Pore-water squeezing from indurated shales

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ABSTRACT

High-pressure mechanical squeezing was applied to sample pore waters from a sequence of highly indurated and overconsolidated sedimentary rocks in a drillcore from a deep borehole in NE Switzerland. The rocks are generally rich in clay minerals (28–71 wt.%), with low water contents of 3.5–5.6 wt.%, resulting in extremely low hydraulic conductivities of 10^{-14}–10^{-13} m/s. First pore-water samples could generally be taken at 200 MPa, and further aliquots were obtained at 300, 400 and 500 MPa. Chemical and isotopic compositions of squeezed waters evolve with increasing pressure. Decreasing concentrations of Cl^-, Br^-, Na^+ and K^+ are explained by ion filtration due to the collapse of the pore space during squeezing. Increasing concentrations of Ca^{2+} and Mg^{2+} are considered to be a consequence of pressure-dependent solubilities of carbonate minerals in combination with sorption/desorption reactions. The pressure dependence was studied by model calculations considering equilibrium with carbonate minerals and the exchanger population on clay surfaces, and the trends observed in the experiments could be confirmed. The compositions of the squeezed waters were compared with results of independent methods, such as aqueous extraction and in-situ sampling of ground and pore waters. On this basis, it is concluded that the chemical and isotopic composition of pore water squeezed at the lowest pressure of 200 MPa closely represents that of the in-situ pore water. The feasibility of sampling pore waters with water contents down to 3.5 wt.% and possibly less opens new perspectives for studies targeted at palaeo-hydrogeological investigations using pore-water compositions in aquitards as geochemical archives.

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1. Introduction

Pore waters in low-permeability, clay-rich sedimentary rocks are natural archives of the ground-water evolution in adjacent aquifers, and the spatial variability of their chemical composition provides constraints on solute-transport processes in aquitard sequences on large scales in space and time. Several studies targeted at these rocks have shown that diffusion is the dominating transport mechanism that governs the solute fluxes within aquitards (e.g. Falck et al., 1990; Rübel et al., 2002; Patriarche et al., 2004a,b; Gimmi et al., 2007; Savoye et al., 2008; Hendry et al., 2010, 2013; Koroleva et al., 2011; Mazurek et al., 2011; Clark et al., 2013). Most of these studies were based on conservative constituents, i.e. anions (Cl^-, Br^-, $\delta^{37}Cl$), stable water isotopes ($\delta^{18}O$, δ^2H) and noble gases (He, $^3He/^4He$, $^{40}Ar/^{36}Ar$). Sampling and analysis of pore waters from low-permeability rocks such as shales are non-trivial tasks and subject to various types of artefacts (Sacchi and Michelot, 2000; Sacchi et al., 2001). Most currently available methods only provide partial information. For example, aqueous extraction or out-diffusion experiments are only suited to quantify

anion concentrations, whereas reactive components are affected by water/rock interaction (mineral dissolution, ion exchange) during the experiments (e.g. Mazurek et al., 2012). Other methods, such as diffusive isotope exchange (Waber and Smellie, 2008) or core outgassing (Rübel et al., 2002) are a priori designed to quantify only the stable isotopic composition of the water and noble-gas concentrations, respectively. Techniques that potentially provide the full pore-water composition, such as advective displacement of pore water (Mäder et al., 2004) or long-term in-situ sampling in rock laboratories (Pearson et al., 2003; Wersin et al., 2011) are technically demanding and not suited to provide substantial data sets pertinent to the spatial distribution of pore-water compositions across low-permeability sequences. Pore-water chemistry can also be deduced from geochemical calculations based on mineral and ion-exchange equilibria (e.g. Pearson et al., 2003; Appelo et al., 2008; Beaucaire et al., 2008; Gaucher et al., 2009; Pearson et al., 2011). However, there are various uncertainties, such as the choice of the solid phases controlling solute concentrations and the quantification of ion-exchange equilibria.

Squeezing of pore water at high pressure is an alternative method that potentially provides full chemical and isotopic compositions of pore waters. This method has been successfully used for bentonite (Muurinen and Carlsson, 2007; Fernández and Villar, 2010), London Clay in the UK (Falck et al., 1990) and is one of the methods for chemical pore-water characterisation in Boom Clay (Belgium; De Craen et al.,

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2004). All of these clays are weakly consolidated (typical water contents 15–25 wt.%), and pressures of 10–70 MPa are sufficient to expel suited quantities of pore water. Squeezing has also been applied on samples of the Opalinus Clay from the Mont Terri underground rock laboratory in Switzerland (Pearson et al., 2003; Fernández et al., 2014) and from the Callovo–Oxfordian shale in eastern France (Fernández et al., 2009). Given the lower water content of 6–8 wt.% in these units, higher squeezing pressures of 70–200 MPa were required to mobilise sufficient quantities of water.

This contribution documents squeezing experiments for clay-rich rocks with even lower water contents down to 3.5 wt.%, obtained from core materials from a deep geothermal borehole in the Swiss Molasse Basin. For these more strongly consolidated rocks, pressures of 200–500 MPa were required to mobilise pore water. Given the progress in modern analytical techniques such as ion chromatography or cavity ring-down spectroscopy, the requirements on sample volume have become less stringent — 0.5 mL is typically sufficient for a full chemical and isotopic analysis. The objectives of the study included a feasibility test of the squeezing method for rocks with very low water contents and the investigation to what degree the squeezed waters can be considered representative of in-situ pore-water composition, and how strongly potential experimental artefacts affect the results.

2. Regional background and sample provenance

The Mesozoic sedimentary sequence of the Molasse Basin in northeastern Switzerland was penetrated in 2011 by a deep cored borehole at Schlattingen (Thurgau, northeastern Switzerland). The primary objective of the campaign was to explore the Triassic aquifers (Muschelkalk and Buntsandstein) for their geothermal potential and possible exploitation. Another objective was the geochemical characterisation of pore waters in the predominantly clay-rich sedimentary sequence between the Late Triassic Keuper and the Late Jurassic Malm aquifers (Fig. 1). This aquitard includes the Opalinus Clay, an Aalenian shale that is currently under investigation as a potential host formation for the deep geological disposal of high-level radioactive waste in Switzerland. In this context, the long-term and large-scale hydrogeological and geochemical characteristics of the Jurassic aquitard are of interest, in order to constrain the long-term evolution of the system.

As shown in Fig. 1, Mesozoic sedimentary rocks overlie Permian sedimentary rocks and the crystalline basement. The sequence is only weakly affected by brittle deformation, in particular normal faulting in the upper part of the Dogger, probably linked to the Bodensee–Hegau graben to the northeast of the site (period of tectonic activity ca. 17–8 Ma). Apart from this, the sequence is essentially undisturbed and dips about 4° towards the southeast. The Mesozoic is unconformably overlain by Tertiary Molasse above 491 m depth. It was subjected to a complex burial and uplift history (Mazurek et al., 2006). For the Benken borehole, located 9 km to the west of Schlattingen, 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, the sequence was uplifted by about 1 km, leading to overconsolidation. The hydraulic conductivity of rock-matrix samples is extremely low. For the Opalinus Clay, reference values are 2E−14 m/s and 1E−13 m/s normal and parallel to bedding, respectively (Nagra, 2002).

Aquifers in the Mesozoic units include the limestones of the Malm and sandy-dolomitic units in the upper Keuper, the upper Muschelkalk and the Buntsandstein (Fig. 1). The Dogger–Lias aquitard is sandwiched between the Malm and Keuper aquifers and is dominated by argillaceous lithologies (shales–marls). Due to problems with borehole stability and the relatively low hydraulic conductivity, no ground-water samples could be obtained from the Malm and Keuper aquifers. The Malm limestones have been strongly affected by karstification during the late Paleogene regional uplift and erosion. The lateral distribution
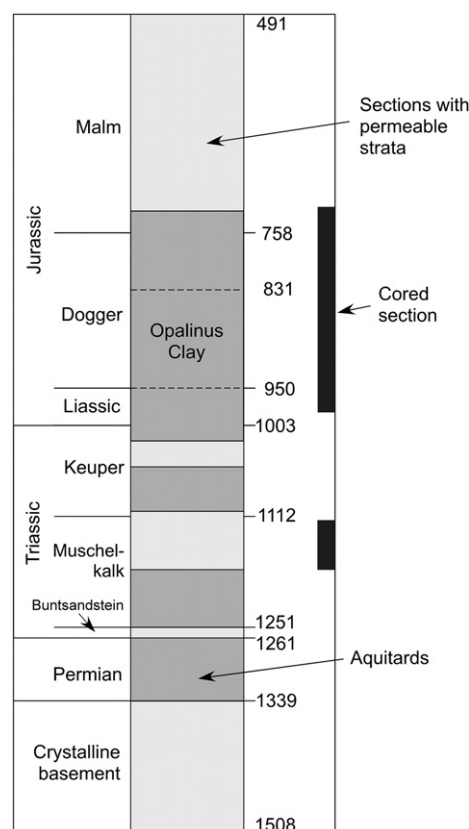

Fig. 1. Simplified hydrogeological profile of the Schlattingen borehole. Numbers indicate depth below surface in m. The Malm is overlain by Tertiary Molasse deposits.

of hydraulic conductivity is highly heterogeneous (range 1E−14 to 1E−4 m/s; Nagra, 2002), and the same is true for ground-water salinity. In the Benken borehole, hydraulic conductivity is relatively low (1E−8 m/s, Nagra, 2002) and the salinity of the Na–Cl–(SO₄) water is relatively high (10 g/L). At Schlattingen, the hydraulic conductivity is even lower, and so an elevated salinity similar to that at Benken can be expected. The underlying local aquifer hosted by Keuper sandstones and evaporites has not been hydraulically tested at Schlattingen. At Benken, it has a hydraulic conductivity of 1E−7 m/s and contains a Na–SO₄–(Cl) water with a salinity of 10 g/L (Nagra, 2002).

3. Methodology

3.1. Sampling

Rock sampling in the Dogger–Lias sequence at Schlattingen was focused on clay-rich lithologies (shales, marls), and the less frequent sandier or calcareous rocks were avoided because of their expected lower water content and higher mechanical strength that render them less suited for squeezing experiments. Sample sections were retrieved on site as full cores (diameter 10 cm) within max. 20 min after core recovery, in order to minimise atmospheric exposure. Existing bedding-parallel breaks in the core caused by disking were used wherever possible; otherwise samples were trimmed by dry cutting on a rock saw. Each sample was cleaned and placed into a plastic coated thick Al bag, which was evacuated and heat sealed. O₂ absorbers and O₂ indicator tablets were added to each sample. Then, all samples were heat-sealed in a second layer (robust plastic bag) for mechanical protection of the Al bag which acts as the main barrier for gas transport. On-site, during transport and in the laboratory, samples were stored cool.