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Precise and accurate isotope fractionation factors ($\alpha^{17}O$, $\alpha^{18}O$ and αD) for water and $CaSO_4{\cdot}2H_2O$ (gypsum)

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Abstract

Gypsum ($CaSO_4{\cdot}2H_2O$) is a hydrated mineral containing crystallization water, also known as gypsum hydration water (GHW). We determined isotope fractionation factors ($\alpha^{17}O$, $\alpha^{18}O$ and αD) between GHW and free water of the mother solution in the temperature range from 3 °C to 55 °C at different salinities and precipitation rates. The hydrogen isotope fractionation factor ($\alpha D_{gypsum\text{-}water}$) increases by 0.0001 units per °C between 3 °C and 55 °C and salinities <150 g/L of NaCl. The $\alpha D_{gypsum\text{-}water}$ is 0.9812 ± 0.0007 at 20 °C, which is in good agreement with previous estimates of 0.981 ± 0.001 at the same temperature. The $\alpha^{18}O_{gypsum\text{-}water}$ slightly decreases with temperature by 0.00001 per °C, which is not significant over much of the temperature range considered for paleoclimate applications. Between 3 °C and 55 °C, $\alpha^{18}O_{gypsum\text{-}water}$ averages 1.0035 $\pm$ 0.0002. This value is more precise than that reported previously (e.g. 1.0041 ± 0.0004 at 25 °C) and lower than the commonly accepted value of 1.004. We found that NaCl concentrations below 150 g/L do not significantly affect $\alpha^{18}O_{gypsum\text{-}water}$, but $\alpha D_{gypsum\text{-}water}$ increases linearly with NaCl concentrations even at relatively low salinities, suggesting a salt correction is necessary for gypsum formed from brines. Unlike oxygen isotopes, the $\alpha D_{gypsum\text{-}water}$ is affected by kinetic effects that increase with gypsum precipitation rate. As expected, the relationship of the fractionation factors for ^{17}O and ^{18}O follows the theoretical mass-dependent fractionation on Earth ($\theta = 0.529 \pm 0.001$). We provide specific examples of the importance of using the revised fractionation factors when calculating the isotopic composition of the fluids.

Keywords: Gypsum hydration water; Fractionation factor; Triple oxygen isotopes; Stable isotopes

1. INTRODUCTION

Gyspum ($CaSO_4{\cdot}2H_2O$) is a common hydrated mineral on Earth and has been recently found to be abundant on Mars (Showstack, 2011; Massé et al., 2012). The oxygen (^{16}O, ^{17}O, ^{18}O) and hydrogen (^{1}H, ^{2}H) isotopes of gypsum hydration water (GHW) provide a rich source of information about the environmental conditions under which gypsum formed (Matsuyaba and Sakai, 1973; Sofer, 1978; Fontes et al., 1979; Halas and Krouse, 1982; Bath et al., 1987; Khademi et al., 1997; Kasprzyk and Jasinska, 1998; Farpoor et al., 2004; Buck and Van Hoesen, 2005; Hodell et al., 2012; Gázquez et al., 2013; Evans et al., 2015; Grauel et al., 2016; Chen et al., 2016, amongst others).

Under certain conditions, the isotopic composition of GHW retains the value of the parent solution and is not altered by post-depositional processes. For example, recent studies of lacustrine gypsum (ca. 43–10 ka; Hodell et al., 2012; Grauel et al., 2016) and Messinian marine gypsum (ca. 5.9 Ma; Evans et al., 2015) suggest that the isotopic values of GHW differ considerably from those expected for isotopic exchange with recent environmental water (e.g. pore waters and groundwater, respectively). In the case of Messinian gypsum, the $\delta^{18}O$ and δD of GHW is highly

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correlated with other indicators of evaporation (e.g. salinity of fluid inclusions) indicating it has retained its original isotopic composition.

Calculating the isotopic composition of the mother fluid requires an accurate knowledge of the fractionation factors for both oxygen and hydrogen isotopes. The isotopic fractionation factor (α) between the mother water and GHW is defined as:

$$\alpha_{\text{gypsum-water}} = \frac{\delta_{\text{gypsum}} + 1000}{\delta_{\text{water}} + 1000}$$

where δ_{gypsum} and δ_{water} denote the isotopic ratio (i.e. $^{17}O/^{16}O$, $^{18}O/^{16}O$ and $^{2}H/^{1}H$) of the hydration water and mother water, respectively, relative to V-SMOW (*Vienna-Standard Mean Ocean Water*).

Early experiments conducted by Baertschi (1953) suggested an $\alpha^{18}O_{\text{gypsum-water}}$ of 1.0035. Subsequently, Gonfiantini and Fontes (1963) and Fontes and Gonfiantini (1967) measured an $\alpha^{18}O_{\text{gypsum-water}}$ value of 1.0037 ± 0.0005 and an $\alpha D_{\text{gypsum-water}}$ value of 0.985 in the temperature range between 17 and 57 °C. Matsuyaba (1971) determined an $\alpha^{18}O_{\text{gypsum-water}}$ of 1.0041 and an $\alpha D_{\text{gypsum-water}}$ value of 0.980 that are in agreement with those reported later by Sofer (1975); 1.0040 and 0.980, respectively. Based on these works, the accepted fractionation factors used in most studies of GHW was rounded to 1.004 and 0.98 for $\alpha^{18}O_{\text{gypsum-water}}$ and $\alpha D_{\text{gypsum-water}}$, respectively. More recently, Hodell et al. (2012) reported a value of 1.0039 ± 0.0004 for $\alpha^{18}O_{\text{gypsum-water}}$ and 0.981 $\pm$ 0.002 for $\alpha D_{\text{gypsum-water}}$ in the temperature range from 12 °C to 37 °C, which did not differ significantly from the accepted values.

The opposite signs of the fractionation factors for oxygen and hydrogen isotopes in GHW have been ascribed to isotopic fractionation between the free solution and the hydration sphere of the dissolved ions. The enrichment by ca. 4‰ in GHW with respect to the mother solution can be explained by the effect of the hydration sphere of Ca^{2+} that is presumably enriched in ^{18}O compared with the free solution (Taube, 1954; Gonfiantini and Fontes, 1963; Oi et al., 2013). In contrast, depletion in ^{2}H by ca. 20‰ may be ascribed to the fact that the hydration sphere of SO_4^{2-} in solution is depleted in ^{2}H with respect to the free water (Oi and Morimoto, 2013).

Previous studies suggest that $\alpha^{18}O_{\text{gypsum-water}}$ is not sensitive to temperature in the range from 12 to 57 °C within analytical uncertainties (Gonfiantini and Fontes, 1963; Hodell et al., 2012; Tan et al., 2014). However, Hodell et al. (2012) found a slight positive temperature dependence (0.00012 per °C) for $\alpha D_{\text{gypsum-water}}$ between 12 °C and 37 °C. The effect of temperature on the isotopic fractionation in the gypsum-water system remains poorly known. In fact, most investigations of hydrothermal gypsum have used the accepted $\alpha^{18}O_{\text{gypsum-water}}$ and $\alpha D_{\text{gypsum-water}}$ of 1.004 and 0.98 (e.g. Matsuyaba and Sakai, 1973), even though these values may differ at the higher temperatures of hydrothermal gypsum precipitation (e.g. 55 °C; Garofalo et al., 2010; Gázquez et al., 2012, 2013, 2016).

Previous estimation of fractionation factors ($\alpha^{18}O_{\text{gypsum-water}}$ and $\alpha D_{\text{gypsum-water}}$) were conducted using several methods of gypsum precipitation (i.e. Gonfiantini and Fontes, 1963), including the hydration of anhydrous $CaSO_4$, evaporation of solutions saturated in $CaSO_4$, and mixing of $CaCl_2$ and Na_2SO_4 solutions. In most cases, results utilizing different methods of gypsum formation have been treated as equivalent (Gonfiantini and Fontes, 1963; Fontes and Gonfiantini, 1967; Tan et al., 2014). Although the fractionation factors from different studies generally agree (Gonfiantini and Fontes, 1963; Fontes and Gonfiantini, 1967; Sofer, 1978; Hodell et al., 2012), the uncertainty remains unsatisfactory for certain geological and paleoclimate applications (see Section 4).

Here we re-evaluate the fractionation factors in the temperature range from 3 °C to 55 °C using two different methods of gypsum formation (hydration of anhydrous $CaSO_4$ and mixing of $CaCl_2$ and Na_2SO_4 solutions) and varying precipitation rates. We discuss the importance of equilibrium and kinetic isotopic fractionation in our experiments and the application to natural gypsum deposits. We also studied the effect of salinity on the fractionation factors with potential implications for gypsum formation from brines. In addition, $\alpha^{17}O_{\text{gypsum-water}}$ has been empirically determined for the first time. This parameter is essential for determining the ^{17}O-excess in paleo-waters from $\delta^{17}O$ and $\delta^{18}O$ measurements of GHW. Lastly, we apply the revised fractionation factors to precisely determine the isotopic composition of the original fluids that are derived from a set of natural gypsum deposits, including gypsum in lakes (Lake Peten Itza; Hodell et al., 2012; Grauel et al., 2016), hydrothermal selenite crystals (Caves of the Naica mine, Chihuahua, Mexico; Garofalo et al., 2010; Gázquez et al., 2012, 2013, 2016) and gypsum precipitated from evaporated seawater (Salinas of Cabo de Gata, Almeria, SE, Spain; Evans et al., 2015).

2. METHODS

Calculating fractionation factors for gypsum involves measuring the relative difference in the isotopic composition of the hydration water and the free water of the mother solution. The measurements can be made very precisely and accurately if both mother and hydration water are measured consecutively by Cavity Ringdown Laser Spectroscopy (CRDS) (Hodell et al., 2012; Steig et al., 2014). Gypsum was precipitated via (i) the hydration of anhydrous $CaSO_4$ and (ii) the mixing of $CaCl_2$ and Na_2SO_4 solutions. Gypsum precipitation experiments were conducted at a range of temperatures and salinities. The effect of precipitation rate on isotope fractionation factors was evaluated by changing the initial concentration of $CaCl_2$ and Na_2SO_4.

2.1. Hydration of anhydrous $CaSO_4$

Following the method of Conley and Bundy (1958), 1.5 g of analytical grade powdered anhydrite (Acros, UK) was hydrated by adding 100 ml of 0.5 M Na_2SO_4 solution. Sodium sulfate acts a catalyst during the hydration reaction of anhydrite. Acceleration of the reaction takes place through the medium of transient surface complexes that are unstable in dilute solution and finally evolve to gypsum (Conley and Bundy, 1958). Importantly, the hydration sphere of Na^+ does not isotopically affect the activity of water in dilute solutions; thus, the addition of Na_2SO_4 does not interfere with isotopic fractionation during gypsum precipitation (Taube, 1954; Gonfiantini and Fontes, 1963). The conversion of anhydrite to gypsum occurs in two steps:

$$CaSO_4(s) + 2H_2O \leftrightarrow CaSO_4 \cdot \frac{1}{2}H_2O + 1.5H_2O$$
$$\leftrightarrow CaSO_4 \cdot 2H_2O(s)$$

where $CaSO_4 \cdot \frac{1}{2}H_2O$ is an intermediate hemihydrate of calcium sulfate (i.e. bassanite) (Wang et al., 2012; Van Driessche et al., 2012).

Prior to the experiment, anhydrite was heated to 400 °C for 3 h to completely remove all hydration and adsorbed water. Subsequent analysis by ATR-FTIR (Attenuated Total Reflectance, Bruker Platinum accessory, coupled to a Fourier Transformation Infrared Spectrometer instrument, Bruker, Tensor II; Department of Earth Sciences, University of Cambridge, UK) detected only anhydrite, with no traces of gypsum or bassanite. The XRD analysis (Appendix 4) of the same material showed insignificant amounts of basanite (0.5%) and gypsum (0.4%).

Experiments were performed in duplicate or triplicate in a conical flask with a greased ground glass stopper and joint to prevent evaporation. Before mixing, the anhydrite and the Na_2SO_4 solutions were temperature equilibrated in an oven at 20 °C, 25 °C, 30 °C, 35 °C and 40 °C for at least 2 h. Anhydrite was added to the solution and then constantly stirred at 700 rpm for 24 h using a wireless magnetic stirrer. After mixing, the flasks containing the solution and the anhydrite were placed again in the oven and temperature was maintained to a precision of ±0.1 °C (1SD).

Experiments at the lower temperatures of 8 °C and 3 °C were conducted in a refrigerator and cold room, respectively, in which temperatures were monitored for the duration of the experiments and varied by less than 0.5 °C. At temperatures greater than 45 °C, the conversion of anhydrite to gypsum was incomplete (e.g. 42 wt% of gypsum at 45 °C or 0 wt% at 60 °C) because of the greater stability of anhydrite relative to gypsum at temperatures above 42 °C (Ostroff, 1964). Thus, we only consider the experiments in which the hydration of anhydrous $CaSO_4$ resulted in over 98 wt% conversion to gypsum (i.e. experiments performed at temperature below 40 °C).

A water sample (200 μL) from each experiment was stored for subsequent isotopic analysis. We found that during temperature equilibration in the experiments at 3 °C, Na_2SO_4 precipitation occurred because of a rapid decrease in solubility at temperatures below 10 °C. For this reason, experiments at 3 °C used a 0.05 M Na_2SO_4 solution.

After 24 h, the solutions were vacuum filtered using Millipore nitrocellulose filters (0.45 μm Φ pore). Samples were then dried at 45 °C for 48 h. Thermogravimetric analysis (Netzsch STA 449 F1 Jupiter) showed that this drying method removed all adsorbed water, but did not result in the loss of hydration water. The mineralogy of the dry precipitates was analyzed by X-ray diffraction.

2.2. Mixing $CaCl_2$ and Na_2SO_4 solutions

Gypsum saturation was achieved by mixing solutions of $CaCl_2{\cdot}6H_2O$ and Na_2SO_4 of varying concentrations to control the rate of precipitation. Experiments with three different initial Ca^{2+} and SO_4^{-2} concentrations (0.5 M, 0.33 M and 0.125 M) were conducted by diluting mother solutions of 0.5 M $CaCl_2{\cdot}6H_2O$ (analytical grade, Sigma–Aldrich) and 0.5 M Na_2SO_4 (analytical grade, Fisher Scientific).

Experiments were conducted at 5 °C, 20 °C, 25 °C, 45 °C and 55 °C using a water bath (±0.1 °C) and solutions were temperature equilibrated for 2 h prior to mixing. A sample of each solution was collected after mixing. In order to promote slower gypsum precipitation, no stirring or shaking of these gypsum precipitation experiments occurred (referred to as *free-drift* experiments hereafter). Experiments at 25 and 55 °C were repeated by setting the shaking mode of the bath at 110 cycles per minute to promote solution homogenization and fast gypsum precipitation (referred to as *shaking* experiments hereafter). Both sets of experiments lasted 10 days. Subsequently, solutions were filtered and the precipitate was dried and analyzed by XRD using the same method employed in the anhydrite hydration experiments (Section 2.1). A sample of each solution was stored after filtering. The saturation index of gypsum (SI_{gyp}) in the initial solution was calculated using PHREEQC (3.1.7) (Parkhurst and Appelo, 2013).

2.3. Gypsum precipitation in brines

Experiments examining gypsum precipitation from brines of varying salinity used the same methodology described in Section 2.1, but varying amounts of NaCl were added to the initial 0.5 M Na_2SO_4 solutions. The NaCl concentrations were 30 g/L, 80 g/L, 150 g/L, 200 g/L and 300 g/L. All the experiments were conducted in duplicate at 20 °C and used the same procedure for filtering, drying, and mineralogical analysis described in Sections 2.1 and 2.2.

2.4. Extraction of gypsum hydration water

GHW was extracted by slowly heating each sample (~200 mg) to 400 °C, *in vacuo*, using a bespoke offline extraction system (Gázquez et al., 2015). The hydration water was recovered by cryogenic trapping at liquid nitrogen temperature.

2.5. Isotopic analyses and calculation of fractionation factors

Oxygen ($\delta^{18}O$) and hydrogen (δD) isotopes in waters and hydration water were measured simultaneously by cavity ring down spectroscopy (CRDS) in the Godwin Laboratory at the University of Cambridge using a L1102-i Picarro water isotope analyzer and A0211 high-precision vaporizer (Hodell et al., 2012). In addition, the original solution and the GHW of 11 experiments of hydration of anhydrous $CaSO_4$ were measured using a L2140-i Picarro CRDS analyzer, capable of analyzing triple oxygen ($\delta^{17}O$ and $\delta^{18}O$) and hydrogen (δD) isotopes (Steig et al., 2014). The samples were analyzed using the same method described by Gázquez et al. (2015). The mother waters collected from each experiment and the corresponding hydration water extracted from the gypsum were measured consecutively by CRDS under the same instrument conditions. This direct comparison minimizes the effect of drift and provides precise and accurate estimates of the fractionation factor that is calculated as the isotopic difference between the sequential samples of the mother water and GHW. By analyzing the waters before and after gypsum precipitation, we found that the isotopic composition of the solution did not change over the course of the experiments within error (Appendix 1); therefore, the values of the initial solutions were used for the calculation of the isotope fractionation factors.

Each sample was analyzed 9 times when using the L1102-i Picarro and 10 times for the L2140-i Picarro by multiple injections of 2 μL of water into the A0211 vaporizer. Memory effects from previous samples were avoided by rejecting the first three analyses. Values for the final 6–7 injections were averaged with a typical in-sample precision (±1SD) of ±0.05‰ for $\delta^{18}O$ and ±0.4‰ for δD for analyses conducted with the L1102-i Picarro analyzer, and were ±0.02‰ for $\delta^{17}O$, ±0.04‰ for $\delta^{18}O$ and ±0.19‰ for δD for samples analyzed using the L2140-i Picarro analyzer. Calibration of results to V-SMOW was achieved by analyzing internal standards before and after each set of 10 or 12 samples. Internal standards were calibrated against V-SMOW, GISP, and SLAP for $\delta^{18}O$ and δD, and against V-SMOW and SLAP for $\delta^{17}O$–$\delta^{18}O$, following the recommendations of Schoenemann et al. (2013). No drift was observed during the analysis and, consequently, no correction was applied. All results are reported in parts per thousand (‰) relative to V-SMOW. External error of the method was ±0.05‰ for $\delta^{17}O$, ±0.1‰ for $\delta^{18}O$ and ±0.7‰ for δD (1SD), as estimated by repeated analysis ($n = 17$) of an analytical grade gypsum standard, extracted together with five samples in each run of the extraction apparatus (Gázquez et al., 2015).

3. RESULTS

3.1. Hydration of anhydrite at low salinities

The $\alpha^{18}O_{gypsum\text{-}water}$ values of the anhydrite hydration experiments varied from 1.0033 ± 0.0001 to 1.0037 ± 0.0001 in the temperature range from 3 °C to 40 °C, with the lowest values at 30 °C and the highest values at 3–8 °C. There was no statistically significant trend over this temperature range given the analytical uncertainty of the measurements ($R^2 = 0.56$; p-value >0.05). In contrast, $\alpha D_{gypsum\text{-}water}$ increased with temperature from 0.9788 ± 0.0003 at 3 °C to 0.9821 ± 0.0009 at 40 °C and showed significant dependence with temperature ($R^2 = 0.89$; p-value <0.05) (Table 1, Fig. 1 and Appendix 1).

The $\alpha^{17}O_{gypsum\text{-}water}$ was determined in the experiments of hydration of $CaSO_4$ and varied in the same manner as $\alpha^{18}O_{gypsum\text{-}water}$ reflecting mass dependent fractionation in the triple oxygen isotope system (Cao and Liu, 2011), with minimum value of 1.0017 ± 0.0001 in the temperature range from 25 °C to 40 °C and maximum of 1.0020 at 8 °C (Table 1). The relation between $\alpha^{17}O_{gypsum\text{-}water}$ and $\alpha^{18}O_{gypsum\text{-}water}$ is given by the parameter θ (Mook, 2000);

$$\alpha^{17}O_{gypsum\text{-}water} = \alpha^{18}O_{gypsum\text{-}water}{}^{\theta};$$

where $\theta = \ln(\alpha^{17}O_{gypsum\text{-}water})/\ln(\alpha^{18}O_{gypsum\text{-}water})$.

θ was found to be 0.5297 ± 0.0012 ($n = 11$) and displayed no correlation with temperature (Table 1).

All gypsum samples yielded a weight loss of hydration water of over 20%, similar to that of the gypsum standard (20.5 ± 0.3%). This suggests that there was complete hydration of anhydrite to gypsum and complete mineral dehydration in our extraction procedure for GHW. Insignificant amounts of bassanite and anhydrite (less than 1 weight %) were detected in all samples (Appendix 4).

3.2. Gypsum precipitation from mixing of $CaCl_2$ and Na_2SO_4 solutions

Experiments of gypsum precipitation from mixing of $CaCl_2$ and Na_2SO_4 solutions produced a mean $\alpha^{18}O_{gypsum\text{-}water}$ value of 1.0034 ± 0.0003 in the temperature range from 5 °C to 55 °C. No measurable differences were found between the free-drift gypsum precipitation and the shaking experiments. No significant relationship was observed with temperature considering the analytical uncertainty of the measurements ($R^2 = 0.73$; p-value >0.05). The $\alpha^{18}O_{gypsum\text{-}water}$ value was unaffected by the different initial SI_{gyp} of the solution within the analytical error (Figs. 1 and 2 and Table 2).

Unlike the oxygen isotope fractionation factor, $\alpha D_{gypsum\text{-}water}$ was affected by changes in both temperature and initial SI_{gyp}. The average $\alpha D_{gypsum\text{-}water}$ was 0.9815 ± 0.0025 between 5 °C and 55 °C. No measurable differences were found between the free-drift gypsum precipitation and the shaking experiments. The experiments conducted at 55 °C produced the highest values of $\alpha D_{gypsum\text{-}water}$ (0.984 ± 0.001) compared with gypsum precipitation at lower temperatures (e.g. 0.977 ± 0.001 at 5 °C). Hydrogen isotope fractionation shows a clear increasing trend with temperature by 0.0001 units per °C ($R^2 = 0.94$; p-value <0.05; taking the average of the experiments at different initial SI_{gyp}). The $\alpha D_{gypsum\text{-}water}$ was affected by the SI_{gyp} of the initial solution, increasing by 0.0033 for each increase of 1 unit in the SI_{gyp}. This linear trend is similar (±0.0012, 1SD) at different temperatures (Appendix 2). Less than 1 weight% of bassanite and anhydrite has been detected in all samples (Appendix 4).

3.3. Gypsum precipitation from brines

The addition of NaCl to the solution does not affect $\alpha^{18}O_{gypsum\text{-}water}$ (1.0033 ± 0.0001) below 150 g/L of NaCl, and results were similar to gypsum precipitation at 20 °C when no NaCl was added (1.0034 ± 0.0001) (Table 3 and Fig. 3). In contrast, $\alpha^{18}O_{gypsum\text{-}water}$ increased to 1.0038 ± 0.0002 at a salinity of 200 g/L and to 1.0047 ± 0.0003 at 300 g/L. The $\alpha D_{gypsum\text{-}water}$ increased linearly with salinity from 0 to 300 g/L NaCl by 0.00003 units per gram of NaCl in solution and showed the greatest value of

Table 1
Isotope fractionation factors ($\alpha^{17}O_{gypsum\text{-}water}$, $\alpha^{18}O_{gypsum\text{-}water}$ and $\alpha D_{gypsum\text{-}water}$) between GHW and its mother solution obtained experimentally by the hydration of anhydrite. See Appendix 1 for complete report. (*Analyses conducted with Picarro L-2140*i* analyzer; #averaged results of samples analyzed by Picarro L-1102*i* and L-2140*i* analyzers).

Temperature (°C)	$\alpha^{17}O^*$	1SD	$\alpha^{18}O^*$	1SD	θ	1SD	n^*	$\alpha^{18}O^\#$	1SD	$\alpha D^\#$	1SD	$n^\#$
3	1.00197	0.00005	1.00372	0.00010	0.5300	0.0011	4	1.0037	0.0001	0.9788	0.0003	4
8	1.00201	0.00009	1.00380	0.00016	0.5293	0.0014	4	1.0037	0.0002	0.9801	0.0006	6
20	n.a	–	n.a	–	–	–	–	1.0034	0.0001	0.9814	0.0011	4
25	1.00181	–	1.00341	–	0.5298	–	1	1.0035	0.0001	0.9810	0.0006	5
30	1.00174	0.00000	1.00329	0.00001	0.5289	0.0014	1	1.0033	0.0001	0.9803	0.0009	2
35	n.a	–	n.a	–	–	–	–	1.0034	0.0000	0.9812	0.0003	4
40	1.00169	–	1.00318	–	0.5314	–	1	1.0034	0.0002	0.9821	0.0009	5

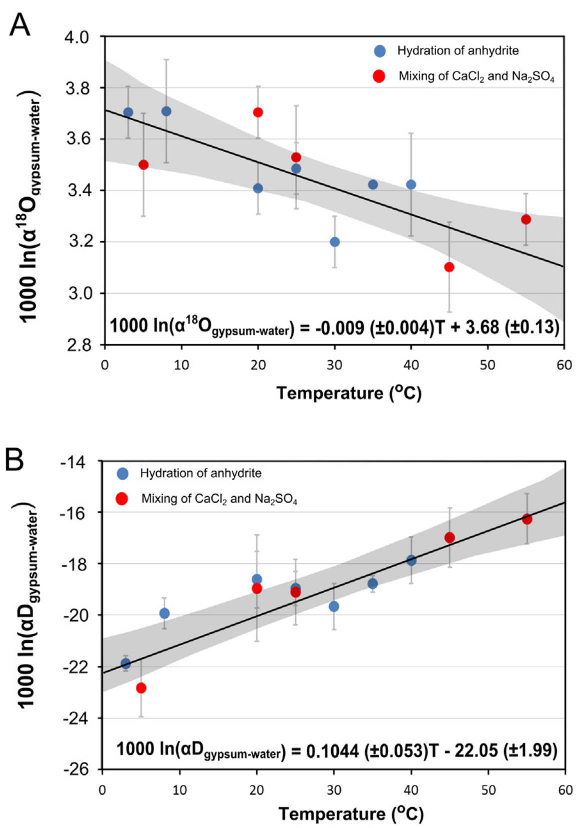

Fig. 1. Isotope fractionation factor (A: $\alpha^{18}O_{gypsum\text{-}water}$ and B: $\alpha D_{gypsum\text{-}water}$) between GHW and its mother solution at different temperatures obtained experimentally by hydration of anhydrite and mixing of $CaCl_2$ and Na_2SO_4 solutions. Note that mixing experiment results are averaged values of gypsum precipitation at different initial SI_{gyp} of the solution (see Table 2 and Appendix 2). Error bars denote 1σ. Gray shades represent the 95% confidence limits.

0.9893 ± 0.0002 at 300 g/L (Table 3). The water content of the solids was $20.7 \pm 0.3\%$ in experiments performed at salinities between 30 and 150 g/L of NaCl, whereas the water yield was slightly lower ($19.7 \pm 0.1\%$) in the experiments at 200 g/L and 300 g/L. Mineralogical analyses by XRD detected only gypsum in the experiments at NaCl concentrations below 150 g/L and small amounts of bassanite and unconverted anhydrite of up to 2.5% and 4.6% respectively at 300 g/L (Appendix 4).

4. DISCUSSION

4.1. Effect of temperature and precipitation rate on the isotope fractionation factors in gypsum hydration water

Most equilibrium fractionation factors between the solution and the solid phase approach unity (i.e. no fractionation between the solution and the mineral, $\alpha = 1$) with increasing temperature (Friedman and O'neil, 1977). In our experiments, $\alpha D_{gypsum\text{-}water}$ increases with temperature in the gypsum formed using two methods (conversion of anhydrite to gypsum and mixing of $CaCl_2$ and Na_2SO_4 solutions). These methods produce similar results for $\alpha^{18}O_{gypsum\text{-}water}$ and $\alpha D_{gypsum\text{-}water}$ in the range of temperature studied within analytical uncertainties (Fig. 1). In the case of $\alpha^{18}O_{gypsum\text{-}water}$, no significantly statistical relationship with temperature was observed when examining separately the results from each method of gypsum precipitation (p-value >0.05 in both cases). However, when combining the results from both methods a slight dependence of $\alpha^{18}O_{gypsum\text{-}water}$ with temperature becomes significant ($R^2 = 0.70$; p-value <0.05; Fig. 1) because of the increased number of observations. The equation for $\alpha^{18}O_{gypsum\text{-}water}$ (expressed as $1000 \ln(\alpha^{18}O_{gypsum\text{-}water})$), as a function of temperature (°C) is:

$$1000 \ln(\alpha^{18}O_{gypsum\text{-}water}) = -0.009\ (\pm 0.004)\ T + 3.68\ (\pm 0.13).$$

whereas the temperature dependence of $\alpha D_{gypsum\text{-}water}$ is given by:

$$1000 \ln(\alpha D_{gypsum\text{-}water}) = 0.104\ (\pm 0.053)\ T - 22.05\ (\pm 1.99).$$

This very small dependence of $\alpha^{18}O_{gypsum\text{-}water}$ on temperature is not relevant for many geological and paleoclimate applications; however, the greater sensitivity of $\alpha D_{gypsum\text{-}water}$ to temperature has implications for the calculation of δD of the mother solution, especially when gypsum forms in hydrothermal environments from hydration of anhydrite (e.g. Matsuyaba and Sakai, 1973; Bath et al., 1987). For example, using the revised fractionation factor value at 55 °C (1.0033 ± 0.0002), the inferred value of $\delta^{18}O$ in the mother water increases by 0.7‰ compared to using the fractionation factor of 1.004 (Gonfiantini and Fontes, 1963; Sofer, 1978). δD value decreases by ~4‰ using the revised fractionation factor (0.984) instead of

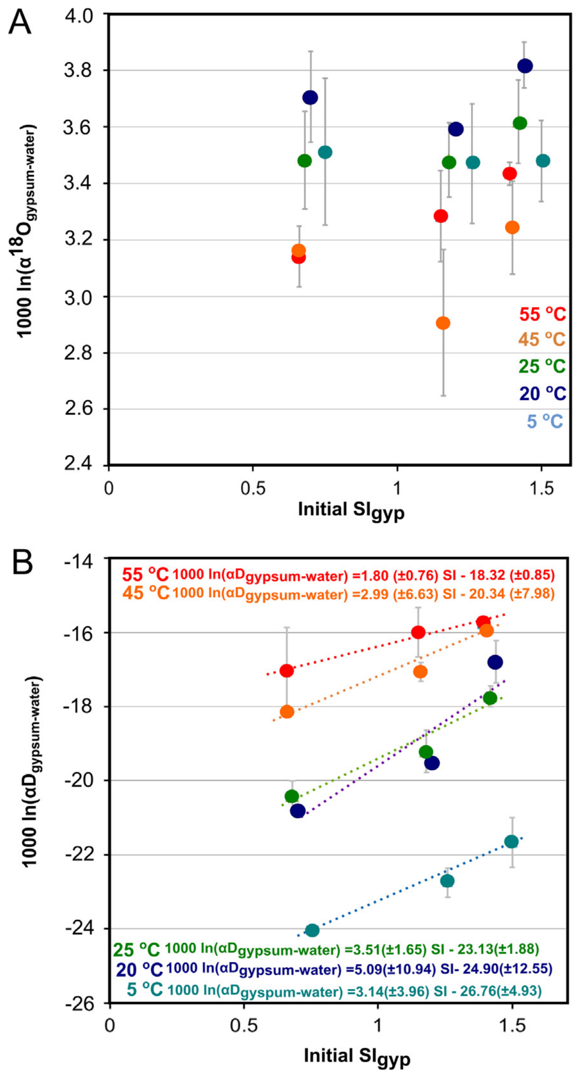

Fig. 2. Isotope fractionation factors ($\alpha^{18}O_{gypsum-water}$ and $\alpha D_{gypsum-water}$) between GHW and its mother solution obtained experimentally by mixing of $CaCl_2$ and Na_2SO_4 solutions at different initial concentrations of Ca^{2+} and SO_4^{2-} and temperatures. Error bars denote 1σ.

the accepted value (0.980; Sofer, 1978). Hence, the temperature of gypsum formation should be considered when choosing which fractionation factors to apply.

At lower temperatures (i.e. from 20 to 40 °C), the two methods of gypsum precipitation produce slightly lower values for $\alpha^{18}O_{gypsum-water,}$ but similar $\alpha D_{gypsum-water}$ values (within analytical error) compared to previously proposed values (Gonfiantini and Fontes, 1963; Fontes and Gonfiantini, 1967; Sofer, 1978; Hodell et al., 2012). For $\alpha^{18}O_{gypsum-water}$, we obtained a value of 1.0034 ± 0.0001 from 20 to 40 °C, which is within the error reported previously (i.e. 1.0037 ± 0.0005 in Gonfiantini and Fontes, 1963; 1.0039 ± 0.0004 in Hodell et al., 2012), but mostly closer to the lower range of values and more precise. For $\alpha D_{gypsum-water,}$ our values from 20 to 40 °C (0.9812 ± 0.0007) are within error of previous measurements (0.981 ± 0.002 between 12 and 37 °C; Hodell et al., 2012), but are also more precise.

By using the proposed $\alpha^{18}O_{gypsum-water}$ value of 1.0034 ± 0.0001, any calculation of mother water in the range from 20 to 40 °C produces a $\delta^{18}O$ of water that is ~0.6‰ higher than if the fractionation factor of 1.004 is used instead (Appendix 5). This results in significant differences for quantitative isotopic studies using GHW, such as the tandem carbonate-GHW paleothermometer (Hodell et al., 2012). Values of $\delta^{18}O$ of mother water that are 0.6‰ greater will lead to water temperatures that are approximately 2 °C higher than those calculated using a fractionation factor of 1.004.

For example, previous studies concluded that the average Last Glacial temperature was colder in lowland Central America by 5–10 °C compared to the Holocene, based on the analysis of coeval GHW and biogenic carbonates from Lake Petén Itzá (Guatemala) and using $\alpha^{18}O_{gypsum-water}$ of 1.004 (Hodell et al., 2012; Grauel et al., 2016). By using $\alpha^{18}O_{gypsum-water}$ of 1.0034, the calculated difference between the Late Glacial and the Holocene is reduced to 3–8 °C, which is closer to expected values for the region (Correa-Metrio et al., 2012). Importantly, the temperature error derived from the analytical uncertainty of our $\alpha^{18}O_{gypsum-water}$ (± 0.0001) is ± 0.5 °C (1SD), which is considerably smaller than that derived using previous fractionation factors (e.g. ± 0.0004 is equivalent to an error of ± 1.6 °C; Hodell et al., 2012). The use of the revised fractionation factors for $\alpha^{18}O_{gypsum-water}$ and $\alpha D_{gypsum-water}$ also produces significant differences for calculations of d-excess in paleo-lake water from GHW of up to 5‰ (Appendix 5). Equally, when the revised fractionation factors are used (1.0034 and 0.981), the evaporation line described by paleo-lake waters

Table 2
Isotope fractionation factors ($\alpha^{18}O_{gypsum-water}$ and $\alpha D_{gypsum-water}$) between GHW and its mother solution obtained experimentally by mixing of $CaCl_2$ and Na_2SO_4 solutions at different initial concentrations of Ca^{2+} and SO_4^{2-} and different temperatures. Initial Ca^{2+} and SO_4^{2-} concentrations are given. SI_{gyp} ranged from 0.66 to 1.50 (Appendix 2). Analyses were conducted with a Picarro L-1102*i* analyzer.

Temperature (°C)	0.25 Ca^{2+}/0.25 SO_4^{2-} (mol/L)				0.166 Ca^{2+}/0.166 SO_4^{2-} (mol/L)				0.065 Ca^{2+}/0.065 SO_4^{2-} (mol/L)			
	$\alpha^{18}O$	1SD	αD	1SD	$\alpha^{18}O$	1SD	αD	1SD	$\alpha^{18}O$	$\alpha^{18}O$	1SD	αD
5	1.0035	0.0001	0.978	0.001	1.0035	0.0002	0.977	0.003	1.0035	0.0003	0.976	0.000
20	1.0038	0.0001	0.983	0.001	1.0036	–	0.980	–	1.0037	0.0000	0.979	0.000
25	1.0036	0.0001	0.982	0.000	1.0035	0.0001	0.981	0.000	1.0035	0.0000	0.980	0.001
45	1.0032	0.0001	0.984	0.000	1.0029	0.0000	0.983	0.000	1.0032	–	0.982	–
55	1.0034	0.0001	0.984	0.001	1.0033	0.0001	0.984	0.001	1.0031	0.0000	0.983	0.001

Table 3
Isotope fractionation factors ($\alpha^{18}O_{gypsum-water}$ and $\alpha D_{gypsum-water}$) between GHW and its mother solution obtained experimentally by hydration of anhydrite from solutions with different concentrations of NaCl at 20 °C. See Appendix 3 for complete data report. Measurements were made using a Picarro L-1102*i* analyzer.

NaCl concentration (g/L)	$\alpha^{18}O$	1SD	αD	1SD	*n*
0	1.0034	0.0001	0.9806	0.0010	4
30	1.0032	0.0001	0.9807	0.0003	2
80	1.0034	0.0003	0.9824	0.0004	2
150	1.0033	0.0001	0.9846	0.0001	3
200	1.0038	0.0002	0.9886	0.0004	2
300	1.0047	0.0003	0.9893	0.0002	2

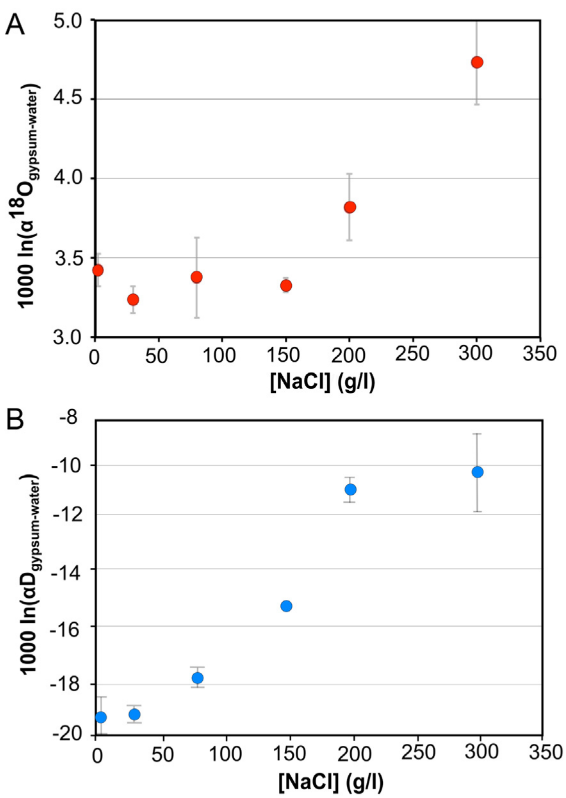

Fig. 3. Isotope fractionation factor (A: $\alpha^{18}O_{gypsum-water}$ and B: $\alpha D_{gypsum-water}$) between GHW and its mother solution at different salinities obtained experimentally by hydration of anhydrite in solutions with different amounts of NaCl. Error bars denote 1σ.

of Lake Petén Itzá produces a more consistent fit to that of the modern lake waters (Fig. 4).

$CaCl_2/Na_2SO_4$ mixing experiments at different initial SI_{gyp} were performed to calculate the effect of precipitation rate on the isotope fractionation factors. Results show that, at different initial SI_{gyp}, within the studied range of saturations (SI_{gyp} = 0.66–1.50) there are no measurable differences in $\alpha^{18}O_{gypsum-water}$ (Table 2), independent of gypsum formation temperature. Unlike $\alpha^{18}O_{gypsum-water}$, the hydrogen fractionation factor, however, increases at a constant rate with SI_{gyp} at all temperatures by 0.003 ± 0.001 per unit of SI_{gyp}.

The studied range of supersaturation is ~5 to ~20 times greater than gypsum saturation under equilibrium conditions (e.g. 0.014 M of dissolved $CaSO_4$ at 25 °C). Equilibrium or near-equilibrium conditions are expected during the precipitation of most natural gypsum deposits. However, the experiments at relatively elevated saturations are useful to ascertain the role of kinetic effects on isotopes fractionation during gypsum precipitation.

The fractionation factors between GHW and free water obtained experimentally are the net result of equilibrium and kinetic effects for oxygen and hydrogen isotopes. The relative importance of the two is governed by the rate of gypsum precipitation. Pure equilibrium-controlled fractionation may occur during slow gypsum precipitation, whereas kinetic isotopic fractionation is more likely at higher precipitation rates. This is demonstrated by the increase in $\alpha D_{gypsum-water}$ with increasing saturation (SI_{gyp}). This suggests that the equilibrium fractionation (i.e. SI_{gyp} = 0) for hydrogen isotopes may be lower than the values obtained from our $CaCl_2/Na_2SO_4$ mixing experiments at different temperatures, in which $\alpha D_{gypsum-water}$ is partially controlled by kinetic effects.

The fact that $\alpha^{18}O_{gypsum-water}$ does not show measurable trends with SI_{gyp} may indicate that kinetic effects are minimal for oxygen isotopes. The $\alpha^{18}O_{gypsum-water}$ is controlled by isotopic fractionation between the free solution and the hydration sphere of Ca^{2+} in solution (Taube, 1954; Gonfiantini and Fontes, 1963; Oi et al., 2013). Our results suggest that different calcium concentrations in the solution and SI_{gyp} do not affect the isotopic values of the hydration sphere of Ca^{2+}, within the range of experimental conditions investigated.

No measurable differences in $\alpha^{18}O_{gypsum-water}$ and $\alpha D_{gypsum-water}$ were observed between the free-drift and the shaking experiments performed at the same SI_{gyp} and temperature. This is because the initial saturations used in our experiments are relatively far from the gypsum precipitation equilibrium. At these saturations levels, there is little difference in the rate of gypsum nucleation and precipitation between both types of experiments, as gypsum crystallization occurs immediately after mixing the initial $CaCl_2$ and Na_2SO_4 solutions.

The relative difference in $\alpha D_{gypsum-water}$ between the experiments conducted at lower initial SI_{gyp} (0.66–0.70) and those at higher SI_{gyp} (1.39–1.44) is 0.0024 ± 0.0010. This suggests that holding all other parameters constant (isotopic composition of the solution, temperature, etc.), faster precipitation of gypsum causes enrichment of hydrogen isotopes in GHW by ~2.4‰ with respect to the

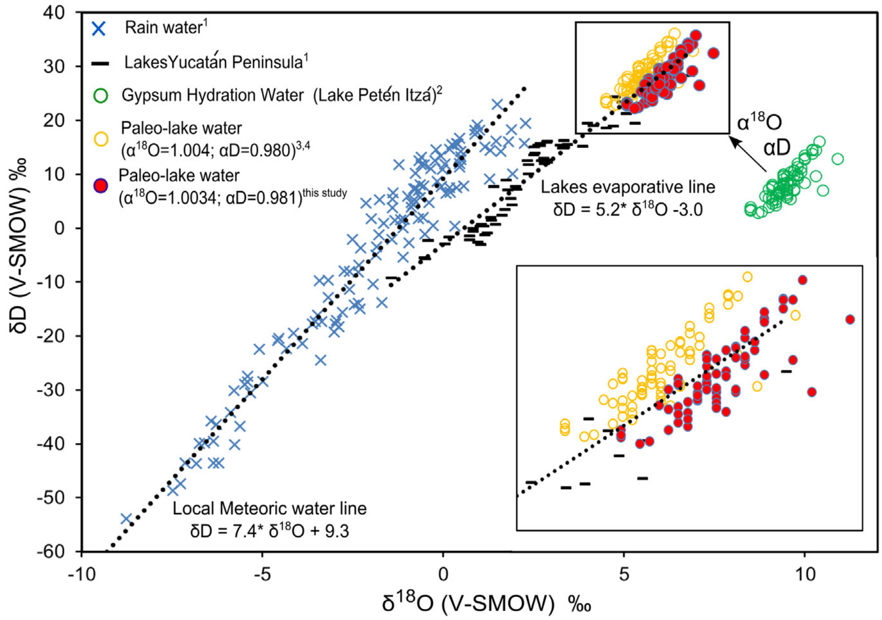

Fig. 4. $\delta^{18}O$ and δD of hydration water and calculated mother water from gypsum from Lake Petén Itzá (Grauel et al., 2016)[2]. $\delta^{18}O$ and δD of the paleo-lake water were obtained by applying the classic fractionations factors ($\alpha^{18}O_{gypsum\text{-}water} = 1.004$ and $\alpha D_{gypsum\text{-}water} = 0.98$; Gonfiantini and Fontes, 1963; Sofer, 1978)[3,4] and the revised fractionation factors ($\alpha^{18}O_{gypsum\text{-}water} = 1.0034$ and $\alpha D_{gypsum\text{-}water} = 0.981$) (see Appendix 5). Isotopic values of rainwaters and Lakes in the Yucatan Peninsula, including Lake Petén Itzá are from Hodell et al. (2012)[1]. Note that when the revised fractionation factors are used, the calculated paleo-lake waters produce a better fit at the upper end of the lake's evaporative line.

experiments with the lowest initial SI_{gyp} (and therefore the slowest rates of precipitation), within the studied range of SI_{gyp}. Unlike the insignificant effect of different initial SI_{gyp} and calcium concentrations on the hydration sphere of Ca^{2+}, the isotopic values of the hydration sphere of SO_4^{2-} are affected by different ionic concentrations and gypsum precipitation rates, within the range of experimental conditions investigated. Although more experiments are needed to explore $\alpha D_{gypsum\text{-}water}$ closer to the saturation point of gypsum, we assume that the relationship between $\alpha D_{gypsum\text{-}water}$ and SI_{gyp} follows the same linear relationship at lower saturations. We extrapolate the $\alpha D_{gypsum\text{-}water}$ values for $SI_{gyp} = 0$ and use it as the expression of pure equilibrium fractionation, with application to cases when gypsum precipitates under near-equilibrium conditions.

The results indicate that at $SI_{gyp} = 0$, the value of $\alpha D_{gypsum\text{-}water}$ should be 0.0046 ± 0.0019 lower than in the experiments with faster gypsum precipitation (i.e. $SI_{gyp} = 1.39$–1.50). Therefore, at the slowest gypsum growth rates, δD in GHW is depleted by ~4.6‰ when compared with the gypsum formed at the faster precipitation rates in our experiments at any given temperature.

This finding has potentially important implications for accurate calculations of δD of the fluid from GHW (particularly for determining *d*-excess values), especially in gypsum crystals formed at low saturation state. This is the case for the megacrystals of the caves in the Naica mine (Chihuahua, Mexico) (García-Ruiz et al., 2007; Gázquez et al., 2012, 2013, 2016), where gypsum speleothems grew from a solution with SI_{gyp} close to 0 and temperature around 47–55 °C. Indeed, the formation period of these crystals could extend over 1 Ma (García-Ruiz et al., 2007; Garofalo et al., 2010; Sanna et al., 2010; Krüger et al., 2013). We analyzed selenite samples from Crystals Cave ($n = 6$) and Ojo de la Reina Cave ($n = 1$) (Appendix 6), both in the Naica mine, using the analytical method described by Gázquez et al. (2015).

Using fractionation factors of 1.004 and 0.98, the $\delta^{18}O$ and δD values of the Naica paleo-aquifer lie above the modern groundwater in north Mexico, and from water from the Naica mine itself (Fig. 5). Using the $\alpha^{18}O_{gypsum\text{-}water}$ of 1.0033 corresponding to the formation temperature of these speleothems (~55 °C in Ojo de la Reina Cave and Crystals Cave; Krüger et al., 2013) the inferred values of paleo-groundwater are in better agreement with those of the modern thermal waters in the Naica mine (Appendix 6 and Fig. 5). Note that when choosing $\alpha D_{gypsum\text{-}water}$, we also consider precipitation rate, which was extremely slow during the formation of these crystals (Sanna et al., 2010; Van Driessche et al., 2011); thus, we selected a $\alpha D_{gypsum\text{-}water}$ value of 0.982 for gypsum formed at 55 °C and SI_{gyp} ~0 (Fig. 2). The agreement between the reconstructed paleo-water and the current thermal water in the Naica aquifer support our linear extrapolation of the observed relationship between $\alpha D_{gypsum\text{-}water}$ and SI_{gyp} to low saturation states.

4.2. Effect of salinity on the isotope fractionation factors in gypsum hydration water

The initial salinity (NaCl concentration) of the solution also controls the fractionation factor between water and gypsum. Results suggest that $\alpha^{18}O_{gypsum\text{-}water}$ is not affected by NaCl concentrations below 150 g/L. Above 150 g/L, the fractionation of oxygen isotopes increases gradually from 1.0034 below 150 g/L to 1.0047 ± 0.0003 at 300 g/L. For hydrogen, the $\alpha D_{gypsum\text{-}water}$ increases linearly with salinity from 0.9806 to 0.9893 between 0 and 300 g/L (Table 3). Therefore, gypsum that precipitates from a 300 g/L NaCl solution has a δD that is ~10‰ lower than gypsum precipitated from freshwater with the same isotopic composition (when all other variables are held constant). Given that gypsum formed from evaporated seawater starts to precipitate when the solution reaches a salinity of ~130 g/L, the effect of salinity on $\delta^{18}O$ hydration water is small for most gypsum precipitates. However, the hydrogen isotopes fractionate by 3‰ less at a salinity of 130 g/L compared to fresh water. This implies that when the conventional fractionation factors are applied to gypsum formed from evaporated seawater (i.e. ~130 g/L), the values of *d*-excess are 10‰ more positive than when the revised fractionation factors are used instead (assuming no salinity effect on $\delta^{18}O$).

To illustrate this point, we analyzed $\delta^{18}O$ and δD in evaporated seawater (ranging 40–300 g/L of total dissolved salts) from different brine pools collected in a natural salt factory during various times throughout the year ($n = 10$; Appendix 7). The brines were analyzed for $\delta^{18}O$ and δD using the distillation method described in Gázquez et al. (2015). As observed in Fig. 6, $\delta^{18}O$ and δD of the mother solution lie on the evaporation line of the brines using the revised fractionations factors for gypsum precipitated at 150 g/L (1.0033 and 0.985, respectively). In contrast, calculated $\delta^{18}O$ and δD values of the mother waters fall above the expected line for the brines when using the traditional fractionations factors of 1.004 and 0.98, respectively (Fig. 6). This demonstrates the importance of using the appropriate fractionation factors when analyzing gypsum formed from marine brines.

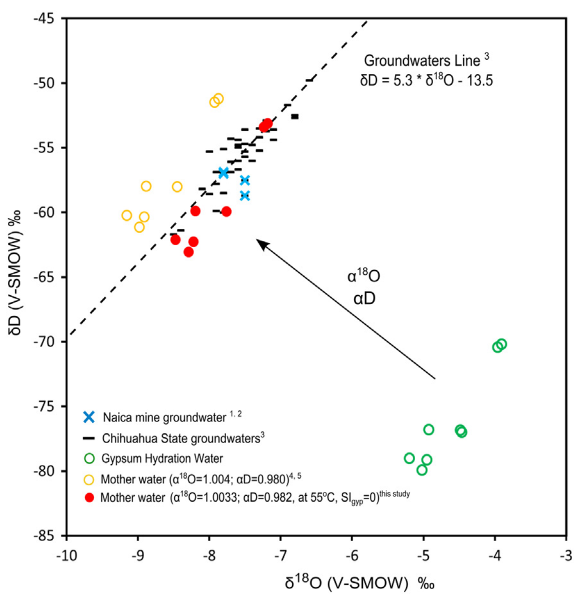

Fig. 5. $\delta^{18}O$ and δD of hydration water and calculated mother water from selenite crystals from the Naica mine (Chihuahua, Mexico). ^{18}O and δD of the paleo-aquifer water were obtained by applying the classic fractionations factors ($\alpha^{18}O_{gypsum\text{-}water} = 1.004$ and $\alpha D_{gypsum\text{-}water} = 0.98$; Gonfiantini and Fontes, 1963; Sofer, 1978)[3,4] and our revised fractionation factors. Note gypsum in Crystals Cave and Ojo de la Reina Cave formed at temperature of 55 °C and SI_{gyp} close to 0 (Krüger et al., 2013); thus, values of $\alpha^{18}O_{gypsum\text{-}water} = 1.0033$ and $\alpha D_{gypsum\text{-}water} = 0.982$ have been used (see Appendix 6). Using the revised fractionation factors proposed here, the calculated $\delta^{18}O$ and δD match the values of the modern Naica mine groundwater (Dames and More, 1977; García-Ruiz et al., 2007)[1,2] and regional groundwater in the Chihuahua region (Mahlknecht et al., 2008)[3].

The effect of NaCl concentration on the fractionation factor between water and gypsum can be attributed mainly to decreases in the activity of water as salinity increases, which is related to the effect of Cl^- on the hydration spheres of Ca^{2+} and SO_4^{2-} (Di Tommaso et al., 2014). As a consequence, the activity and isotopic ratios of water in brines are not the same as for fresh water (Sofer and Gat, 1975). Another explanation of the effect of NaCl on the fractionation factor is that the precipitation of intermediate hydrated calcium sulfate phases (e.g. bassanite) could affect the fractionation factors between water and gypsum at high salinities. Indeed, the stability of bassanite increases with increasing NaCl concentration (Ostroff, 1964; Ossorio et al., 2014). Considering these results, the salinity of the solution from which gypsum precipitated should be considered for calculations of the original $\delta^{18}O$, δD, and derived d-excess from gypsum precipitated from brines (i.e. evaporative marine gypsum).

4.3. Triple oxygen isotope fractionation in gypsum hydration water

The parameter θ, which describes the relationship between $\alpha^{17}O$ and $\alpha^{18}O$ ($\alpha^{17}O_{gypsum\text{-}water} = \alpha^{18}O_{gypsum\text{-}water}{}^{\theta}$), has been determined for water-GHW. We observed $\theta = 0.5297 \pm 0.0012$ (1SD) in the experiments of hydration of anhydrite and θ is independent of temperature. Our observed θ value is close to the greatest theoretical values of this parameter in any mass-dependent fractionation process of triple oxygen isotope, which ranges from 0.52 to 0.5305 (Matsuhisa et al., 1978; Cao and Liu, 2011; Bao et al., 2016). This θ value agrees with that given by Barkan and Luz (2005) in vapor–liquid water equilibrium ($\theta = 0.529 \pm 0.001$), as well as other equilibrium mass-dependent reactions for the triple oxygen isotope system (Miller, 2002; Cao and Liu, 2011; Bao et al., 2016). Although no dependence of θ with temperature has been detected in our experiments, this parameter increases with temperature in most water–mineral systems during oxygen isotope fractionation. However, in the temperature range from 0 to 50 °C no measurable trends (within analytical uncertainties of the current methods) are expected for most geochemical systems, including CO_2–water, quartz-water and calcite-water (Cao and Liu, 2011). This agrees with our observations in the GHW-water system.

The relationship between the $\delta^{17}O$ and $\delta^{18}O$ in the hydrological cycle (known as ^{17}O-excess) was defined by Barkan and Luz (2007) as:

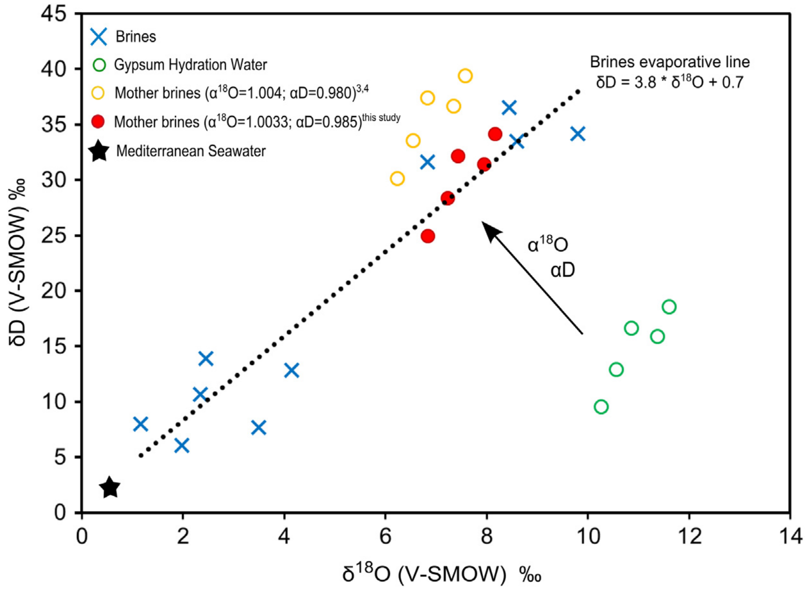

Fig. 6. $\delta^{18}O$ and δD of hydration water and calculated mother water from gypsum formed by seawater evaporation in pools of a natural salt factory (Cabo de Gata, SE Spain). ^{18}O and δD of the original brines were obtained by applying the classic fractionations factors ($\alpha^{18}O_{gypsum\text{-}water} = 1.004$ and $\alpha D_{gypsum\text{-}water} = 0.98$; Gonfiantini and Fontes, 1963; Sofer, 1978)[3,4] and the revised fractionation factors proposed here for salinity of 150 g/L of NaCl ($\alpha^{18}O_{gypsum\text{-}water} = 1.0033$ and $\alpha D_{gypsum\text{-}water} = 0.985$). Using our revised fractionation factors, the calculated $\delta^{18}O$ and δD match the values of the brines in these pools (Appendix 7).

$^{17}O\text{-excess} = \ln(\delta^{17}O + 1) - 0.528 \ln(\delta^{18}O + 1).$

As an example of application, we apply the fractionation factors to infer the ^{17}O-excess of the paleo-groundwater of the Naica aquifer from GHW in selenite speleothems from Crystals Cave and Ojo de la Reina Cave (Appendix 6). The mean ^{17}O-excess was 30 ± 10 per meg (1SD) (using fractionations factors at 55 °C; $\alpha^{18}O_{wat\text{-}gyp}$ of 1.00334 and $\alpha^{18}O_{wat\text{-}gyp}$ of 1.00177 for $\alpha^{17}O_{wat\text{-}gyp}$; the last calculated using the value of $\theta = 0.5297$). Importantly, the use of the fourth and fifth digits of the fractionation factors is required for precise determination of ^{17}O-excess from GHW. Although no ^{17}O-excess measurements in the modern water of the Naica aquifer have been reported to date, these results are similar to the ^{17}O-excess values obtained by Li et al. (2015) in fresh waters from the southern US (i.e. 24 $\pm$ 31 in Las Cruces, New Mexico). This agreement suggests that ^{17}O-excess in GHW records the ^{17}O-excess of the solution from which gypsum formed when corrected using the appropriate fractionation factors.

A potential application of the triple oxygen isotope system might be to determine the origin of hydrated minerals in meteorites. For example, hydrogen isotopes in gypsum and jarosite ($KFe_3^{3+}(OH)_6(SO_4)_2$) in a Martian meteorite found in Antarctica (Roberts Massife 04262) show signs of isotopic re-equilibration with different types of terrestrial water (Greenwood et al., 2009). Considering the large differences in $^{17}O_{excess}$ between Mars and Earth (Franchi et al., 1999), triple oxygen would be useful to determine if hydrated minerals preserved a Martian signal. Ultimately, the triple oxygen isotopic composition of Martian gypsum (Showstack, 2011; Massé et al., 2012) could be measured either *in situ* using an isotopic analyzer onboard a rover, or eventually on Earth from a sample return mission.

5. CONCLUSIONS

The isotopic composition of gypsum hydration water is a useful palaeoclimatic proxy to trace geological and hydrogeological processes. Precise and accurate calculations of $\delta^{17}O$, $\delta^{18}O$ and δD of the mother solution and their derived values of d-excess and ^{17}O-excess require accurate fractionation factors, including their dependence on temperature, salinity and gypsum precipitation rate. Modern analytical methods utilizing CRDS permit the determination of isotopic fractionation factors for gypsum at a precision and accuracy that is an order of magnitude better than conventional methods.

We demonstrate that using the revised $\alpha^{18}O_{gypsum\text{-}water}$ and $\alpha D_{gypsum\text{-}water}$ (instead of the traditional values) provides better agreement with expected values for a set of natural gypsum samples. Choosing appropriate fractionation factors is particularly relevant for gypsum formed in hydrothermal systems and in brines. In addition, we found that using the revised fractionation factors result in temperatures that are about 2 °C cooler when applying the tandem method of paleotemperature estimation using $\delta^{18}O_{carbonate}$ and $\delta^{18}O_{GHW}$ (Hodell et al., 2012).

Our results of triple oxygen isotopes in natural gypsum samples suggest that GHW preserve the ^{17}O-excess value of its mother water. Given that ^{17}O-excess has been shown to be less sensitive to temperature than the *d*-excess during evaporation (Luz and Barkan, 2010), combining the ^{17}O-excess and *d*-excess recorded by GHW may provide information about the relative effects of humidity and temperature change at the time of gypsum formation in evaporative environments. ^{17}O-excess is also relevant for meteorite studies and planetary geology because the triple oxygen isotope composition on Earth differs substantially from that of other planets (Franchi et al., 1999; Ali et al., 2016).

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.gca.2016.11.001.

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