Isotope diffusive exchange experiments for deriving porewater isotope composition in low-permeability rocks – Improvements in experimental procedure and data processing

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ARTICLE INFO

ABSTRACT

Over the last decades, several methods have been developed for determining the porewater stable isotope composition (δ^2H, δ^{18}O) in low-permeability, argillaceous rocks and pertinent to the acquisition of spatially highly-resolved tracer profiles for investigating subsurface transport processes over large scales of time and space. One of these methods is the so-called isotope diffusive exchange technique (IDE) where the porewater of the rock equilibrates via the vapour phase with a test water of known isotope composition. In this study we aim for 1) identifying and assessing important parameters and artefacts these experiments are sensitive and prone to, respectively, 2) evaluating their impact on the porewater isotope composition derived from such experiments and 3) testing the reproducibility and accuracy of the method. For this, the experimental data and the calculated porewater isotope composition of 752 isotope diffusive exchange experiments, performed on drillcore samples from variable lithologies, were examined under these aspects. The investigations are complemented by comparison between porewater and groundwater isotope values in regions of water-conducting zones and an interlaboratory comparison. Ultimately, this allowed defining a stringent procedure for the evaluation of the experimental data and classifying experiments as 'reliable', less reliable' and 'failed'. For calculating the porewater isotope composition, a new approach was developed that accounts for sample-scale heterogeneity of the water content. This procedure of data evaluation and processing resulted in smooth isotope profiles with only little scatter across largely different lithologies. The interlaboratory comparison attests the method a very good reproducibility. The comparison with groundwater isotope data reveals slightly enriched δ^{18}O and δ^2H signatures by 0.3–0.6 and 1.7–2.7‰ VSMOW, respectively, for some samples investigated by the IDE method. No stringent explanation exists at this stage for these differences, but it must be emphasized that these deviations are small compared to the typical natural variations observed in profiles of these tracers. This demonstrates that porewater isotope data obtained by the IDE method represent the conditions in the in situ porewater reasonably well when strictly following the proposed procedures of the experimental setup, the evaluation of experimental data and the calculation of porewater isotope compositions.

1. Introduction

Argillaceous rock formations show very low hydraulic conductivities and a large retention capacity for cations, which has put such lithologies into focus as potential host rocks for geological disposal of radioactive waste. In several countries, campaigns are under way aiming for characterizing the detailed transport properties of such formations at depth.

In this context, profiles of natural chemical and isotope tracers in the porewater across the potential host rock and its confining units are of particular importance for investigating transport processes over large scales of time and space (e.g., Mazurek et al., 2009, and references therein). To this end, the water isotope composition of the porewater (δ^{18}O and δ^2H) serves as an ideal tracer besides dissolved conservative tracers such as chloride, bromide and helium. In low-permeability

argillaceous rocks, solute transport is typically diffusion-dominated and porewater cannot be obtained by conventional techniques for isotope and chemical analyses. Moreover, exploration in the context of site characterization campaigns typically relies on surface-based boreholes and, thus, information on the porewater composition has to be obtained by indirect methods based on drillcore samples.

Approaches to physically extract porewater from drillcore samples and analyse its composition include the advective displacement technique, AD (Mäder et al., 2004; Mäder, 2018) and high-pressure squeezing, SQ (Entwisle and Reeder, 1993; Fernández et al., 2003, 2014; Mazurek et al., 2015; Nakata et al., 2018) both allowing rather complete chemical and isotope analyses of the extracted water. Alternatively, complete information about the porewater composition can be obtained by long-term in situ sampling in underground rock laboratories (e.g. Pearson et al., 2003; Vinsot et al., 2008; Wersin et al., 2011). These methods are technically demanding, time and cost intensive or not feasible on extracted cores and, thus, not suited for acquiring spatially highly resolved tracer profiles.

Alternatively, over the past two decades, several other techniques have been developed for specifically investigating the porewater isotope composition, $\delta^{18}O$ and δ^2H, in low-permeable rocks. These are more time- and cost-efficient and, hence, better suited for routine analysis of a large number of samples – i.e., for providing substantial data sets pertinent to porewater isotope profiles of high spatial resolution. These techniques include the vacuum distillation technique, VD (e.g. Araguás-Araguás et al., 1995; Moreau-Le Golvan, 1997; Clark et al., 2013), radial diffusion experiments, RD (e.g. van der Kamp et al., 1996; Savoye et al., 2006), the isotope diffusive exchange technique, IDE (Rogge, 1997; Rübel et al., 2002), the direct vapour equilibration method, DVE (Koehler et al., 2000) and the direct vapour equilibration method using laser spectrometry, DVE-LS (Wassenaar et al., 2008; Hendry et al., 2015).

There are distinct differences between these methods and their applicability to low-permeability rocks. Most importantly, in the IDE and DVE techniques the porewater and rock are not subjected to experimentally induced changes in pressure or temperature as this is the case for AD, SQ and VD. The two techniques further differ from all others in a way that the porewater composition is not derived from a liquid phase that is in contact with the rock sample. Changes in pressure or temperature with the extracted liquid phase being in contact with the rock during the experiment might induce unwanted mineral reactions that potentially modify the in situ porewater isotope composition and trigger isotope fractionation.

Differences in the applicability of the various methods to different rock types concern limitations related to the required minimum water content in order to obtain a sufficiently large volume of extracted water for isotope analysis (around 3 wt% for AD, SQ) and/or the required signal change in the isotope analyses outside the analytical uncertainty (RD, DVE-LS). In contrast, the IDE technique, which was originally also developed for argillaceous rocks with elevated water content (Rogge, 1997; Rübel et al., 2002), has more recently been adapted to low water-content rocks (<1 wt%) such as crystalline rocks and limestones (e.g. Eichinger et al., 2006, 2015; Waber and Smellie, 2008; Waber, 2012). An additional adaption of the IDE technique includes that by de Haller et al. (2014, 2016) for porewater salinities distinctly exceeding that of seawater.

Over the past two decades, all of these methods were applied worldwide in numerous studies mainly conducted in the framework of site characterization programmes for the deep geological disposal of radioactive waste in sedimentary and crystalline rocks. A first comprehensive compilation of porewater isotope studies performed on sedimentary rocks of various European sites is given by Mazurek et al. (2009 and references therein). These are complemented by additional studies in Europe (e.g. Gimmi et al., 2007; Savoye et al., 2006; Koroleva et al., 2011; Mazurek et al., 2011; Waber, 2012; Bensenouci et al., 2013; 2014; Waber and Rufer, 2017; Wersin et al., 2018) and various studies in North America (e.g. van der Kamp et al., 1996; Koehler et al., 2000; Hendry et al., 2004, 2013, 2015; Wassenaar et al., 2008; Hobbs et al., 2011; Clark et al., 2013).

These studies showed that all different methods based on rock samples provide more or less diverging results, some also with respect to isotope data obtained from long-term in situ sampling of borehole water (Pearson et al., 2003; Mazurek et al., 2009; Hendry et al., 2015). Obviously, all these methods – including AD and SQ – are prone to various experimental artefacts that can bias the experimentally determined isotope composition. This has been shown in numerous method comparisons between, e.g., the IDE and VD techniques (Rübel et al., 2002; Altinier et al., 2007; Mazurek et al., 2009, 2017), the IDE, VD and RD techniques (Altinier et al., 2007), as well as the SQ and DVE-LS techniques (Hendry et al., 2013, 2015; Nakata et al., 2018). For consolidated argillaceous rocks reasonable agreement was found between borehole water collected in situ and the IDE and SQ techniques (for squeezing pressure <150 MPa; Pearson et al., 2003; Mazurek et al., 2009, 2017). For weakly consolidated glacial till and shales good agreement was observed between water collected directly from piezometer boreholes and the DVE-LS and SQ techniques (squeezing pressure of 50 MPa; Hendry et al., 2004; 2013, 2015). For consolidated rocks, the ultimate proof of the accuracy of the above described methods relies on applying these methods to rocks that host groundwater for which isotopic equilibrium can be expected based on groundwater residence times. However, owing to the difficulties of predicting groundwater occurrences at great depth and the rather large sample spacing used in previous studies, such comparisons are limited to a very few examples and only exist for the IDE technique (Waber, 2005, 2012; Waber et al., 2012; Waber and Rufer 2017).

In this study we focus on the IDE technique and the various parameters and artefacts the experiments are sensitive and prone to, respectively. Their importance is described in various studies (Pearson et al., 2003; Gimmi and Waber, 2007; Waber and Smellie, 2008; Hobbs et al., 2011; de Haller et al., 2016; Waber and Rufer, 2017), however, the understanding of their impact on the calculated porewater isotope composition often remained on a qualitative level. Thus, we aim for taking a step in the direction of bridging the gap between qualitative and quantitative understanding of the impact of experimental parameters and artefacts on the calculated porewater isotope compositions, as well as testing the reproducibility and accuracy of the method. Between 2019 and 2022, Nagra (the Swiss National Cooperative for the Disposal of Radioactive Waste) conducted a deep drilling campaign in the context of their site selection program for a deep geological repository for radioactive waste in northern Switzerland (for details see Mazurek et al., 2023). From 8 deep boreholes a large number of drillcore samples dedicated to porewater investigations – including IDE experiments – were collected at a very high spatial resolution of 3–12 m. Special emphasis was given to water-conducting zones for comparison of IDE derived porewater isotope data and those obtained from corresponding deep groundwaters. Based on the assessment of this large dataset under the aspects mentioned above, a stringent procedure for the evaluation of the experimental data is defined, allowing a systematic assessment of the robustness of IDE-derived porewater isotope compositions in low to moderate salinity systems. These investigations are complemented by an interlaboratory comparison for testing the reproducibility of the IDE technique.

2. Samples

From 8 deep boreholes drilled by Nagra between 2019 and 2022, a total number of 752 drillcore samples were investigated by the IDE technique. This led to porewater isotope profiles at a very high spatial resolution of 3–12 m, which are presented by Gimmi et al. (2023). The samples span the entire 800–900 m thick Mesozoic sequence, i.e., from the Upper Malm down to the base of the Trias, thus, covering a wide range of different lithologies with variable water contents (i.e.

claystones, sandstones, carbonates and evaporites; see Mazurek et al., 2023).

The preservation of the original saturated state of the drillcore samples upon recovery is mandatory for all porewater investigation. For this, the on-site sampling followed a stringent protocol as described by Rufer and Stockhecke (2019) aiming for minimizing desiccation, oxidation and outgassing of the samples until their preparation and analyses in the laboratory. This involved rapid vacuum-sealing into gas-tight bags (PET-Aluminium-Polyethylene compound foil) immediately after core recovery.

3. Experimental method

3.1. General principles of the isotope diffusive exchange method

The IDE method developed by Rogge (1997) and Rübel et al. (2002) is based on the molecular diffusive exchange of water (and thus of oxygen and hydrogen isotopes) between the porewater in the rock sample and a small quantity of test water of known isotope composition. The isotope exchange occurs via the vapour phase in a vapour-tight container until equilibrium between the isotope compositions of porewater and test water is achieved. Providing that equilibration is complete, the original oxygen and hydrogen isotope composition of the porewater (C_{pw} of ^{18}O and ^2H), as well as the porewater mass (m_{pw}) of the sample can be derived from the following isotope mass-balance relationships (Rogge, 1997; Rübel et al., 2002):

$$m_{pw}C_{pw} + m_{tw} \, C_{twi} = (m_{pw} + m_{tw})C_{twf} \tag{1}$$

where the subscripts *tw* and *pw* denote the test water and porewater, respectively, *C* is the isotope concentration, expressed as $\delta^{18}O$ and δ^2H, and *m* is the mass of water. The left side of the equation describes the system before isotopic equilibration (i = initial), whereas the right side describes the system after equilibration (f = final) assuming zero loss of water from the system.

The test water mass, m_{tw}, and the isotope composition of the test water, $\delta^{18}O_{tw}$ and δ^2H_{tw}, before and at the end of the experiment are known. Solving equation (1) for the three unknowns of the porewater, i. e., m_{pw}, $\delta^{18}O_{pw}$ and δ^2H_{pw}, requires two experiments with test water of different isotope composition. Each equilibration experiment then reveals two independent equations of the type (1) for $\delta^{18}O_{pw}$ and δ^2H_{pw}. Combining these equations, the original isotope composition C_{pw} of the porewater ($\delta^{18}O_{pw}$ and δ^2H_{pw}) can be calculated:

$$C_{pw} = \frac{m_{tw2} \, m_{rw1} \, C_{twf1} \left(C_{twf2} - C_{twi2}\right) - m_{tw1}m_{rw2} \, C_{twf2} \left(C_{twf1} - C_{twi1}\right)}{m_{tw2} \, m_{rw1} \left(C_{twf2} - C_{twi2}\right) - m_{tw1}m_{rw2} \left(C_{twf1} - C_{twi1}\right)} \tag{2}$$

where the indices 1 and 2 denote the two different experiments. Note that the mass of porewater in an experiment is defined by the mass of wet rock m_{rw} and its water content w_w (relative to the wet weight of the sample). According to Rogge (1997) and Rübel et al. (2002), the mass balances remain correct at complete equilibration, even if a small amount of test water is transferred to the sample during the experiment. Working with rock samples of elevated water content, these authors generally assumed that the water content of the two subsamples is identical and thus cancels out in eq. (2).

Once the porewater isotope composition is determined, it is possible to back-calculate porewater contents w_w based on the experiment with a test water strongly depleted in ^{18}O and ^2H according to:

$$w_w = \frac{m_{tw} \left(C_{twf} - C_{twi2}\right)}{m_{rw} \left(C_{pw} - C_{twf}\right)} \tag{3}$$

Rogge (1997) and Rübel et al. (2002) showed that the propagated experimental uncertainty of the calculated porewater isotope concentration increases with increasing difference in isotope ratio between porewater and test water, whereas the propagated uncertainty of the porewater content decreases with increasing difference in isotope concentration between porewater and test water. Thus, in order to minimize these uncertainties, a test water with δ^2H and $\delta^{18}O$ values close to those of the porewater should be used for determining the isotope composition, whereas the difference should be as large as possible for determining the porewater content.

3.2. Experimental set-up

The preconditioned drillcore samples were unpacked in the laboratory and approximately 1.5 cm of rim material, potentially contaminated by the drilling fluid and pre-exposed to the atmosphere was removed from the intact core. The saturated censec3.2tral rock was gently disaggregated into 4–5 cm-sized fragments. Depending on lithology, about 200–300 g of rock were weighted and placed in vapour-tight glass containers along with a small crystallization dish containing 3–5 mL test water (section 4.2) of known salinity (0.3–0.7 M NaCl; section 4.3) and isotope composition. Similar to the original method by Rogge (1997) and Rübel et al. (2002) two test waters of different isotope composition were defined based on considering the effect of the isotope composition of the test water on the propagated uncertainties of the method (section 3.1) and previous work (Pearson et al., 2003; Gimmi et al., 2007; Waber and Rufer, 2017; Wersin et al., 2018): 1) Tap water from the laboratory water supply showing $\delta^{18}O$ and δ^2H values ranging from −12.20 to −10.31‰ VSMOW and −87.7 to −80.0‰ VSMOW, respectively (named 'LAB' test water), over the 3 years of the drilling campaign, and 2) melt water of an Antarctic ice core showing $\delta^{18}O$ and δ^2H values ranging from −27.29 to −26.11‰ VSMOW and −208.4 to −201.8‰ VSMOW, respectively (named 'NGW' test water). Aliquots of the original test waters were collected immediately before and after preparation of an individual sample series (i.e. morning and evening) and analysed for their isotope composition.

The preparation time during which an individual sample was exposed to atmospheric conditions was limited to generally less than 5 min to minimize evaporation effects. The glass containers were then stored in a Styrofoam box for 35 days at 23 °C to allow for complete equilibration. The equilibration time of 35 days is based on the work by Rogge (1997) who examined this parameter for a variety of different lithologies. This study was later confirmed and complemented by time-dependent IDE experiments performed by Rübel et al. (2002) and Altinier et al. (2007), specifically focussing on clay-rich rocks. To ensure complete equilibration for all the different lithologies encountered in the investigated boreholes, and for practical reasons with respect to the large number of samples that were processed, the same (conservative) equilibration time was used for all the different lithologies.

After equilibration, the test water was transferred into vapour-tight 1.5 mL glass vials for isotope analyses and the water content of the different subsamples used for the experiments were measured by gravimetry. All individual and total weights of experiment components were measured before and after the experiments (section 4.1).

3.3. Analyses of stable water isotopes

Stable oxygen and hydrogen isotope ratios ($\delta^{18}O$ and δ^2H) of the equilibrated and the original test waters were analysed using a Picarro L2120-i cavity ring down spectrometer (CRDS) attached to a V1102-i vaporizer. Raw data of $\delta^{18}O$ and δ^2H were obtained by a tenfold measurement of each sample. Post-run correction of raw data (memory and drift) followed the methodology described by van Geldern and Barth (2012). The measurements were normalized to the international VSMOW-scale using a set of four in-house reference waters calibrated against primary international IAEA standards (VSMOW2 and SLAP2).

The in-house reference waters span a calibration interval between −27.08 and −2.13‰ VSMOW for $\delta^{18}O$ and −208.8 and −6.1‰ VSMOW for δ^2H, respectively. The analytical uncertainty of the isotope measurements was determined based on multiple measurements of internal IAEA standard and corresponds to ±0.1‰ VSMOW for $\delta^{18}O$ and ±1.0‰ VSMOW for δ^2H, respectively. Note that the CRDS technique allows measuring accurate water isotope compositions also at salinities above that of seawater without the need of an additional correction for fractionation effects associated with salt hydration (e.g. Mazurek et al., 2013; Skrzypek and Ford, 2014).

4. Choice and evaluation of experimental parameters

In order to identify artefacts or processes that potentially affect IDE experiments and, ultimately, the calculated porewater isotope composition, a rigorous monitoring and parameter evaluation is required. This includes aspects of mass changes, the ratio of porewater to test water, the impact of test water salinity and the gravimetric water content. Once identified, some of the artefacts or processes can be corrected. Ultimately, this allows classifying calculated porewater isotope compositions as 'reliable', 'less reliable' or 'unreliable' (section 5).

4.1. Weight control and evaporation correction

Before and after the experiment all individual and total weights of experiment components (glass container and crystallization dish) were measured in their empty and filled state (i.e. containing rock sample and test water, respectively). This allows monitoring any change in mass of rock and test water during the experiment and, thus, identifying potential evaporation of a liquid phase (container leakage), as well as transfer of water from the rock to the test water or vice versa.

In most cases, the difference in weight of the entire experiment container before and after the experiment was within the propagated analytical uncertainty (±0.04 g). If the loss of mass was larger, it was compared to the mass change of the rock sample and the test water during the experiment, i.e., mass transfers between the two. If the loss of mass from the total system was larger, corrections were applied to the measured isotope value of the equilibrated test water by Rayleigh-fractionation calculations (e.g. Clark and Fritz, 1997) before calculating the porewater isotope ratio, assigning thus the mass loss to evaporation of the test water.

4.2. Mass of rock and test water

The mass of test water and rock sample have to be optimized in order to ensure a reasonable ratio of porewater to test water yielding a change in the isotope signal of the equilibrated test water outside the analytical uncertainty. While this was not specifically taken into account in previous studies focussing on argillaceous rocks with high water contents, it was considered in porewater studies of crystalline rocks (e.g. Eichinger et al., 2006; Waber and Smellie, 2008). This is equally important in low-porosity sedimentary rocks, such as micritic limestones or evaporites and especially if their porewater isotope composition is close to that of the LAB test water. This effect is illustrated in Fig. 1. Obviously, at porewater to test water ratios of <0.1 the shift in the isotope signal of the equilibrated test water falls within the analytical uncertainty (for the assumed C_{pw} and C_{twi} in Fig. 1) and cannot be reliably resolved. For rocks with water contents of around 1 wt%, the corresponding rock to test water ratios are <8 g/mL. In order to account for variations of porewater isotope composition and water contents along the investigated stratigraphic profile, a conservative approach was chosen with rock to test water ratios of 40 g/mL (200 g of rock and 5 mL test water) for clay-rich lithologies, sandstones and dolomites, whereas for low-porosity lithologies, such as massive limestones and anhydrites a higher ratio of 100 g/mL (300 g of rock and 3 mL test water) was used. Note that in most cases the porewater content of a rock sample is not known when starting an experiment and thus, it must be estimated.

4.3. Salinity of the test water

The salinity of the test waters is important in three aspects: 1) it serves to lower the water vapour pressure and, thus, minimizes condensation in the experiment container. 2) It needs to be adjusted with respect to the (expected) porewater salinity to prevent excessive water transfer between the test water and the rock (i.e. owing to large differences in the water activity between the two reservoirs). 3) The liquid-vapour equilibrium fractionation of oxygen and hydrogen isotopes varies as a function of the amount and type of salts contained in a solution (Craig and Gordon, 1965; Stewart and Friedman, 1975; Horita et al., 1993).
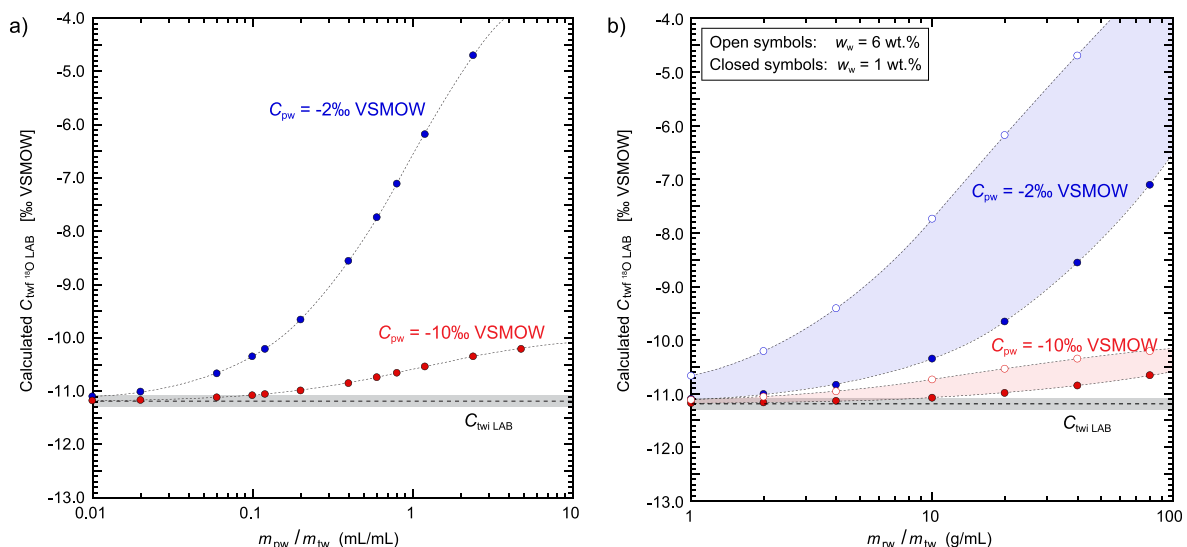

Fig. 1. Calculated oxygen isotope composition of the equilibrated LAB test water (C_{twf}) as a function of (a) the ratio of porewater to test water and (b) the ratio of saturated rock sample to test water for different porewater isotope compositions (C_{pw}) and water contents (w_w). For the isotope composition of the original test water (C_{twi}) the value reflects an average composition as was used for samples from the Bülach 1-1 borehole (section 5.1). The grey bar represents the analytical uncertainty of the isotope measurements (section 3.3).

Adding NaCl salt to the test water is a standard procedure since the work of Rogge (1997) and Rübel et al. (2002). These authors further point out that for Na–Cl-type systems slight differences in salinity between porewater and test water will have no effect on the liquid-vapour equilibrium fractionation of ^{18}O, but does have some effect on ^{2}H, which at room temperature can be expressed as ~2.7‰ × ΔM where ΔM denotes the difference in molality between the two solutions. The effect of different salt concentrations and compositions of the test water and the porewater has later been investigated by de Haller et al. (2014, 2016).

In the investigated boreholes, the lithologies in the interval Malm – Upper Keuper typically host low-to moderately saline Na–Cl-type porewater with chloride concentrations of around 0.1–0.4 M (Kiczka et al., 2023; Wersin et al., 2023). Thus, a test water salinity of 0.3 M NaCl was used for these rock intervals. Accordingly, the difference between porewater and test water was at maximum 0.2 M and the effect on δ^{2}H is < 0.6‰, i.e., less than the analytical error, while there is no effect on δ^{18}O.

In the evaporitic lithologies of the Lower Keuper and Muschelkalk higher porewater salinities were expected. Thus, test water salinities of up to 0.7 M NaCl were used for these rock intervals. Note that the porewater salinity is essentially unknown at the time the experiments start and, thus, it has to be estimated based on experience from similar geologic environments and/or rapid determination of the chloride concentrations of the porewater by, e.g., aqueous leaching and electrode measurements. The latter was applied for the evaporitic lithologies investigated in this study.

4.4. Gravimetric water content

After the termination of the experiment, the initial water content of the different subsamples used in the experiments was determined by gravimetry, i.e., by drying the subsamples at 105 °C to constant weight. For this, the wet mass of the sample after the experiment was corrected for any uptake of test water by the rock during the experiment. Gravimetric measurements were performed on a weekly basis except for the first week of drying during which a higher frequency was used (2–3-day intervals). The criteria for the attainment of constant weight were 1) mass changes of ≤0.005 g over a 14-day drying interval or 2) two subsequent measurements with each showing an increase in mass of >0.005 g (owing to oxidation reactions).

Analysis of the gravimetric water content of the two subsamples has three purposes, which are 1) identifying problematic samples with low ratios of porewater to test water (section 4.2), 2) identifying problematic samples in terms of sample heterogeneity (section 5.1) and 3) an independent check of the robustness of the calculated porewater isotope composition (section 5.4). The impact of these aspects on the calculated porewater isotope compositions are further described below.

5. Improvements in data processing and evaluation

5.1. Calculation of the porewater isotope composition

Calculating the porewater isotope composition according to the isotope mass balance equation (eq. (2)) assumes equality of the water contents of the two subsamples (Rübel et al., 2002). This might well apply to argillaceous rocks with elevated water contents, however, in lithologically heterogeneous rocks with heterogeneous porosity distribution, the water content can vary on a cm – dm scale. For such rocks, the assumption of homogeneity of the water content is not necessarily valid on the sample-scale. When calculating the porewater isotope composition of samples for which the water content of the two subsamples differs significantly, the application of eq. (2) leads to biased concentrations, with the bias not appearing in the propagated uncertainties. Therefore, an alternative approach is presented that explicitly considers the ratio q, defined as the ratio of the gravimetric water contents of the two different subsamples used in the experiments

with LAB and NGW test water, w_{w1}/w_{w2}. This new procedure eliminates the bias introduced by sample-scale heterogeneity of the water content (i.e. porosity). The isotope concentration of the porewater is then calculated as:

$$C_{pw} = \frac{a\,q\,C_{twf1} - b\,C_{twf2}}{a\,q - b} \qquad (4)$$

with:

$$a = m_{tw2}\,m_{rw1}\left(C_{twf2} - C_{twi2}\right) = m_{tw2}\,m_{rw1}\Delta C_{tw2} \qquad (5)$$

$$b = m_{tw1}\,m_{rw2}\left(C_{twf1} - C_{twi1}\right) = m_{tw1}\,m_{rw2}\Delta C_{tw1} \qquad (6)$$

and

$$\Delta C_{tw2} = \left(C_{twf2} - C_{twi2}\right),\, \Delta C_{tw1} = \left(C_{twf1} - C_{twi1}\right) \qquad (7)$$

This formalism is valid even for cases where q deviates substantially from 1, and approaches eq. (2) for cases where q tends to 1. Note that instead of using $q = w_{w1}/w_{w2}$, it is also possible to formulate eq. (4) with the corresponding masses of porewater, which leads to the same result.

Fig. 2 shows that in clay-rich lithologies the ratio q is reasonably constant showing values of around 1. This validates the applicability of eq. (2) in previous studies of, e.g., Rübel et al. (2002), Gimmi et al. (2007), Koroleva et al. (2011) and Wersin et al. (2018), which exclusively focused on clay-rich rocks with elevated water contents. In contrast, for limestones, dolomites and anhydrite-bearing lithologies, where the respective mineral fractions often vary on a small scale (e.g. intercalations of more clay-rich material), the ratio q can substantially deviate from 1. Such lithologies constitute a significant portion of the Mesozoic sedimentary rock sequence investigated in this study.

The new method for calculating the porewater isotope composition from IDE experiments clearly reduces the scatter of isotope profiles compared to the previous method, where equality of the water content was assumed for the two subsamples. As an example, this effect is illustrated in Figs. 3 and 4 for the Bülach 1-1 borehole (for details
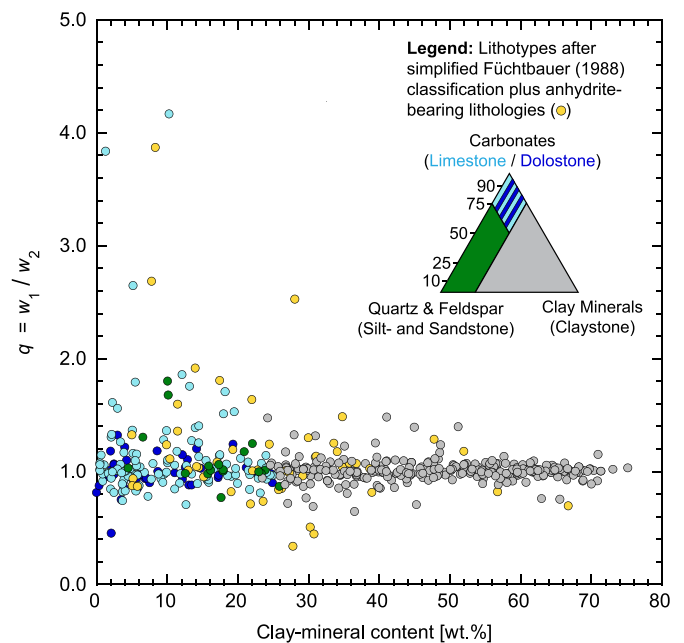
Fig. 2. Data from all 8 boreholes (n = 561) for samples with additional mineralogical data available (Mazurek et al., 2023). Ratio q of the gravimetric water contents of the LAB and the NGW subsamples used for the isotope diffusive exchange experiments (w_{w1} = gravimetric water content of LAB subsample, w_{w2} = gravimetric water content of NGW subsample) as a function of clay-mineral content (Füchtbauer, 1988).
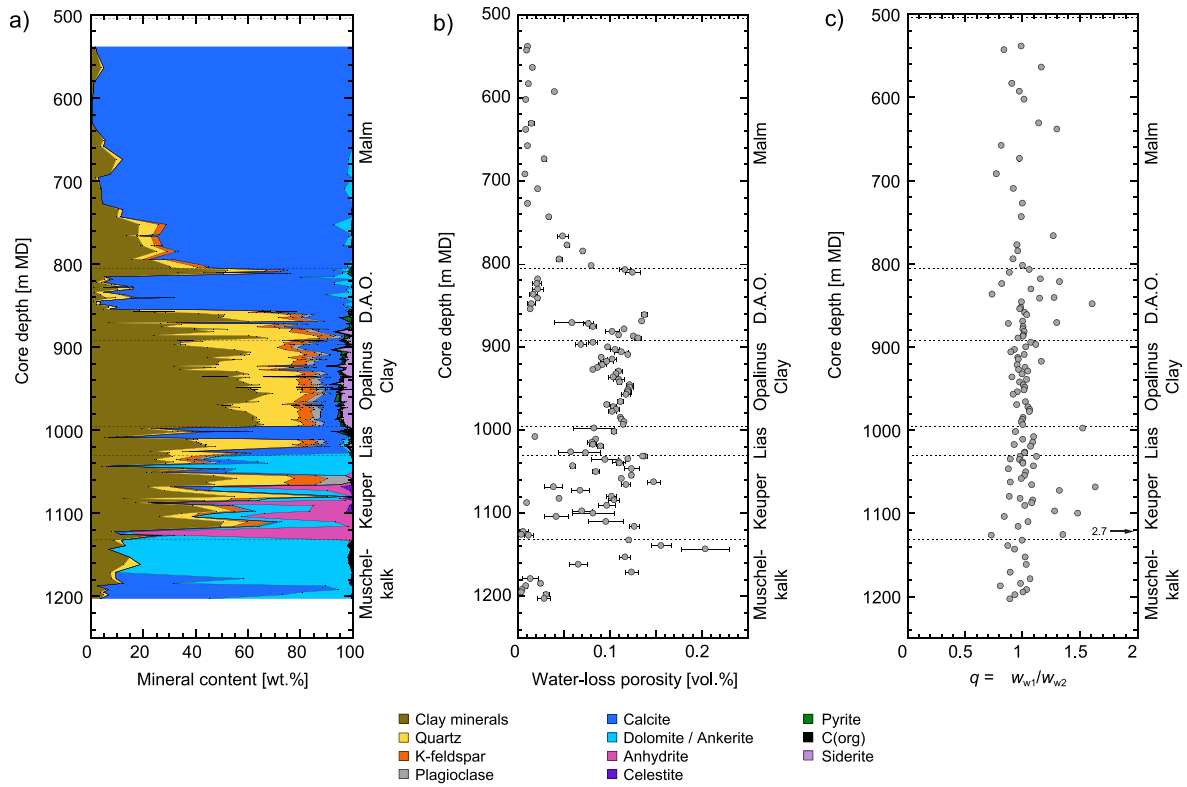
Fig. 3. Depth profiles of a) mineralogy, b) water-loss porosity and c) ratio $q = w_{w1}/w_{w2}$ for the Bülach1-1 borehole. The ratio q of the gravimetric water contents of the LAB (w_{w1}) and the NGW (w_{w2}) subsamples used in the IDE experiments scatter most in low-porosity limestones, as well as in anhydrite-bearing lithologies. The value indicated with a black arrow falls outside the plotted range. D.A.O. = Dogger above Opalinus Clay.

regarding the borehole location see Mazurek et al., 2023). Fig. 3 shows the depth profiles for mineralogy and water-loss porosity (Mazurek et al., 2023) compared to the ratio q of the two subsamples used for the IDE experiments. Constant levels of water-loss porosity and q are observed for the clay-rich Opalinus Clay and Lias, whereas in the over- and underlying units both parameters show significant scatter. Most scatter of q is observed for the low-porosity limestones of the Malm and the lithologically heterogeneous rock sequences of the Dogger above the Opalinus Clay (limestone – marl intercalations) and of the Keuper (anhydrite – marl intercalations).

Fig. 4 shows the porewater isotope composition in the Mesozoic rock sequence at the Bülach 1-1 borehole calculated using eq. 2 – i.e., assuming equal water content for the two subsamples (Fig. 4a) – compared to that obtained from using eq. (4) considering the ratio q (Fig. 4b). Clearly, the porewater isotope profiles calculated according to eq. (2) show significant scatter in rock sections where $q \neq 1$ with the bias not appearing in the propagated uncertainties. In contrast, the scatter is greatly reduced when calculating the isotope composition according to eq. (4), particularly in rock sections where $q \neq 1$, resulting in overall much smoother profile shapes. Given the high sample frequency and the low diffusivity of these rocks (see van Loon et al., 2023; Gimmi et al., 2023), the smooth porewater isotope profiles obtained using eq. (4) are more plausible.

For comparison, porewater isotope data from high-pressure squeezing (SQ) and advective displacement (AD) experiments are also shown in Fig. 4. Rock samples subjected to these methods are all clay-rich showing water contents of >3 wt%. In general, porewater δ^2H values derived by IDE and SQ experiments agree well within the propagated uncertainty of IDE experiments and the analytical error of SQ experiments. Due to experimental artefacts no reliable δ^2H data could be derived from AD experiments conducted on samples from the Bülach 1-1 borehole (Kiczka et al., 2023). Regarding $\delta^{18}O$, both SQ and AD solutions show slightly depleted isotope signatures (by 0.2–0.8‰ VSMOW)

compared to the data from IDE experiments.

5.2. Propagated error of porewater isotope composition and important sensitivities

Based on first-order error propagation, the error of the porewater isotope composition calculated with eq. (4) is:

$$\sigma_{C_{pw}}^2 = \left(d\frac{\sigma_{m_{tw1}}}{m_{tw1}}\right)^2 + \left(-d\frac{\sigma_{m_{tw2}}}{m_{tw2}}\right)^2 + \left(-d\frac{\sigma_{m_{rw1}}}{m_{rw1}}\right)^2 + \left(d\frac{\sigma_{m_{rw2}}}{m_{rw2}}\right)^2$$
$$+ \left(-d\frac{\sigma_q}{q}\right)^2 + \left(-d\frac{\sigma_{C_{twi1}}}{\Delta C_{tw1}}\right)^2 + \left(d\frac{\sigma_{C_{twi2}}}{\Delta C_{tw2}}\right)^2 \qquad (8)$$
$$+ \left(\left[\frac{aq}{aq-b} + \frac{d}{\Delta C_{tw1}}\right]\sigma_{C_{twf1}}\right)^2 + \left(\left[-\frac{b}{aq-b} - \frac{d}{\Delta C_{tw2}}\right]\sigma_{C_{twf2}}\right)^2$$

with

$$d = \frac{m_{tw1}m_{tw2}\,m_{rw1}\,m_{rw2}\,q\Delta C_{tw2}\Delta C_{tw1}\left(C_{twf1} - C_{twf2}\right)}{\left(m_{tw2}\,m_{rw1}\Delta C_{tw2}q - m_{tw1}\,m_{rw2}\Delta C_{tw1}\right)^2} = \frac{aqb\left(C_{twf1} - C_{twf2}\right)}{\left(aq - b\right)^2}$$
$$(9)$$

and a and b as defined in eqs. (5) and (6).

The error, σ_q, is calculated from the analytical error of the water contents according to:

$$\sigma_q = q\left(\left[\frac{\sigma_{w_{w1}}}{w_{w1}}\right]^2 + \left[\frac{\sigma_{w_{w2}}}{w_{w2}}\right]^2\right)^{0.5} \qquad (10)$$

The expressions for the individual error terms in eq. (8) appear comparably simple, but a, b, d and also ΔC_{tw1} or ΔC_{tw2} depend in a complicated way on all parameters (see, e.g., middle term in eq. (9)). As a result, it is not possible to easily infer the interdependencies of the errors on each parameter. For instance, it is not just the relative error (e.
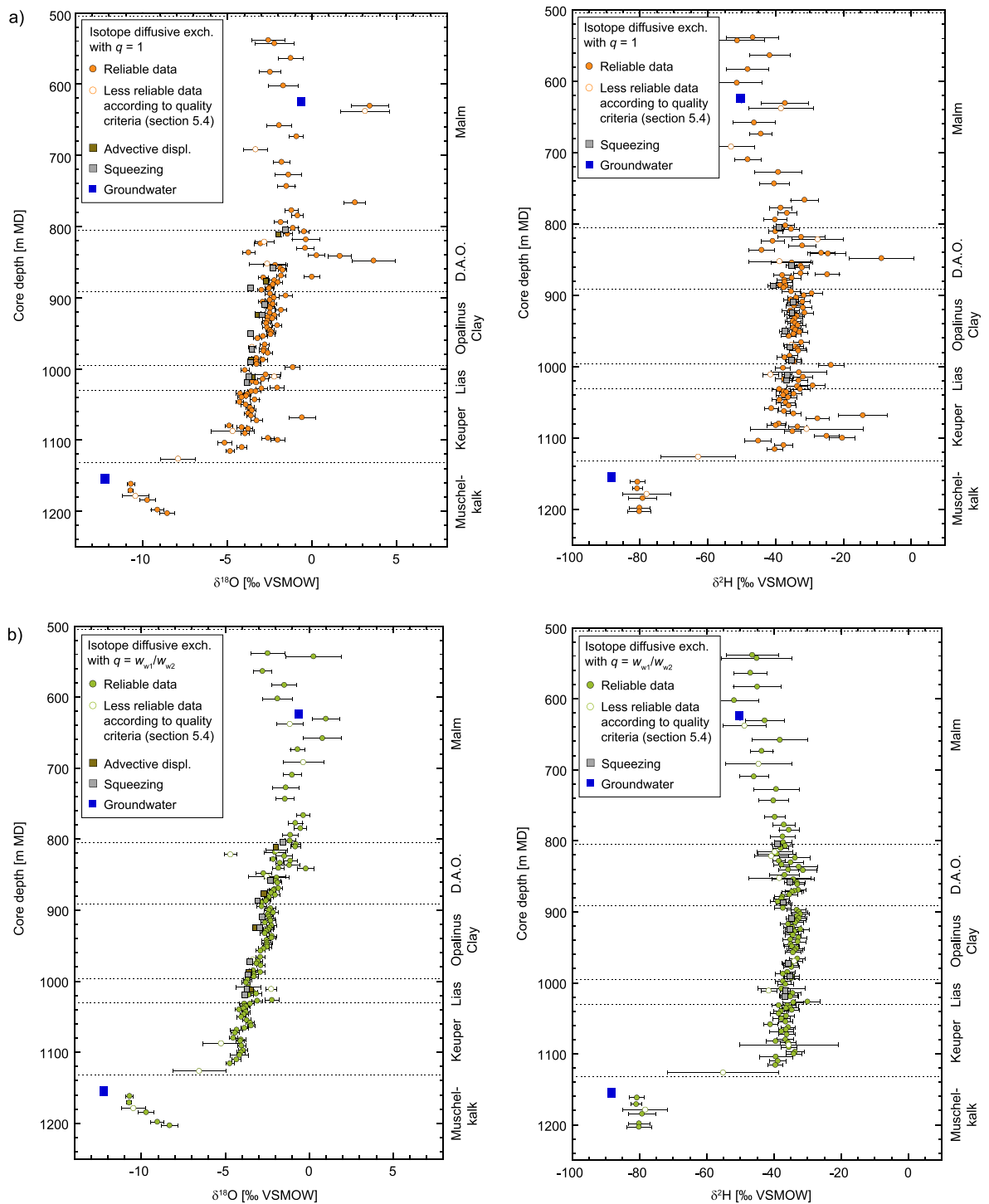
Fig. 4. Porewater δ¹⁸O (left) and δ²H (right) profiles for the Bülach 1-1 borehole calculated in two different ways. a) Values calculated according to eq. (2) assuming equal water contents of the subsamples used for the LAB and NGW experiments (old approach). The profiles show large scatter in rock sections where $q \neq 1$. b) Values calculated according to eq. (4) accounting for differences in the water content of the two subsamples by the ratio q. Open symbols refer to samples showing elevated uncertainties owing to experimental artefacts (classified as 'less reliable'; section 5.4). Porewater isotope data obtained from SQ and AD experiments (Kiczka et al., 2023) are shown for comparison. D.A.O. = Dogger above Opalinus Clay.
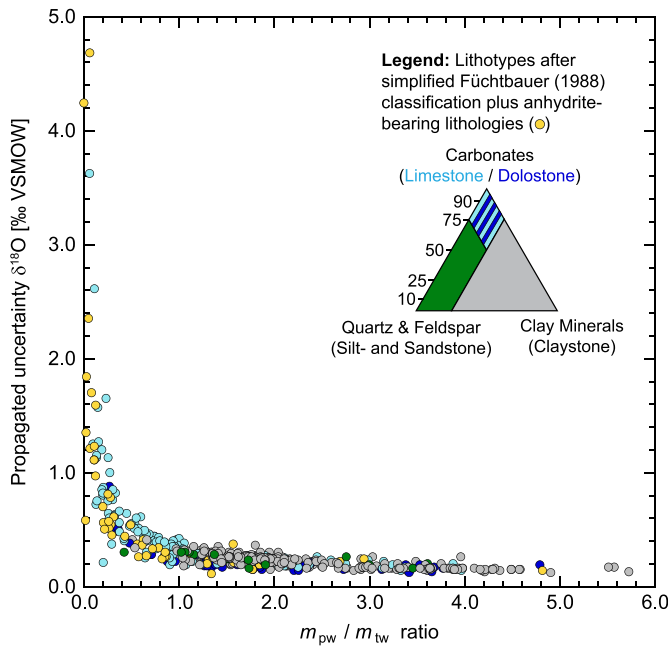
Fig. 5. Data from all 8 boreholes (n = 561) for samples with additional mineralogical data available (Mazurek et al., 2023). Propagated uncertainties of calculated porewater δ18O values using the $q = w_{w1}/w_{w2}$ approach. At the given ratios of mass porewater to volume of test water (m_{pw}/m_{tw}) in the experiments, the uncertainty increases exponentially at very low m_{pw}/m_{tw} ratios (Füchtbauer, 1988).

g., $\sigma_{m_{tw1}}/m_{tw1}$) that matters in the first error terms in eq. (8). Also, the last two terms remain finite even when ΔC_{tw1} or ΔC_{tw2} is approaching zero, that is, when the pore water signature is very similar to the test water signature.

Typical analytical errors used to derive $\sigma_{C_{pw}}$ are $\sigma_m = 0.002$ g, $\sigma_q = 5\cdot10^{-4}$, and $\sigma_{C_{tw}} = 0.1‰$ for δ18O and 1.0‰ for δ2H.[1] With these values and m_{wr} of 200–300 g, m_{tw} of 3–5 g, $q \approx 1$, and typical ranges of values for all other parameters, the last four terms in eq. (8), that is, those that depend on the analytical error $\sigma_{C_{tw}}$ of the isotope analysis, generally dominate the total error $\sigma_{C_{pw}}$ of the calculated pore water concentration. On average (median), the last four squared error terms in eq. (8) contribute about 10% (error of initial test water of LAB experiment), 0.5% (error of initial test water of NGW experiment), 85% (error of final test water of LAB experiment) and 4% (error of final test water of NGW experiment), to the total squared error $\sigma^2_{C_{pw}}$.

Overall, the propagated uncertainty exponentially increases at very low m_{pw}/m_{tw} ratios of <0.5 (Fig. 5). Thus, the ratio m_{pw}/m_{tw} is a sensitive parameter of IDE experiments. This has to be kept in mind particularly for low-porosity rocks such as limestones, anhydrite-rich rocks and partly dolostones.

5.3. Calculation of the water content by isotope mass balance

Theoretically, four values of w_w can be calculated from the two isotope ratios δ18O and δ2H and the two subsamples (LAB and NGW experiments; eq. (3)). However, only the water contents obtained for a single subsample with the two tracers are independent; the water contents of the two subsamples are related by the imposed condition $q = w_{w1}/w_{w2}$ during the evaluation of C_{pw}. The propagated error of the calculated water contents is:

$$\sigma_{w_w} = \left(\frac{w_w}{m_{tw}}\sigma_{m_{tw}}\right)^2 + \left(\frac{w_w}{m_{rw}}\sigma_{m_{rw}}\right)^2 + \left(\left[\frac{w_w}{C_{twf} - C_{twi}} + \frac{w_w}{C_{pw} - C_{twf}}\right]\sigma_{C_{twf}}\right)^2$$
$$+ \left(\frac{w_w}{C_{twf} - C_{twi}}\sigma_{C_{twi}}\right)^2 + \left(\frac{w_w}{C_{pw} - C_{twf}}\sigma_{C_{pw}}\right)^2$$

(11)

It can be seen that the uncertainty in the calculated water content decreases with increasing difference between final and initial isotope value in the test water as well as between the expected porewater isotope value and the final test water value as already shown by Rübel et al. (2002). Accordingly, back-calculated water contents obtained from the NGW experiments tend to have lower errors, and only these water contents are presented and compared to gravimetric water contents obtained by drying of the NGW rock samples (Fig. 6).

The scatter of the w_w back-calculated from the new isotope values ($q \neq 1$ method) with respect to the gravimetric water content of the NGW subsample is relatively small. It is smaller compared to that of w_w back calculated from the isotope values calculated assuming $q = 1$ (Fig. 6). Overall, these observations support the use of the new evaluation method. Note that the water content calculated from isotope mass balance is by average 11 ± 6% larger than the gravimetric water content (solid black regression line in Fig. 6). Pearson et al. (2003) and Mazurek et al. (2009, 2023) show that the gravimetric water content is generally well correlated with the clay-mineral content of the rocks. Thus, the observed systematic difference in the two water contents might be associated with minor exchange with water of different isotope composition adsorbed on clay mineral surfaces (i.e. bound water; Pearson et al., 2003; Gimmi and Waber, 2007) during IDE experiments. Isotope exchange with structural oxygen and hydrogen of clay-minerals as, e.g., observed for smectite at elevated temperatures (Kanik et al., 2022) is considered irrelevant at ambient temperatures and short time periods. Moreover, the difference in the two water contents is independent of the clay-mineral content (Fig. 7) and clay-mineral
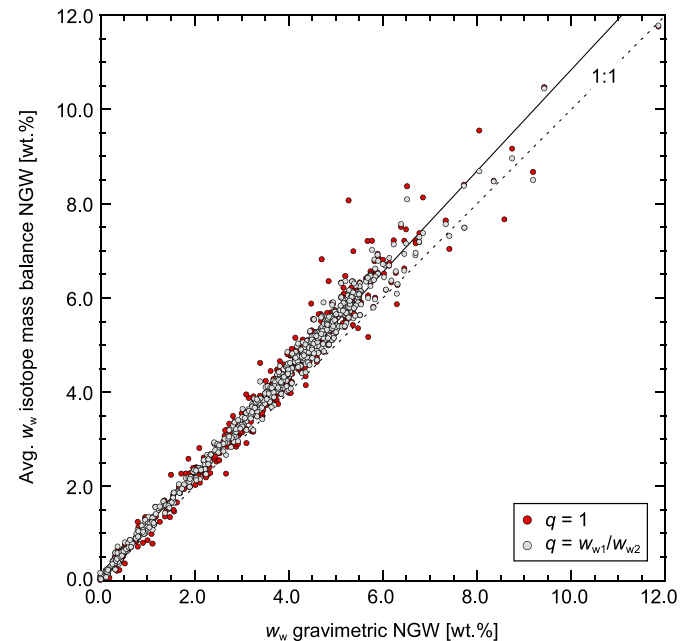

Fig. 6. Data from all 8 boreholes (n = 717) excluding failed experiments based on quality criteria in section 5.4. Water content obtained by water-loss at 105 °C of subsample NGW vs. average water content calculated from δ18O and δ2H mass balance from NGW diffusive exchange experiments, using either the old eq. (2) with $q = 1$ or the new eq. (4) with $q = w_{w1}/w_{w2}$ for calculating the porewater isotope concentration. The linear regression (solid black line) for the $q = w_{w1}/w_{w2}$ method has a slope of 1.11 (see text for details).

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[1] Values of 18O and 2H in δ notation represent nearly linearly scaled and normalized concentrations. Accordingly, they can be treated like concentrations in these calculations or in transport simulations (e.g., Gimmi et al., 2007).
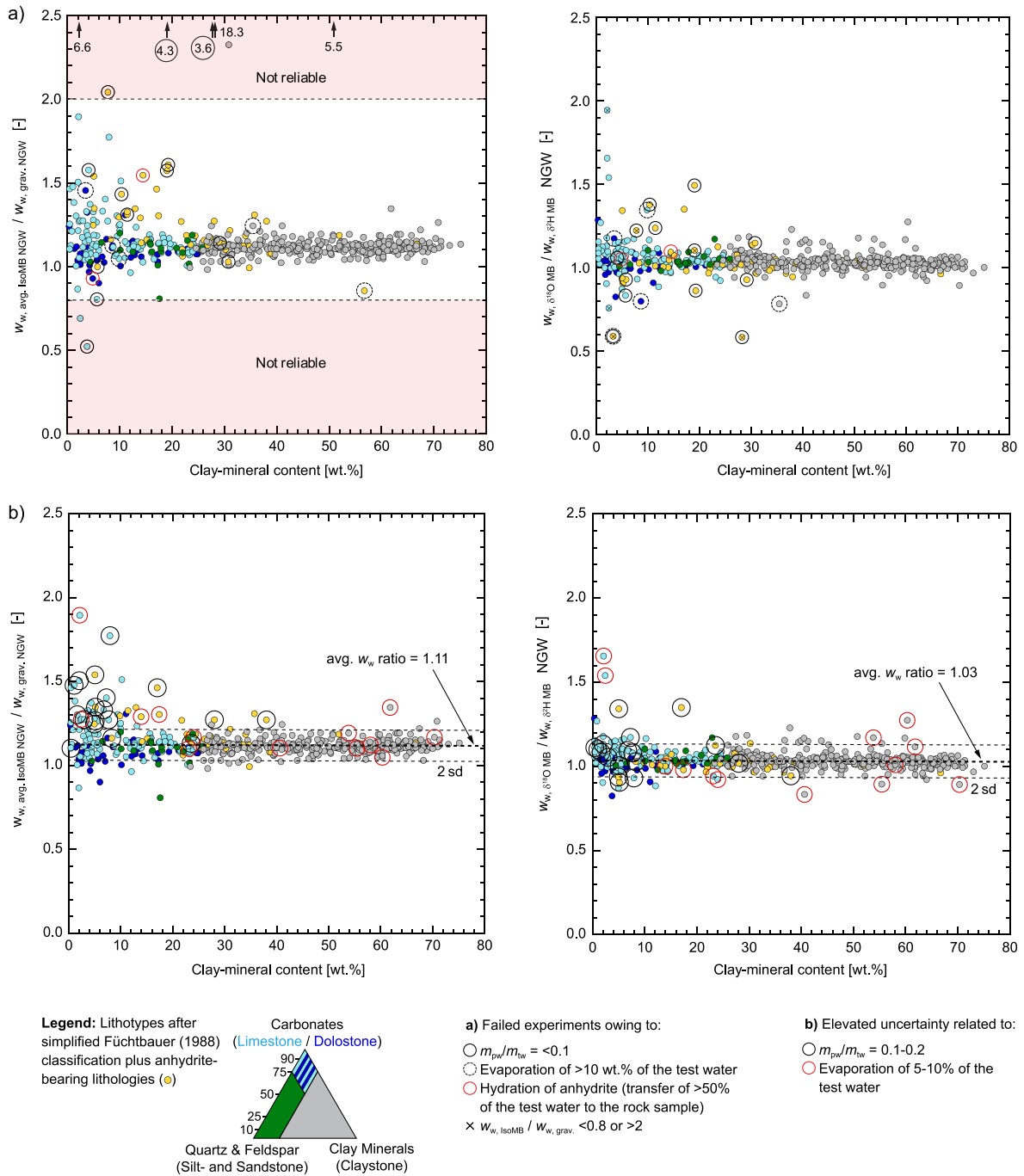
Fig. 7. Different water content ratios as function of the clay mineral content. Left: ratio of the average water content obtained by isotope mass balance and the gravimetric water content of the NGW subsample. Right: ratio of the water contents obtained by $\delta^{18}O$ and δ^2H mass balance from the NGW experiment. Data from all 8 boreholes (n = 561) for samples with additional mineralogical data available (Mazurek et al., 2023). The top figures a) show all data. The samples marked with a circle were afflicted by experimental artefacts and they constitute clear outliers in the porewater isotope profiles. These experiments were classified as failed and corresponding isotope data is not considered reliable. In the bottom figures b) failed experiments are excluded. Samples marked with a circle are also afflicted by experimental artefacts but to a lower degree and they do not constitute outliers in the porewater isotope profiles. The calculated porewater isotope compositions are kept by accepting the somewhat larger uncertainties and they are classified as less reliable (see text). sd denotes standard deviation (Füchtbauer, 1988).

composition (Mazurek et al., 2023), thus, rendering these hypotheses unlikely. A third option is restricted to very high porewater salinities at which the difference in the two water contents could be associated with minor exchange with water of different isotope composition bound in hydration shells of solutes in the porewater (de Haller et al., 2014). For the low to moderate salinity porewaters investigated here, ultimately, no stringent explanation exists at this stage.

5.4. Robustness of calculated porewater isotope compositions and quality control criteria

In principle, for a successful IDE experiment the water contents calculated from $\delta^{18}O$ and δ^2H mass balance should both agree within the propagated uncertainty. Similarly, the water contents obtained from isotope mass balance and by gravimetry should be identical (within the propagated uncertainty). However, as shown in Fig. 6 the former is

systematically larger than the latter. Because of the systematic difference, the observed relation between the two water contents can nevertheless be used as an argument for identifying samples that are affected by experimental artefacts. From additionally considering that the water content is generally well correlated with the clay-mineral content of the rocks (Pearson et al., 2003; Mazurek et al., 2009, 2023), the relationship between the water content ratios and the clay-mineral content is viewed as a key proxy for assessing the robustness of the experimental and the analytical data and, ultimately, of the calculated porewater isotope composition. This is illustrated in Fig. 7a, which shows the ratios of the different water contents as a function of clay-mineral content for all the investigated samples. Generally, the scatter of the data increases with decreasing clay-mineral content with some samples showing ratios of the two water contents clearly deviating from one. These samples were at the same time clearly identified as distinct outliers in the depth profiles of porewater isotope compositions. The IDE experiments of these samples were all afflicted by, e.g., very low porewater to test water ratios, evaporation effects, mass transfer between rock and test water or potentially incomplete equilibration. The corresponding experiments were classified as failed and the calculated isotope compositions for such samples are unreliable. Even after discarding such experiments, the ratios of the differently derived water contents still show some scatter, especially at low clay-mineral contents (Fig. 7b). Most of these samples were also afflicted by experimental artefacts, but to a distinctly lower degree. Most importantly, they cannot be identified as distinct outliers in the depth profiles of porewater isotope compositions, i.e., they agree well (within the propagated uncertainty) with the porewater isotope compositions obtained from unaffected neighbouring samples. Such experimental data are retained by accepting the somewhat larger uncertainties and by classifying the calculated porewater isotope compositions as less reliable.

The specific criteria for classifying experimental and calculated data as reliable, less reliable or unreliable (failed experiments) are summarized as follows.

- Evaporation during the experiment (i.e., leaking of the experiment containers): Although Rayleigh-distillation calculations were applied to correct for evaporation effects, it appears that losses of more than 10% of the initial mass of the test water render the calculated porewater isotope values unreliable. Corresponding experiments were thus considered as failed. For losses of 5–10% of the initial mass of the test water, the data were kept providing that the experiments do not show any further unconformities. The calculated porewater isotope values from such experiments were classified as less reliable.
- Reasonable mass ratio of porewater to test water: Porewater to test water ratios as low as 0.1–0.2 were accepted, but the calculated isotope composition of the porewater was then classified as less reliable. Ratios of <0.1 lead to unreliable results and were rejected.
- Mass transfer between rock and test water. Two different cases have to be discerned:
  1) Mass transfer of test water to rock: This can either be caused by a higher salinity of the porewater compared to that of the test water or hydrating mineral phases such as, e.g., anhydrite. In anhydrite-free lithologies some rare cases of transfer of test water to the rock of up to 54% of the initial mass of test water were observed, however, without any major effect on the calculated porewater isotope composition (i.e. based on good agreement with the calculated porewater isotope composition of neighbouring samples that are unaffected by any mass transfer). Anhydrite-bearing lithologies are exceptional as the hydration of anhydrite and associated isotope fractionation bias the calculated porewater isotope composition. The extent and effect of this fractionation in IDE is currently unknown. If the transfer of test water to anhydrite-bearing rock was larger than 50% of the initial mass of test water, the calculated isotope composition of the porewater was clearly unreliable and the results were rejected.

  2) Mass transfer of porewater to test water caused by a higher salinity of the test water compared to that of the porewater: In general, the calculated porewater isotope data and water contents derived from samples affected by such mass transfers agree well with those of unaffected neighbouring samples (i.e. within the propagated uncertainty). Transfers of porewater to the test water of up to 7.4% of the initial mass of the porewater were observed without any major effect on the calculated porewater isotope composition.

Overall, it appears that – apart from anhydrite-bearing lithologies – IDE experiments are not very sensitive to mass transfers between rock and test water.

- Ratio of the average water content from isotope mass balance to the gravimetric water content of the NGW subsample: For samples not affected by any artefacts described above, any disagreement between water contents derived from isotope mass balance and gravimetry is not yet fully understood. The differences may reflect incomplete equilibration (for ratios <1), differences in salinity between test water and porewater, or evaporation during sample preparation. Generally, samples with ratios smaller than 0.8 or larger than 2 clearly constitute outliers in the isotope profiles and, thus, such data were rejected.
- Stable isotope analyses of test water solutions within the required precision and accuracy.

Neglecting the data that are classified as less reliable according to the quality criteria above, the average ratio of water contents derived from δ^{18}O and δ^{2}H mass balance is 1.03 ± 0.10 (2 sd), whereas the ratio of the average water contents derived by isotope mass balance and the gravimetric water contents is slightly larger (1.11 ± 0.09). As shown in Fig. 7b the two-sigma deviation of the different water content ratios includes some data classified as less reliable, but it excludes some data classified as reliable. Thus, the two-sigma deviation of the water content ratios of about ±0.10 cannot be viewed as a strict quality criterion for the experiments, but it can be used as a first-order assessment of the robustness of the experimental data.

6. Interlaboratory comparison

For reasons of quality assurance, porewater isotope profiles of the boreholes Trüllikon 1-1, Marthalen 1-1, Bözberg 2-1 and Stadel 2-1 (for details see Mazurek et al., 2023) acquired in this study were complemented with IDE experiments and isotope analyses performed at Hydroisotop GmbH following the same experimental and analytical protocols. This allows an independent testing of the reproducibility of the IDE technique. In general, these complementing samples are located ≤5 m vertically from the samples investigated at the University of Bern. Given the diffusivity of the low-permeability rocks (van Loon et al., 2023) and the magnitude of local gradients in the porewater isotope composition (Gimmi et al., 2023), minor differences between the two sample sets can be expected. However, the narrow spacing of <5 m is considered reasonably close for assessing the reproducibility of the IDE method, certainly in the rather homogenous Opalinus Clay.

The obtained porewater isotope compositions of the interlaboratory comparison of IDE experiments performed at the two laboratories is shown in Fig. 8. For some samples somewhat larger differences in the porewater isotope composition derived by the two laboratories are observed, especially for δ^{18}O. Most of these samples originate from clay-poor rocks and/or depth intervals with comparatively larger local gradients in the porewater isotope composition (Gimmi et al., 2023). In general, the porewater isotope values obtained from IDE experiments performed at Hydroisotop GmbH integrate well into the porewater isotope profiles derived from the samples investigated by the University of Bern (e.g. Gimmi et al., 2022). Thus, overall, a very good
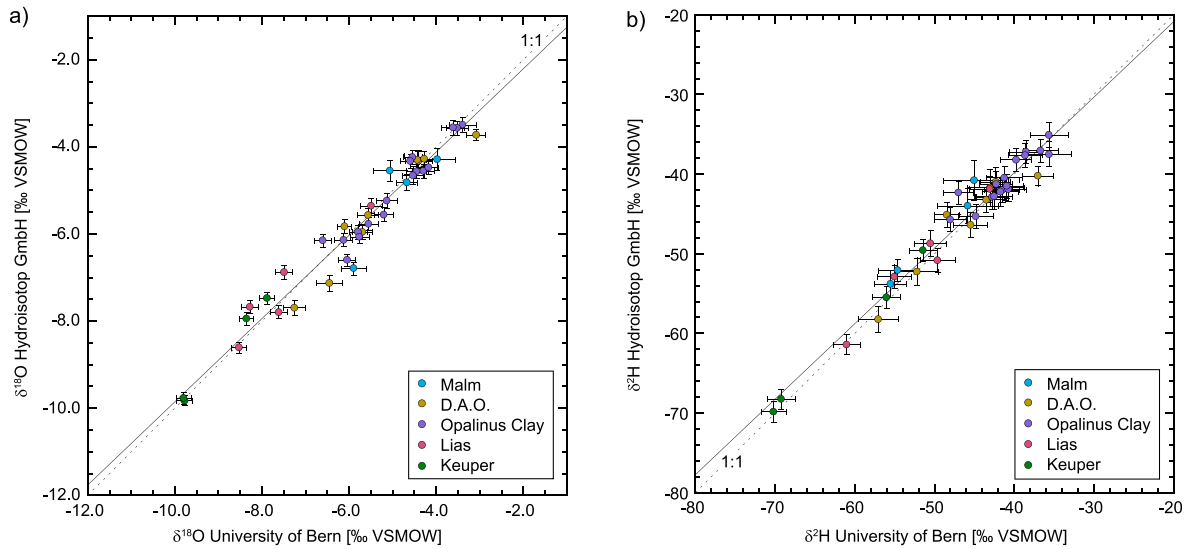
Fig. 8. Interlaboratory comparison of porewater $\delta^{18}O$ (a) and δ^2H (b) values obtained by IDE experiments performed by the University of Bern and Hydroisotop GmbH following the same protocol. Experiments were performed on adjacent samples, located maximum 5 m apart from each other. The solid black line represents the linear regression, whereas the stippled black line represents a 1:1 correlation. D.A.O. = Dogger above the Opalinus Clay.

reproducibility is observed for the IDE experiments performed in the context of Nagra's deep drilling campaign.

7. Comparison with groundwater data

An ultimate test of the accuracy of porewater isotope data obtained by IDE experiments of drillcore samples is the comparison of such data to groundwater collected from the same depth intervals. Given the long residence time of deep groundwater in aquifers confining the low-permeability Dogger – Lias sequence in northern Switzerland (typically >10 ka; Waber and Traber, 2022), identical isotope compositions can be expected for porewater and groundwater in the water-conducting zones.

The isotope compositions of groundwater sampled from the aquifers in the Malm, Hauptrogenstein, Keuper and Muschelkalk cover a large range from −0.6 to −12.4‰ VSMOW in $\delta^{18}O$ and −45 to −89‰ VSMOW in δ^2H (Fig. 9). Porewater isotope compositions derived from IDE

experiments and compared to the groundwater data reflect the composition of 1–5 drillcore samples (average values for multiple samples) that are located within or maximum 7 m away from the major groundwater inflow zones. Porewater isotope compositions from IDE experiments agree within the propagated uncertainty with the Malm, the Dogger above the Opalinus Clay and most of the Keuper groundwater (Fig. 9). For groundwater isotope compositions more negative than about −8‰ VSMOW for $\delta^{18}O$ and −70‰VSMOW for δ^2H, which concerns groundwater in the Keuper and Muschelkalk aquifers, the corresponding porewater isotope compositions tend to be slightly enriched in ^{18}O and ^2H (Fig. 9). In absolute terms the differences are up to 0.5‰ VSMOW in $\delta^{18}O$ and 2.1‰ VSMOW in δ^2H for the Keuper aquifer, whereas slightly larger differences of up to 0.6‰ VSMOW in $\delta^{18}O$ and 2.7‰ VSMOW in δ^2H are observed for the Muschelkalk (based on the regression line in Fig. 9).

No stringent explanation exists at this stage for the observed differences between the isotope composition of the groundwaters and those of
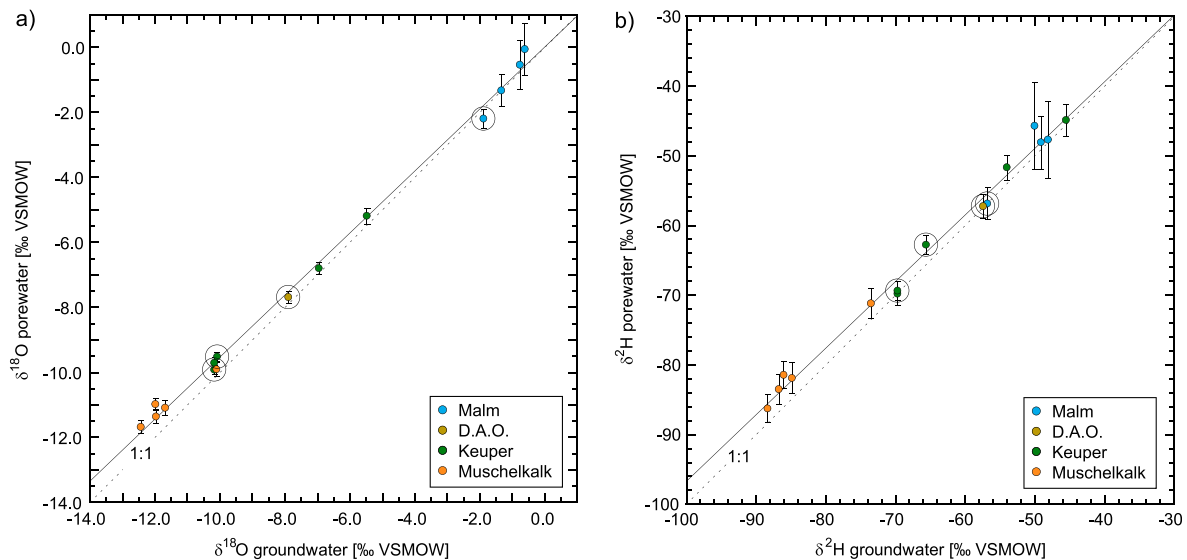

Fig. 9. Data from all boreholes. Comparison of porewater and groundwater $\delta^{18}O$ (a) and δ^2H values (b). Porewater isotope data are obtained from IDE experiments performed on drillcore samples that are located within or maximum 7 m away from the major groundwater inflow zones. D.A.O. = Dogger above Opalinus Clay. Black circles indicate samples for which IDE experiments were performed by Hydroisotop GmbH.

the porewater obtained by IDE experiments, however, the following considerations provide some constraints. Evaporation during the IDE experiments can be excluded as the calculated deuterium-excess (defined as $\delta^2H - 8 \times \delta^{18}O$) of the groundwater and the corresponding porewater agree within the uncertainty. The clay-mineral contents of the porewater samples are <5 wt% for the Malm, 25–54 wt% for the Keuper, and 2–23 wt% for the Muschelkalk (Mazurek et al., 2023). Porewater Cl concentrations are 4–8 g/L for the Malm samples and highly variable for the Keuper and the Muschelkalk samples (<1–9 g/L; Wersin et al., 2023). The observed differences between the isotope composition of the porewater and the groundwater do not correlate with the clay-mineral content of the investigated samples and neither with the porewater salinity. This excludes isotope exchange with bound water on clay-mineral surfaces or salinity effects as explanations for the observed differences.

The regression lines in Fig. 9 indicate that the difference in isotope composition between porewater and groundwater increases as the isotope composition of the porewater approximates that of the test water used in the LAB experiment ($\delta^{18}O$ and δ^2H values ranging from −12.20 to −10.31‰ VSMOW and −87.7 to −80.0‰ VSMOW, respectively; section 3.2). Thus, for the Muschelkalk samples used for the IDE experiments, ΔC_{tw1} values as low as 0.2‰ VSMOW were observed, although they generally show water contents larger than 1 wt%. The propagated errors of the calculated porewater isotope composition remain finite even for small ΔC_{tw1} (section 5.2), and they are smaller than the observed differences in Fig. 9. The small ΔC_{tw1} might nevertheless have an effect on the IDE experiments and the calculated porewater isotope composition; however, the underlying processes are not understood at this stage. It may thus be reasonable to adjust the isotope composition of the test waters with respect to that expected for the porewater to avoid too small values for ΔC_{tw1}.

As shown and discussed in section 5.3, water contents back-calculated from isotope mass balance are systematically larger (around 11%) compared to those obtained from gravimetry. The reason is not known and a contribution to the differences observed between the isotope compositions of porewater and groundwater cannot be excluded.

8. Conclusions

Investigating a large number of IDE experiments (752) and the vertical distribution of the obtained porewater isotope compositions, allowed a quantitative assessment of important parameters and artefacts, to which IDE experiments are sensitive and prone, respectively. Ultimately, this allowed defining a stringent procedure for the evaluation of the experimental data and classifying experiments as 'reliable', less reliable' and 'failed'. For calculating the porewater isotope composition, a new approach was developed: Originally, equality of the water contents of the two subsamples used in IDE experiments was assumed for calculating the porewater isotope composition. However, in lithologically heterogeneous rocks with heterogeneous porosity distribution, this assumption is not necessarily valid, which may lead to a bias in the calculated isotope concentrations, with the bias not appearing in the propagated uncertainties. Therefore, an alternative approach was presented that explicitly considers the ratio q, defined as the ratio of the gravimetric water contents of the two different subsamples used in the experiments. This new approach eliminates the bias introduced by sample-scale heterogeneity of the water content (i.e. porosity). This procedure of data evaluation and processing resulted in smooth isotope profiles with only little scatter across largely different lithologies. This highlights the applicability of the IDE method to all kind of different lithologies, i.e., not only in argillaceous rocks for which it has mainly been applied to date. This is further supported by the very good reproducibility of the method indicated by an interlaboratory comparison. Limitations refer to: 1) Anhydrite-bearing lithologies where isotope fractionation resulting from mineral hydration introduces a bias and 2)

very low-porosity limestones with water contents of <1 wt%, for which the amount of rock sample and test water must carefully be adjusted.

A systematic difference of ~11% is observed between the water contents calculated from isotope mass balance and those obtained by gravimetry. Furthermore, porewater isotope signatures derived from IDE experiments are identical or slightly enriched in ^{18}O and ^2H compared to isotope data of corresponding groundwater, where isotopic equilibrium is expected based on groundwater residence times. Ultimately, no stringent explanation for these differences exists at this stage, however, the following considerations provide some constraints: 1) In IDE experiments, the rock sample and its porewater are not subjected to changes in pressure and temperature and the analyte solution is not in direct contact with the rock sample, therefore excluding unwanted reactions with solid phases. 2) Based on the lack of correlation between the clay-mineral content and the above described differences in isotope composition between pore- and groundwater and between water contents obtained by gravimetry and isotope mass balance, it appears unlikely that substantial exchange with isotopically different water bound on clay minerals (diffusive double layer, interlayer) occurred during the IDE experiments. 3) Similarly, based on the good agreement of deuterium-excess between pore- and groundwater, evaporation during IDE experiments or sample preparation cannot explain these differences. 4) The observed differences do not correlate with the porewater salinity, therefore excluding substantial exchange with isotopically different water in the hydration shell of solutes during IDE experiments (as shown for highly saline solutions). 5) For some samples the difference between the isotope composition of the porewater and that of the test water used for the LAB experiments was small, resulting in only small isotope shifts between original and equilibrated test water (>0.2‰ VSMOW). Such samples show comparatively larger differences between the isotope composition of the pore- and the groundwater. 6) A few samples show ratios of the average water content from isotope mass balance to the gravimetric water content of the NGW subsample of smaller than 1. Such samples are potentially affected by incomplete equilibration during the IDE experiments.

Overall, it is important to emphasise that on the scale relevant for investigating large-scale transport processes in the subsurface (e.g. aquifer-aquitard-aquifer interactions), the resolution and accuracy of the IDE technique is good, i.e., the natural variations observed in isotope tracer profiles is typically much larger than the minor differences between porewater in water-conducting zones and the corresponding groundwaters. This demonstrates that porewater isotope data obtained by the IDE method represent the conditions in the in situ porewater reasonably well for a wide range of different lithologies when strictly following the proposed procedures regarding setup of the experiment, evaluation of the experimental data, calculation of porewater isotope compositions and assessment of their quality.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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