

# New determination of gypsum isotope fractionation factor

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## INTRODUCTION

Gypsum is a low temperature mineral of relevance for the understanding of evaporitic (Orti, 2011) and late hydrothermal scenarios (Garcia-Ruiz et al., 2008). Gypsum deposits are spread all over the geological record and their crystals may contain important information about the history of the seas. Because of its composition (calcium sulfate with two molecules of water), gypsum is a key material to understand the history of water in Mars (McCollom and Hynek, 2005), and because of its transformation to the dehydrated phase (anhydrite) upon changes in pressure and temperature, gypsum is the origin of many geotechnical problems (Cooper, 2002).

Besides fluid inclusions, the formation temperature of minerals is usually decoded by the study of isotopic analysis. At present, only one experimentally obtained fractionation factor for oxygen is found in the literature for gypsum precipitated from solution at 25 °C (Lloyd, 1967) with an apparent isotope fractionation of 2 ‰ between dissolved sulfate and gypsum. According to Lloyd this result is in fair agreement with data of natural evaporation pans, where  $\delta^{18}\text{O}$  of gypsum was enriched by 3.6 ‰ compared to dissolved sulfate. However, it is not certain whether the latter represents either an equilibrium isotopic fractionation or a kinetic effect. In this work the isotopic fractionation between oxygen and sulphur of dissolved sulphate and precipitated gypsum was determined. The influence of temperature, salinity and saturation index (SI) has been tested.

## METHODOLOGY

Gypsum crystallization was carried out by chemical reaction in stoichiometric

conditions, using as reagents calcium chloride dihydrate and sodium sulfate anhydrate. Chemical reactions were conducted at different salinities by varying the concentration of sodium chloride. Three initial conditions were used: 0.035 M  $\text{CaSO}_4$  + 0.2 M NaCl, 0.035 M  $\text{CaSO}_4$  + 4.5 M NaCl and 0.08 M  $\text{CaSO}_4$  + 4.5 M NaCl. This series of experiments was performed in the temperature range from 4 °C to 80 °C. All stock solutions were filtered (0.45  $\mu\text{m}$  filter) and tempered before mixing. The mixture of these reagents was carried out in glass bottles and then sealed with Teflon in order to avoid evaporation. The reaction products were filtered (0.45  $\mu\text{m}$  filter) and washed with ethanol (Fig. 1).



Fig. 1 Gypsum crystals grown at 40 °C.

For sulphur and oxygen isotopic analysis representative samples of 0.1 g of gypsum were dissolved in 50 mL of milli-Q water and sulphate was precipitated as  $\text{BaSO}_4$  by the addition of excess  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  after acidifying the sample with HCl (pH<2) and boiling it to prevent  $\text{BaCO}_3$  precipitation.

The sulphur isotope ( $\delta^{34}\text{S}$ ) composition of gypsum and reaction solutions was determined with an Elemental Analyser (Carlo Erba 1108) coupled to an IRMS (Delta C Finnigan Mat) and the oxygen isotope ( $\delta^{18}\text{O}$ ) was measured with a Thermo-Chemical Elemental Analyser

(TC/EA Thermo-Quest Finnigan) coupled to an IRMS (Delta C Finnigan Mat). Notation is expressed in terms of ‰ relative to the Vienna Standard Mean Ocean Water (V-SMOW) and Vienna Canyon Diablo Troilite (V-CDT) standards. The isotope ratios were calculated using international and internal laboratory standards. To improve the precision of measurements, preliminary experiments provided us with an isotopic composition of the raw material as well as a notion of the fractionation values. Therefore, when measuring isotope composition of sulphur, three international  $\text{BaSO}_4$  standards (IAEA-SO5, IAEA-SO6, NBS-127) and one internal standard (YCEM) were used for calibration at the start and end of every run. Additionally, every 8 samples the standards with a value closest to that of our samples (IAEA-SO5 and YCEM) were also measured. For oxygen, at the start and end of every run 3 standards (NBS-127, YCEM and  $\text{H}_2\text{SO}_4$ ) were measured three times. Every 4 samples two standards (YCEM and  $\text{H}_2\text{SO}_4$ ) with values closest to our samples were measured two times. To reduce even further the fluctuations of measuring conditions oxygen and sulphur samples were measured as a group. Reproducibility is  $\pm 0.1$  ‰ for  $\delta^{34}\text{S}$ , and  $\pm 0.3$  ‰ for  $\delta^{18}\text{O}$ .

## RESULTS AND DISCUSSION

Figure 2 summarizes the sulphur and oxygen isotopic compositions of gypsum precipitated from solution as function of temperature and for different saturation indexes. As expected, due to the larger mass difference, oxygen isotopes show the highest fractionation factor and a significant dependence on temperature is found for two experimental conditions (Fig. 2a,b). On the other hand, the sulphur isotope composition of precipitated gypsum only shows for one experimental condition (Fig. 2b) a feeble

**palabras clave:** yeso,  $\delta^{34}\text{S}$ ,  $\delta^{18}\text{O}$ , fraccionamiento isotópico

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dependence on temperature.

To verify how long it takes to reach a stable isotope composition we conducted a series of experiments at 4 and 40 °C. The fractionation factor was determined as a function of reaction time (i.e. time the precipitated product was in contact with the mother solution).

At 40 °C, for all three initial solution conditions tested no significant effect of the reaction time is detected (Figure 2d-f). Even so, from these experiments we get an estimate of the “natural” scatter of the isotopic composition, which is approximately 0.5 ‰. Although, for oxygen, we find a higher scatter, up to 1 ‰, for the experiments conducted at high ionic strength (Fig. 2c). At 4 °C, for oxygen fractionation, a significant dependence on time is found (Fig. 2g-i). After one month no equilibrium was reached. At least, for all three initial conditions, two months of reaction time were necessary to reach a stable (i.e. equilibrium) value of the fractionation. After seven months of reaction no significant difference is observed. We know that gypsum growth kinetics are considerably slower at low temperatures (4 °C, Van Driessche et al., 2010), and one would assume that after one month the precipitation process (i.e. growth of crystals) is still on going. But, for sulphur, no time dependence is found (after one month the obtained value is already very similar to those determined after 7 months) indicating that the precipitation must have stopped almost completely after one month. Hence, these results strongly support the fact that the fractionation of oxygen is a slower process, especially at low temperatures, compared to that of sulphur.

From these results we conclude that fractionation is influenced by temperature, but it strongly depends on the initial solution conditions: for low salinity and low SI a clear dependence of fractionation of gypsum and sulphate from solution with temperature is detected. At high salinities, similar to evaporitic environments, the values obtained in this work are in reasonable agreement with the values used in literature up to now.

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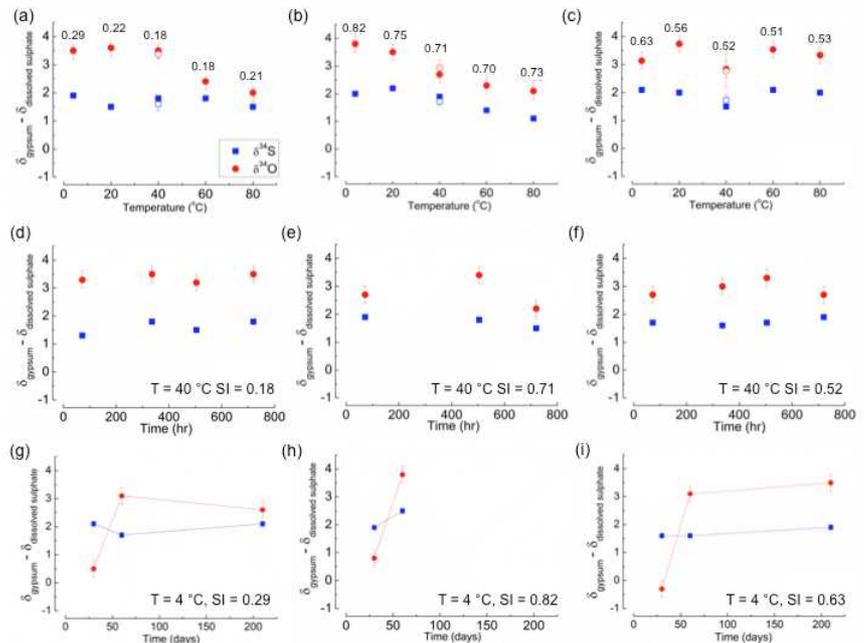


Fig. 2. Oxygen (red) and sulphur (blue) isotope fractionation between gypsum and dissolved sulphate as a function of temperature (a,b,c) and time (d-i) for three different initial solution conditions: (a,d,g) 0.03 M CaSO<sub>4</sub> + 0.2 M NaCl, (b,e,h) 0.08 M CaSO<sub>4</sub> + 4.5 M NaCl, (c,f,i) 0.08 M CaSO<sub>4</sub> + 4.5 M NaCl.

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