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Constraining porewater chemistry in a 250 m thick argillaceous rock sequence

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ABSTRACT

The geochemistry of an argillaceous rock sequence from a deep borehole in NE-Switzerland was investigated. The focus was to constrain the porewater chemistry in low permeability Jurassic rocks comprising the Liassic, the Opalinus Clay formation, the 'Brown Dogger' unit and the Effingen Member (Malm). A multi-method approach including mineralogical analysis, aqueous and Ni-ethylenediamine extraction, squeezing tests and pCO_2 measurements as well as geochemical modelling was applied for this purpose. A consistent dataset was obtained with regard to the main solutes in the porewaters. A fairly constant anion-accessible porosity of ~50% of the total porosity was deduced for all analysed samples which displayed variable clay-mineral contents. Sulphate concentrations were shown to be constrained by a sulphate-bearing phase, presumably by celestite or a Sr–Ba sulphate. Application of a simple equilibrium model, including cation exchange reactions, calcite and celestite equilibrium showed good agreement with squeezing data, indicating the suitability of the modelling approach to simulate porewater chemistry in the studied argillaceous rocks. The modelling highlighted the importance of correct determination of the exchangeable cation population. The analysis corroborates that squeezing of the studied rocks is a viable and efficient way to sample porewater.

1. Introduction

Argillaceous rock formations are generally characterised by low hydraulic conductivity and thus solute transport is governed by diffusion. Because of this property, they may act as natural barriers, and thus serve as caprocks for oil and gas reservoirs or as host rocks for radioactive waste repositories. It is important to constrain the porewater chemistry in such low permeability clayrocks because it affects the transport of solutes or, more specifically, of contaminants such as radionuclides. The intimate association of water with the nanoporous clayrock, however, makes the sampling and characterisation of porewater chemistry a difficult task (Sacchi et al., 2000). Thus, virtually every extraction method may create disturbances and alter the in-situ porewater chemistry.

Presumably because of the aforementioned experimental difficulties, there are comparatively few published studies of porewater chemistry in clayrocks. Most of these have been focussed on the investigation of porewaters of clay-rich formations proposed as host rocks for geological radioactive waste disposal. In a pioneer synthesis study, Pearson et al. (2003) compiled data from different experimental extraction techniques and seepage waters from the Opalinus Clay formation in the Mont Terri underground rock laboratory (URL) in Switzerland. Based on these data, the authors proposed a fairly simple chemical equilibrium modelling approach for describing porewater compositions. The same type of approach was initially applied to define porewater chemistry for the Callovo-Oxfordian formation at the URL at the Bure site in France (Gaucher et al., 2006) and was later refined (Appelo et al., 2008, Gaucher et al., 2009). The sensitivity of different equilibrium-type models was evaluated for Opalinus Clay porewaters (Pearson et al., 2011). Earlier geochemical characterisation and modelling of porewaters in the weakly consolidated Boom Clay at the URL at Mol (Belgium) was reported in Beaucaire et al. (2000). More recently, characterisation and modelling studies were conducted on the strongly consolidated Toarcian/Domerian clayrock at the Tournemire URL site in France (Beaucaire et al., 2008; Tremosa et al., 2012).

A systematic finding in these and other (e.g. Mazurek et al., 2012) studies was the effect of anion exclusion arising from the negative structural charge of smectite and illite, which are abundant in such argillaceous rocks. Considering anion exclusion, consistent profiles for chloride could be obtained by applying aqueous extraction, squeezing and water sampling in boreholes (e.g. Pearson et al., 2003, Mazurek

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et al., 2012). The derived anion-accessible porosity was in many instances found to be around 50% of the total porosity (Pearson et al., 2003; Gaucher et al., 2006, 2009; Mazurek et al., 2011) for different argillaceous rocks with variable clay-mineral content.

A further finding in all studied clayrocks was the important role of cation exchange in constraining major cations, such as Na^+, Ca^{2+}, Mg^{2+} and K^+. Using a "classical" cation exchange model calibrated for smectite and illite data, fairly consistent results could be obtained for different clayrock samples of Callovo-Oxfordian shale and Opalinus Clay (Tournassat et al., 2007, 2009; Gaucher et al., 2009; Pearson et al., 2011). Differences encountered between modelled and measured data seemed often to be related to methodological uncertainties in cation exchange capacity (CEC) and exchangeable cations analyses (e.g. Tournassat et al., 2009).

Mineral equilibria reactions pose a further constraint to solute chemistry of clayrocks, which contain variable types and contents of carbonates. Calcite equilibrium has been invoked in all modelling studies mentioned above. Dolomite, siderite and, in the case of Opalinus Clay, ankerite are also encountered, but whether these phases are in equilibrium with the pore fluid is less obvious (Tournassat et al., 2008; Gaucher et al., 2009; Pearson et al., 2011). Pyrite is generally the main sulphur-bearing phase in argillaceous rocks. High sulphate levels found in aqueous extracts and squeezed samples may arise from pyrite oxidation during sampling, storage and/or porewater extraction procedure (De Craen et al., 2006; Gaucher et al., 2009). The latter authors showed for aqueous extraction data from carefully stored Callovo-Oxfordian shale cores that sulphate in the porewater was likely controlled by celestite, the presence of which as infill in bioclasts and veins was later confirmed (Lerouge et al., 2011). For Opalinus Clay porewater, control of sulphate remains ambiguous. Fixed SO_4/Cl at seawater ratio was considered in earlier work based on aqueous extraction data (Pearson et al., 2003), but the possibility of control by celestite has been discussed (Pearson et al., 2011). In a recent petrographic study of Opalinus Clay cores of the deep borehole in Benken (NE Switzerland), diagenetically formed Sr–Ba sulphate as well as celestite as infill in faults was observed (Lerouge et al., 2014).

This contribution documents the geochemical analysis of a 250 m thick, strongly consolidated argillaceous rock sequence in the Swiss Molasse Basin comprising the Opalinus Clay formation and its confining units (Nagra, 2002). The data were obtained from carefully conditioned drillcores of a deep geothermal borehole. A multi-method approach was applied including petrophysical measurements, X-ray diffraction (XRD), scanning electron microscopy (SEM), aqueous extraction, squeezing, analyses of CEC and exchangeable cations and CO_2 partial pressure measurements. The objective was to constrain the porewater chemistry, thus to extend the geochemical database for Opalinus Clay as host rock for a geological waste repository and to acquire data on the underlying and overlying argillaceous units. The latter display more variability in terms of clay-mineral contents, particularly the overlying unit termed 'Brown Dogger'. The specific goals were (i) to test the robustness of the equilibrium modelling approach for describing porewater compositions in the analysed rock sequence, (ii) to determine anion-accessible porosities and their relation to mineralogy based on chloride data, and (iii) to evaluate processes constraining sulphate in the porewater.

2. Geological setting

A deep geothermal borehole was drilled to a final depth of 1508 m at Schlattingen (Thurgau, Switzerland) at the Eastern border of the Swiss Molasse Basin in the year 2011. The primary objective of the campaign was to explore the Triassic aquifers (Muschelkalk and Buntsandstein) and the crystalline basement for their suitability as a geothermal resource. A further objective was to extend the geological and geochemical database of the Opalinus Clay and the adjacent argillaceous units. The Schlattingen borehole is located 9 km ENE from the well-investigated deep borehole at Benken (Nagra, 2002, Gimmi et al., 2007) and is in the vicinity of a potential siting area for a high-level radioactive waste repository (Nagra, 2014).

As shown in Fig. 1, the borehole penetrated through Mesozoic and Permian sedimentary rocks dipping at ~4° to the SE into the crystalline basement (Variscan gneisses). The Mesozoic is unconformably overlain by Tertiary and Quaternary deposits at 491 m depth (not shown). The basin was subjected to a complex burial and uplift history (Mazurek et al., 2006). For the Benken borehole, a maximum burial of 1650 m and a maximum temperature of 85 °C were obtained for the Opalinus Clay, and these values are considered to be representative for Schlattingen as well. Since maximum burial at 5–10 Ma, the sequence was uplifted by about 1 km, leading to overconsolidation.

The studied Jurassic argillaceous rock sequence can be roughly divided into four units (Fig. 1): The top (~25 m thick) corresponds to the Effingen Member (lower Malm) and is made up of silty to sandy calcareous marls to limestones. The underlying unit (~77 m thick), termed 'Brown Dogger', exhibits rather variable lithology. It consists predominantly of clayrocks and marls but also includes sandy-calcareous beds. The third unit is the ~120 m thick Opalinus Clay (Aalenian), consisting of fairly homogeneous silty to fine sandy clayrocks. The lowest ~53 m thick unit termed Lias is also rather clay-rich and is mainly made up of a variable sequence of marls and clayrocks. Based on analogy with the Benken borehole, it can be expected that the clay-rich sequence is bounded by the underlying aquifer in the middle Keuper and the overlying Malm aquifer.

The evolution and the relationships of diagenetically-formed minerals in Opalinus Clay have been studied by Wersin et al. (2013) and Lerouge et al. (2014) on cores obtained from the Schlattingen and Benken boreholes, respectively. Sediment deposition occurred in a shallow marine environment. Early diagenesis, i.e. processes near the interface between water and the unconsolidated sediment, had the most significant impact. Minerals precipitated include pyrite, siderite and minor calcite, dolomite and ankerite. The most significant imprint of

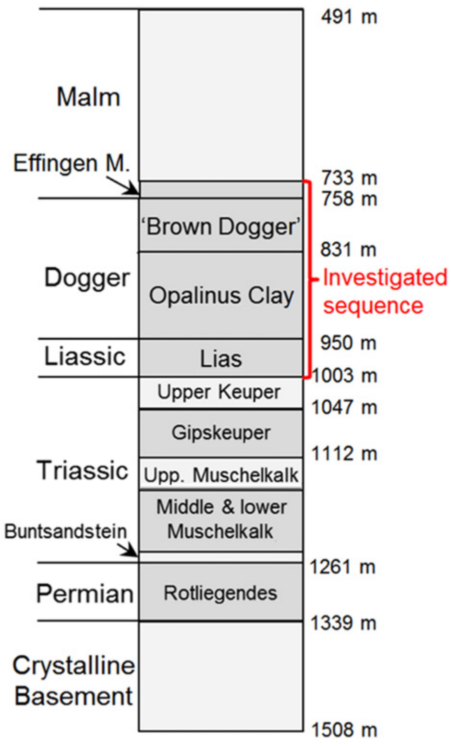

Fig. 1. Simplified geological profile encountered in the Schlattingen borehole (section above 491 m depth not shown). Light sections contain permeable strata, grey shaded units represent aquitards.