related completeness of the thermodynamic database that is used to make this choice, and (iii) the accuracy of the thermodynamic values that are tabulated as a function of temperature. In addition, dissolution/precipitation kinetic considerations and the underlying hypotheses on reactive surface area and kinetic rates can also interfere with the final result.

The goal of our study was to tackle the problem of how to predict pore water composition as a function of temperature using a stepwise approach combining modeling and experiments carried out on clay-rock samples that are representative of expected geological storage sites. In a first step, a set of pore water compositions were calculated at 80 °C (i) by using a modified version of a model previously published for predicting composition at 25 °C (Gaucher et al., 2009) and (ii) by applying a set of hypotheses made on the reactivity of mineral phases at 80 °C. We then chose a reference composition at 80 °C, and designed long-term solid–solution equilibration experiments accordingly to check the validity of the modeling predictions. In a final step, a comparison was made between the pore water composition predictions (and their underlying assumptions) and the actual solution and solid phase compositions that were determined before, during and after the experiments. This manuscript is organized with that stepwise approach in mind.

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