

## Characterisation of the Opalinus Clay pore water composition at Mont Terri

Mettler Suzanne & Wersin Paul

Nagra, Wettingen, Switzerland

The geochemistry of the Opalinus Clay pore water represents an important scientific basis for predicting the behaviour of radionuclides following their release into the Opalinus Clay. Sampling of pore water and correct determination of its geochemistry is, however, technically challenging. The Mont Terri Opalinus Clay has a low water content of 6 to 8.6 wt % (mean of 7.4 wt %), around half of which is bound to the clay surfaces (3.2 to 4.4 wt %). The very low permeability of the clay rock ( $\sim 2 \times 10^{-13}$  m/s) is reflected in low seepage in sampling boreholes, showing maximum rates of a few tenths of ml per day. Its isolation from the atmosphere also makes it very prone to contamination by air.

Current knowledge is built on an integrated approach combining field data, laboratory data and geochemical modelling. Most of the field data were obtained from the water sampling experiments (WSA) at Mont Terri, which involved pore water sampling and flow-through monitoring of pH, Eh and conductivity in boreholes sealed with sampling packer systems. The field data were accompanied by laboratory experiments on cores from boreholes drilled through the Opalinus Clay, including analysis of the gases released from the cores and of mineralogy, as well as squeezing (expulsion of water under high loads of 70 to 500 MPa) and leaching experiments. In the latter, the core samples are equilibrated in pure water or in salt solutions; from measurement of the leachates, Cl, Br and possibly SO<sub>4</sub> concentrations can be derived. A similar technique is used to determine the cationic occupancy of the clay surfaces (Na, K, Ca, Mg and Sr).

Interpretation of results was preceded by careful screening of the data to identify perturbing effects such as oxidation by air or methodological artefacts. Such effects can be revealed by chemical or isotopic indicators. Thus, a higher SO<sub>4</sub>/Cl ratio is often a result of pyrite oxidation; a shift in the <sup>13</sup>C isotopic signal of CO<sub>2</sub> and CH<sub>4</sub> may also point to oxidizing effects caused by drilling or sampling. Systematic differences between data from different sources help to identify methodological artefacts. For example, squeezing results above 200 MPa showed a decrease in the concentrations of Cl, SO<sub>4</sub>, Na, K, Br and TOC), which could be related to ultra-filtration effects. Geochemical modelling was also used to investigate the data sets for perturbing effects. This tool is essential for understanding how aqueous chemistry is controlled, the aim being to reproduce the processes that led to the measured data. The geochemical modelling was based on the assumption of equilibrium between pore water and rock, all components being controlled either by mineral solubility (calcite, dolomite, pyrite, quartz, siderite), gas solubility (carbon dioxide) or cationic exchange reactions. An unresolved question is how to account for the non-unique porosity, since the accessible pore space depends on the chemical species: an anion such as Cl<sup>-</sup>, for example, will not access the bound water due to electrostatic repulsion with the clay surfaces.

The Opalinus Clay water can be classified as Na-Cl type water. The high salinity (TDS of 13,000 to 18,500 mg/l) of the samples, as well as SO<sub>4</sub>/Cl and Br/Cl ratios close to those of seawater (0.05 and 0.0015, respectively), are clear signals of its origin. Its current composition can be explained by slow dilution of seawater and reaction with neighbouring rocks over the past 180 million years. The pH is neutral and is controlled by the carbonate system and a slight contribution of small organic acids to alkalinity is likely; within the formation, the clay surfaces participate in the buffering. The redox conditions are most probably controlled by the sulphide/sulphate and pyrite/sulphate redox couples. The variation in salinity observed across the Opalinus Clay at Mont Terri can be correlated with small systematic differences in the chemistry.

Most effort in recent field experiments was invested in minimising perturbations and optimising sampling. Thus, N<sub>2</sub> drilling techniques were developed to avoid oxidation of the cores and the boreholes by air. Measures such as aseptic drilling and disinfection of borehole equipment were used to prevent microbial growth, based on experience with recent experiments. The last generation of experiments, the Pore Water Chemistry experiments (PC and PCC), were designed as circulation experiments with a synthetic pore water (PC) or an inert gas (PCC) through the borehole; they are equipped for online sampling and monitoring. However, a new type of perturbation, namely microbially induced sulphate reduction, affected the data produced in the PC experiment, where microbial growth was unwillingly facilitated by contamination with organic carbon. Microbial growth can be considered as another experimental artefact: space and nutrient flow were provided in an environment where these are usually restricted. The best field data available at the present time are considered as those originating from seepage water of the boreholes sealed by a sampling packer and maintained under a protective atmosphere (PCC).

## REFERENCES

- F. J. Pearson, D. Arcos, A. Bath, J.-Y. Boisson, A. M. Fernandez, H.-E. Gäbler, E. Gaucher, A. Gautschi, L. Griffault, P. Hernan and H. N. Waber. (2003): Mont Terri Project – Geochemistry of Water in the Opalinus Clay Formation at the Mont Terri Rock Laboratory. Reports of the FOWG, Geology Series N° 5.
- A. Vinsot, T. Fierz, C. Cailteau, J. Pironon, S. Pepa, P. Wersin, P. de Cannière, H.-E. Gäbler, N. Badertscher, L. Eichinger. (2005). Gas equilibration and pore water sampling experiment in the Opalinus Clay at the Mont Terri Rock Laboratory. 2nd International Meeting “Clays in natural and engineered barriers for radioactive water confinement: Tours (France). March, 14-18, 2005.
- P. Wersin, P. De Cannière, F. J. Pearson, E. Gaucher, P. Höhener, L. Eichinger, S. Mettler, U. Mäder, A. Vinsot, H.-E. Gäbler, K. Hama, P. Hernan. (2005). Results from an in-situ pore water chemistry experiments in Opalinus Clay: Evidence of microbially-mediated anaerobic redox processes. 2nd International Meeting “Clays in natural and engineered barriers for radioactive water confinement: Tours (France). March, 14-18, 2005.