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 ($\alpha D_{gypsum-water}$) increases by 0.0001 units per °C between 3 °C and 55 °C and salinities <150 g/L of NaCl. The $\alpha D_{gypsum-water}$ 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 $\alpha^{18}O_{gypsum-water}$ 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, $\alpha^{18}O_{gypsum-water}$ averages 1.0035 ± 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 $\alpha^{18}O_{gypsum-water}$, but $\alpha D_{gypsum-water}$ 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 $\alpha D_{gypsum-water}$ 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.

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 ± 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