Adapting the diffusive exchange method for stable isotope analysis of pore water to brine-saturated rocks

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ABSTRACT

The isotope diffusive exchange technique was originally developed to indirectly measure the hydrogen and oxygen stable isotope composition (δ^2H and δ^{18}O values) and content of pore water (WC) in low permeability rocks. This study aims to benchmark developments of the technique adapted for high salinity (low water activity) pore waters by: 1) investigating the factors that might influence the results of the isotope diffusive exchange technique for saline solutions through solution-solution experiments; and 2) apply the adapted diffusive exchange method to rock samples previously equilibrated with synthetic solutions of known chemical and isotopic composition. Two different rocks were used in the benchmarking tests: Queenston Formation red shale from Ontario, Canada; and Opalinus Clay from the Mont Terri Underground Research Laboratory (URL), Switzerland.

Solution-solution experiments showed that the main sources of error included a mismatch between the water activities (a_w), a major chemical mismatch, and/or a significant weight difference between the test and sample solution. Samples with a_w spanning from 1 to 0.5 can be matched with adequate precision using a set of test waters with an a_w of 0.99, 0.805, and 0.5. The a_w of the test water must be equal or lower than the sample because equilibration is faster at low a_w (i.e. higher salinities). Experiments with contrasting chemistry between test and sample solutions (NaCl vs CaCl$_2$), induced a deviation in the δ^2H and δ^{18}O values (<5‰ and <2‰, respectively) calculated for the sample water. This deviation can be minimized by matching the a_w of the test solution with salts that correspond to the dominant dissolved species in the sample pore water. The mass of test water must be no <0.5 times the mass of the sample water to maintain acceptable errors. This means the technique is adapted for rocks having a WC >0.5 wt%. The WCs are generally estimated with errors of about 10% for all solution-solution experiments.

To prepare rock samples containing pore waters of known composition, rocks were equilibrated with 0.3 and 5 m NaCl, and 2.5 and 5 m CaCl$_2$ synthetic solutions. Based on time series chemical analyses of the solutions, equilibrium was attained in about 1 and 4 days for the Opalinus Clay and Queenston shale samples, respectively. Benchmarking experiments were then conducted by applying the diffusive exchange method to determine the pore water isotopic compositions of these equilibrated rock samples and comparing to the known values of the equilibrated solution. The water stable isotope compositions are identical within 2σ error and do not depend on salinity or type of salt (NaCl, CaCl$_2$). The adapted diffusive exchange method allows reliable stable isotope analysis of pore waters at all salinities when a_w and chemistries of the pore and test waters are similar.

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1. Introduction

The accurate determination of stable isotope compositions (δ^2H and δ^{18}O values) of pore waters in low permeability rocks is important for safety assessments of deep geological repositories. Water isotopes, together with other geochemical tracers, provide information on the timing and dominant transport mechanisms (advection versus diffusion) of solute (e.g., Altinier et al., 2006; Gimmi et al., 2007; Hobbs et al., 2011; Mazurek et al., 2011; Mazurek and de Haller, 2017; Pearson et al., 2003). Intact, preserved samples of drill core are used to examine pore water compositions within the rock along profiles perpendicular to the stratigraphy. The geochemical profiles reflect the chemical evolution of the groundwater in the aquifers and aquitards through geological time, driven by advection and/or diffusion transport. Data of the highest quality are required for the reliable modeling of the solute diffusion parameters of low permeability rocks used to evaluate the soundness of potential nuclear waste repositories. Although initially focused on applications to the nuclear waste management, the adapted diffusive-exchange technique can also be of use in other types of hydrological studies involving brines and low permeability rocks.

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The determination of the stable isotope composition of pore water in low permeability rocks is challenging; available techniques include the analysis of: i) seepage water that accumulates over time (months or years) in confined intervals of drill holes (e.g. Gascoyne et al., 1996; Pearson et al., 2003; Smellie et al., 2003); ii) water obtained through vacuum distillation of pore water-saturated rock (Altinier et al., 2006; Clark et al., 2013); iii) water recovered through advective displacement of the pore water from a drill core (Mäder et al., 2004); and iv) water collected by squeezing pore water-saturated rock (Mazurek et al., 2015). Measurement artifacts and uncertainties can be related to evaporation, incomplete pore water distillation, isotope fractionation during extraction by squeezing and interaction with water structurally bound to clay minerals. Practical limitations of these techniques include sampling time, and the difficulty to physically expel pore water (advective displacement, squeezing) from certain rock types. In contrast to the techniques mentioned above, the water isotope diffusive-exchange method (Rübel et al., 2002) is used to determine the pore water isotope composition of intact rock pieces indirectly, without mechanical or thermal extraction procedures. The technique was developed to measure the $\delta^{18}O$ and δ^2H values of pore water and the water content in low hydraulic conductivity (4E-15 to 3E-14 m/s) Jurassic clay-rich rocks from Switzerland (Opalinus Clay, Mazurek et al., 2011). The principle is that a known mass of pore water-saturated rock is isotopically equilibrated through the vapor phase with two test waters of different isotopic composition and known mass in two separate, sealed containers (Fig. 1). After equilibration, when the isotopic composition of the sample pore water and the test water are the same, the isotope compositions of the two test waters are measured and these values allow the calculation of the $\delta^{18}O$ and δ^2H of pore water and the water content.

The isotope diffusive-exchange technique works well for the characterization of the isotopic composition of pore waters that are less saline than seawater (Pearson et al., 2003; Gimmi and Waber, 2004; Gimmi et al., 2007; Altinier et al., 2006; Waber and Smellie, 2008), but major modifications of the protocol are needed to adapt the method to higher salinity pore waters, such as those found in Ordovician age sedimentary rocks of southwestern Ontario, Canada (Hobbs et al., 2011). High salinity pore waters introduce three complications: i) the water activity (a_w) of the test water has to be matched (by the addition of salts) to the a_w of the pore water in the rock to minimize water mass transfer between test water and sample, thus avoiding a possible reduction in the volume of test water available for analyses, and reducing the risk of isotopic disequilibrium; ii) the determination of the hydrogen isotope composition of saline waters using the common procedure of Cr-reduction in a Thermo Fisher Scientific H-Device (Bremen, Germany) is not possible because salts would accumulate on the Cr plate, block the syringe, and induce uncontrolled isotopic fractionation; and iii) differences between the compositions of the test solution and the pore water of the sample can affect the final isotopic composition of the test solution because the liquid-vapor isotope fractionation coefficient of water depends on
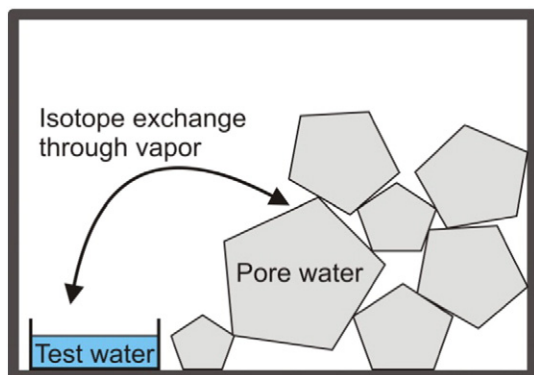
both the salinity and on the type of salt (Horita et al. 1993a and 1993b), such that at equilibrium, test and sample waters may have different isotopic compositions. Alternatively, measurements of the δ^2H value by H_2 equilibration (Coplen et al., 1991) and of $\delta^{18}O$ by CO_2 equilibration in a Thermo Fisher Scientific GasBench II (Bremen, Germany) headspace analyzer are possible, however, the measured isotopic signatures will be shifted from their true values, because salts change the isotopic fractionation factor between water and vapor (Horita et al. 1993a and 1993b). Although these deviations can be corrected empirically knowing the brine chemical composition and the vapor-liquid equilibration temperature (Horita et al. 1993a and 1993b), a more direct alternative requiring no correction is desirable; consequently, the test solution must be distilled prior to isotopic analysis. Water isotopes analysis by cavity ring-down spectroscopy (CRDS) may allow the direct analysis of brines (Skrzypek and Ford, 2014), thus eliminating the distillation procedure required when analyzing by isotope ratio mass spectrometry (IRMS). However, the technique shows important limitations, especially at high salinities and when divalent cations are involved, and Wassenaar et al. (2014) consider that CRDS is not adapted for the direct analysis of saline solutions.

The change in isotopic fractionation between liquid water and vapor with salt addition is related to the creation of two types of liquid waters with distinct isotopic compositions: the free water (FW), which interacts with the vapor; and the water bound to the cations (BW), which has limited interaction with the vapor, except through the isotopic equilibration with the FW. During diffusive exchange experiments, the FW and the BW of both reservoirs (test water and sample) equilibrate through the vapor phase, such that at equilibrium, the isotopic composition of the waters (FW + BW) in both reservoirs is the same. Therefore, if quantitative distillation is applied to the test water before isotopic analysis, the measured water isotope ratios correspond to the composition of the bulk water (FW + BW). Data can therefore be used in the same way as described by and Rübel et al. (2002).

Water activity (a_w) of rock or liquid samples can be measured directly from the relative humidity of the air immediately surrounding the sample (pore water saturated rock or liquid). The correlation between a_w and salinity is shown in Fig. 2 for the most common Cl-bearing salts encountered in pore waters: NaCl, KCl, CaCl$_2$, and MgCl$_2$. The a_w of the different salt solutions can be calculated up to saturation using Pitzer equations (Pitzer, 1987). In addition to dissolved species in the pore water (or osmotic effects), other factors can contribute to the measured a_w of a core sample (matrix effects), including i) surface
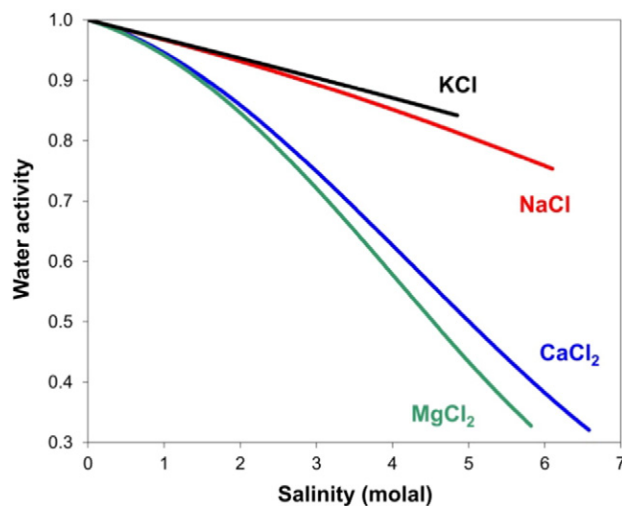

Fig. 1. Principle of the diffusive exchange technique.

Fig. 2. Water activity versus salinity of NaCl, KCl, CaCl$_2$, and MgCl$_2$ solutions. Lines end at saturation with a solid phase (KCl, NaCl, CaCl$_2$ * 6H$_2$O, or MgCl$_2$ * 6H$_2$O) and were calculated using Pitzer equations and the program Geochemist's Workbench®.