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On site measurements of the redox and carbonate system parameters in the low-permeability Opalinus Clay formation at the Mont Terri Rock Laboratory

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Abstract

An *in situ* water sampling experiment was performed in the Opalinus Clay formation (Switzerland), with the aim of obtaining undisturbed pore water samples for its characterization. The study was made from a dedicated borehole, named BDI-B1, drilled in March 2002 in the DI niche of the Mont Terri Rock Laboratory, located at the north-western part of the formation, a few meters away of the underlying Jurensis Marl formation. Five water sampling campaigns have been completed, and *on site* measurements of the key parameters of the water, such as pH, Eh, Fe(II), S^{2-} and alkalinity, were performed under controlled conditions inside an anoxic glove box.

The chemical composition of the seepage waters obtained from the borehole is Na–Cl type, with an ionic strength of about 0.4 M. The Cl concentrations fit the concentration profile of the Opalinus Clay pore water obtained in previous experiments from boreholes and squeezed water samples. The highest salinity is found in this zone of the Opalinus Clay, with around 12 g/L of chloride.

A perturbation of the rock system was produced during the first stages of the experiment due to a packer failure. As a consequence, the borehole was exposed to air during the first phase of the experiment. The main perturbations induced were: (1) pyrite oxidation that caused an increase of sulphate, calcium, magnesium and bicarbonate content in the waters; and (2) the inflow of ^{3}H-bearing water vapour that could penetrate the EDZ. This fresh water infiltration could have mixed with the original formation water, and tritium contents of up to 3.8 TU were measured in the first water sampling campaigns. Nevertheless, after some time the hydrogeochemical conditions of the formation were recovered, and the long-term instrumentation and monitoring of the borehole made possible to obtain different parameters of the formation. Successive water sampling campaigns show a tendency to the stabilization of the main parameters of the water, such as sulphate and pH to values of 1600 mg/L and 7.6, respectively. The *on site* determination of the key parameters of the pore waters such as pH, Fe(II) and alkalinity has allowed to model the main water–rock interaction processes of the Opalinus Clay formation. A redox potential of −196 mV at pH 7.6 was obtained.

Keywords: Pore water chemistry; *In situ* pore water sampling; *On site* measurements; Opalinus Clay; Pyrite oxidation; Water–rock interaction

1. Introduction

Argillaceous formations of low permeability are considered in many countries as potential host rocks for the disposal of high level radioactive wastes (HLRW). In order to determine their suitability for waste disposal, evaluations of the hydrogeochemistry and transport mechanisms from such geologic formations to the biosphere must be undertaken.

In this context, the knowledge of the pore water chemistry is essential for performance assessment purposes. This

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information allows to establish a reliable model for the main water–rock interactions, which control the physicochemical parameters and the chemistry of the major element of the system.

One of the main research lines undertaken at the Mont Terri Rock Laboratory (Switzerland) is the understanding of the geochemical behaviour of the Opalinus Clay formation (Gautschi et al., 1993; Bradbury and Baeyens, 1998; Thury and Bossart, 1999; Arcos et al., 2001; Waber et al., 2001; Rübel et al., 2002; Pearson et al., 2003; Delgueldre et al., 2003). This field of knowledge covers a broad spectrum, such as the hydrogeochemical evolution of the pore water, the movement of solutes through the formation and the retention of dissolved species by the clay minerals.

In order to improve the understanding of the pore water chemistry and the water–rock interactions in argillaceous rocks, different experiments were performed in the Mont Terri Rock Laboratory. The Water Sampling experiments (WS-A, WS-B, WS-C, WS-E) aimed to obtain representative values of the pore water composition in the whole Opalinus Clay formation by applying different techniques (*in situ* water sampling from boreholes, squeezing technique at high pressures, etc.). A complete characterization of different water samples from the WS-A1, A2, A3, A4, A5 and A6 boreholes (Fig. 1) was performed (chemical, isotopic and gas analyses) to explore the hydrogeochemical system in the Opalinus Clay formation and to follow its evolution with time (Pearson et al., 2003).

However, the different methods used up to now to obtain pore water perturb the system in one way or another, and introduce sampling artifacts into the resulting data. Some types of perturbations, such as dissolved gas loss or oxidation are common to all sampling techniques. The carbonate chemistry of the pore water in the Opalinus Clay is not well understood. Likewise, pH and Eh field values are not stable when the samples are exposed to air during the measurement (Pearson et al., 2003).

In this context, a new water sampling experiment has been performed at Mont Terri in the borehole BDI-B1 to progress in the evaluation of different techniques for the sampling, analysis and characterization of pore water geochemistry. The aims of this experiment were: (a) to obtain unaltered pore water samples, minimizing sampling artifacts and possible perturbations in the system, such as oxidation and degassing; and (b) to measure *on site* the key parameters of the water, such as Fe(II) and S^{2-} (redox couples). Other key parameters measured were pH, Eh, EC and alkalinity.

This water sampling experiment was planned on the basis of the experience gained from the WS experiments and all contributions of the Geochemical Modelling (GM) Group, where many problems concerning the WS experiments were pointed out and new mechanisms and methodologies were proposed (Pearson et al., 2003). The data obtained show that a number of methodological difficulties are linked to the characterization of the *in situ* conditions in relation to pH, Eh, alkalinity and p_{CO_2} in the highly saline pore waters of the Opalinus Clay formation. These parameters are needed both for site characterization and geochemical modelling of water–rock reactions and transport processes. Besides, Eh, pH and salinity are important parameters in relation to pore water chemistry for the prediction of radionuclide solubilities. For this reason, the knowledge of the key parameters of the pore water and the determination of major ion concentrations are so important.

In this paper, the hydrogeochemical data of the water collected from the Opalinus Clay in the borehole BDI-B1 during five sampling campaigns are presented. This includes *on site* measurements of the key parameters of the waters (pH, Eh, EC, Fe(II), S^{2-} and alkalinity). This borehole is located in the DI niche, a few meters away from the underlying Jurensis Marl formation. Therefore, these data can be integrated within the set of data obtained in

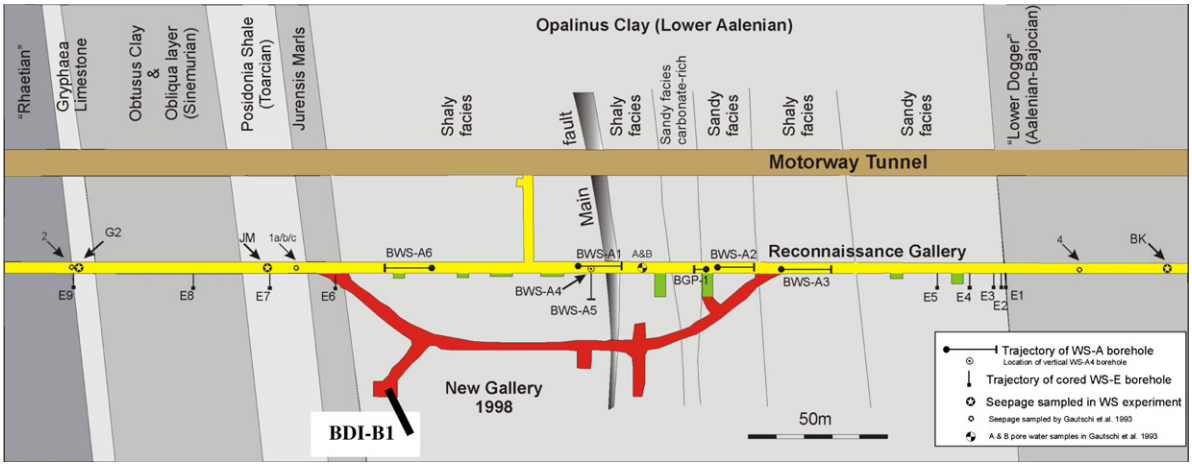

Fig. 1. Geological plan of the Mont Terri Rock Laboratory, showing the sub-divisions of the Opalinus Clay according to lithostratigraphical facies and the location of the 'main' fault. Borehole BDI-B1 is located at the DI niche. The location of other water sampling (WS) boreholes is also shown (Bath and Gautschi, 2003).