Stable strontium isotope fractionation in synthetic barite

Inoka H. Widanagamage [a], Edwin A. Schauble [b], Howie D. Scher [c],
Elizabeth M. Griffith [d],*

[a] *Department of Geology, Kent State University, 221 McGilvrey Hall, Kent, OH 44242, USA*
[b] *Department of Earth, Planetary, and Space Sciences, University of California, 595 Charles Young Drive East, Box 951567, Los Angeles, CA 90095, USA*
[c] *Department of Earth and Ocean Sciences, University of South Carolina, Columbia, SC 29208, USA*
[d] *Department of Earth and Environmental Sciences, University of Texas at Arlington, 500 Yates St., Arlington, TX 76019, USA*

Abstract

The mineral barite ($BaSO_4$) accommodates strontium (Sr) in its crystal structure, providing an archive of Sr-isotopes ($^{87}Sr/^{86}Sr$ and $\delta^{88/86}Sr$) in the highly stable sulfate mineral. We investigated mass dependent stable Sr-isotope fractionation ($\Delta^{88/86}Sr = \delta^{88/86}Sr_{solid} - \delta^{88/86}Sr_{solution}$) during inorganic precipitation of barite from a barium-rich solution by addition of sulfate under controlled conditions and compared this to equilibrium isotopic fractionation calculated using Density Functional Theory modeling. Sr-substituted barite is predicted to have lower $^{88}Sr/^{86}Sr$ than any other studied species, and at 25 °C will be about 0.6–0.7‰ lower than the two modeled $Sr(H_2O)_8^{2+}$-bearing salts that could approximate aqueous Sr^{2+}. This agrees in direction and order of magnitude with experimental results that estimate equilibrium Sr-isotope fractionation in barite to be 0.3‰ lower than aqueous Sr^{2+} at ~20 °C. The high ionic strength of some of the precipitating solutions (up to 1 M) and potential differences in the average coordination number of aqueous Sr^{2+} add to uncertainty in a direct comparison of the calculated equilibrium isotopic fractionation values with the experimental results.

Stable Sr-isotope fractionation varied along with the distribution coefficient of Sr [Kd(Sr) = [Sr/Ba]$_{barite}$/[Sr/Ba]$_{solution}$], which is a function of both temperature and barite saturation state. However the relationship between mass dependent isotopic fractionation and Kd(Sr) is different for conditions of changing temperature versus barite saturation state. With increasing temperature (from 5 to 40 °C), the barite phase became isotopically lighter ($\Delta^{88/86}Sr = -0.29‰$ to $-0.41‰$). Conversely, with increasing saturation state (saturation index of barite = 3.0–4.3) the barite phase became isotopically heavier ($\Delta^{88/86}Sr = -0.25‰$ to $-0.10‰$). These observations suggest chemical kinetic effects control isotopic fractionation rather than equilibrium temperature effects. The relationship with saturation state indicates the potential presence of a diffusive boundary layer. Barite crystal morphology appears to be affected by the diffusion rate of solute (sulfate) to the growing crystal surface relative to the overall growth rate of barite crystals during precipitation.

1. INTRODUCTION

The controls on mass dependent stable strontium (Sr) isotopic fractionation during barite ($BaSO_4$) precipitation were investigated to highlight potential isotopic and elemental fractionation mechanisms during trace element incorporation. This was done by precipitating barite in the laboratory from solution under various conditions (solution Sr/Ba, temperature, and saturation state) that may influence equilibrium and/or kinetic mass dependent stable Sr-isotope fractionation. Results from the experiments are compared with theoretical estimates of

* Corresponding author. Tel.: +1 817 272 0771.
  E-mail address: lgriff@uta.edu (E.M. Griffith).

equilibrium mass dependent stable Sr-isotope fractionation from Density Functional Theory (DFT) and their dependence on temperature and mineralogy including Sr coordination—this study being the first comprehensive theoretical study of Sr-isotopes relevant to natural aqueous species and precipitates.

Strontium has four naturally occurring stable isotopes: ^{84}Sr, ^{86}Sr, ^{87}Sr, and ^{88}Sr with relative abundances of 0.56%, 9.86%, 7.00%, and 82.58%, respectively. ^{87}Sr forms as the result of radioactive decay of rubidium-87 (^{87}Rb). Strontium is distributed as a trace element in sedimentary minerals (e.g., sulfates, silicates and carbonates). In radiogenic Sr-isotope studies, the isotopic ratio of stable ^{88}Sr/^{86}Sr is assumed to be constant and is used to correct for instrument and laboratory induced mass dependent fractionation during the measurement of ^{87}Sr/^{86}Sr. However, recent work using external corrections for the mass fractionation effect during measurement has revealed significant mass dependent isotopic fractionation of stable Sr-isotopes. Variations are seen in many types of natural samples such as marine carbonates, soils, rocks, plants, hydrothermal fluids, and river waters (Fietzke and Eisenhauer, 2006; Ohno and Hirata, 2007; Halicz et al., 2008; Rüggeberg et al., 2008; Krabbenhöft et al., 2009, 2010; de Souza et al., 2010; Knudson et al., 2010; Böhm et al., 2012; Raddatz et al., 2013; Stevenson et al., 2014; Vollstaedt et al., 2014).

Stable Sr-isotope fractionation mechanisms during aragonite and calcite precipitation have been investigated in the most detail to date (e.g., Fietzke and Eisenhauer, 2006; Böhm et al., 2012). Fietzke and Eisenhauer (2006) found two different temperature dependent Sr-isotope fractionation trends during the precipitation of biogenic and inorganic aragonite, which they suggested to be kinetic isotopic fractionation dependent on the relative mass differences between ^{88}Sr and ^{86}Sr and the presence or absence of Sr^{2+}-aquocomplexes. Natural coral samples (*Pavona clavus*) exhibited a strong temperature dependence of 0.033‰/°C between 23 and 27 °C while the temperature dependent isotopic fractionation of experimentally precipitated inorganic aragonite was only 0.0054‰/°C between 10 and 50 °C. Since kinetic isotopic fractionation is inversely correlated with mass, the stronger temperature dependence of the modern coral samples was interpreted as kinetic isotopic fractionation of pure Sr^{2+} ions (lower mass) whereas the inorganic aragonite had less significant temperature-dependent kinetic isotopic fractionation due to the influence of heavier Sr^{2+}-aquocomplexes (Fietzke and Eisenhauer, 2006).

Böhm et al. (2012) found that Sr-isotope fractionation in inorganic calcite during their precipitation experiments was predominantly controlled by precipitation rate. Larger mass dependent stable isotopic fractionation occurred at higher precipitation rates and no significant fractionation was seen at very low rates. This kinetic fractionation behavior probably involves chemical kinetic fractionation of hydrated Sr^{2+} ions, i.e., preferential desolvation of isotopically light Sr^{2+} (Böhm et al., 2012). Furthermore, using their calcite precipitation experiments at constant temperature and initial $(Sr/Ca)_{aq}$ they estimated that equilibrium Sr-isotope fractionation between inorganic calcite and

aqueous Sr^{2+} is very close to zero, similar to the equilibrium Ca isotopic fractionation between inorganic calcite and aqueous Ca^{2+} proposed by Fantle and DePaolo (2007). Two samples of inorganic calcite precipitated in veins during low temperature alteration of ocean crust basalt at very low precipitation rates confirmed this observation (Böhm et al., 2012). Therefore, it appears that measurable mass dependent Sr-isotope fractionation during carbonate crystal formation in most natural environments is likely a process occurring at the surface of the crystal under non-equilibrium conditions. Stevenson et al. (2014) found a similar trend in cultured coccolithophores of increasing discrimination against the heavier Sr-isotopes with increasing growth rate, which is controlled by temperature.

Earlier work by Ohno and Hirata (2007) suggested that the magnitude of Sr-isotope fractionation between carbonates and aqueous Sr^{2+} (0.1‰/amu) could be explained by isotopic fractionation under equilibrium conditions because it is 4-times smaller than that seen for Ca (DePaolo, 2004). Alternatively this could be explained by similar kinetic mechanisms affecting both Ca and Sr-isotope fractionation in carbonates as Böhm et al. (2012) suggested.

Barium is an alkaline earth metal, which is chemically similar to strontium. Barium forms a divalent cation (Ba^{2+}) with an ionic radius of 1.35 Å in 6-fold coordination, slightly larger than 1.21 Å for strontium (Sr^{2+}) (Krauskopf, 1979). Barite can be used to study Sr-isotope systematics because Sr^{2+} can readily substitute for Ba^{2+} in barite and the resulting high affinity of Sr in barite (~10,000 ppm Sr; Averyt et al., 2003). Studying mass dependent isotopic fractionation of Sr in barite could also be a useful tool to predict what stable isotope fractionation mechanisms are important in controlling similar isotopic systems such as calcium and magnesium.

We present results of stable Sr-isotope fractionation of laboratory precipitated barite and theoretical estimates of equilibrium Sr-isotope fractionation to elucidate the mechanisms that control isotopic fractionation under conditions similar to those in modern continental settings where barite precipitates from Ba-rich fluids (e.g., Younger, 1986; Senko et al., 2004; Bonny and Jones, 2007). This knowledge will inform and constrain future work on stable Sr-isotope fractionation in natural biologically-influenced barite precipitation.

2. NOTATIONS AND METHODS

2.1. Notation

The Sr-isotope composition of a sample is expressed as the deviation from a standard value, using δ-notation in per mil (‰):

$$\delta^{88/86}Sr = \left[\left(^{88}Sr/^{86}Sr_{sample} - ^{88}Sr/^{86}Sr_{standard} \right) / ^{88}Sr/^{86}Sr_{standard} \right] \times 1000$$

(1)

where $^{88}Sr/^{86}Sr_{sample}$ refers to the $^{88}Sr/^{86}Sr$ isotopic ratio of the sample and $^{88}Sr/^{86}Sr_{standard}$ refers to the $^{88}Sr/^{86}Sr$ isotopic ratio of SRM 987 (Fietzke and Eisenhauer, 2006).