Controls on stable Sr-isotope fractionation in continental barite

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ABSTRACT

Barite precipitation typically occurs when barium rich fluids mix with sulfate rich fluids, however barite found in the modern continental environment suggests that biological activity can play an important role in barite formation by oxidizing sulfur and/or concentrating barium within microenvironments. These activities induce barite precipitation, and carry with them implications for studies of barite genesis. Strontium (Sr) is incorporated into the barite crystal structure during barite formation preserving a radiogenic and stable Sr-isotope signature in barite, providing information about its formation. Here we present Sr-isotope results from three artesian sulfidic springs with ongoing barite precipitation (Zodletone Spring, Oklahoma; Stinking Spring, Utah; and Doughty Springs, Colorado) to explore the controls on stable Sr-isotope fractionation during barite precipitation in a continental setting. Apparent stable Sr-isotope fractionation for all three sites ranged from −0.6‰ to ~0.0‰ similar to previously published calculated values for equilibrium conditions and measured values of synthetic barite. However, clear relationships do not exist between water and barite chemistry in the natural systems, indicating that barite does not precipitate directly from solution, but heterogeneously within diverse microenvironments created by microbial biomass or on sediment surfaces. The dynamic microenvironments in a continental setting influence the apparent stable Sr-isotope fractionation during barite precipitation because of changing saturation conditions, Sr concentration and/or precipitation of different mineral phases (e.g., celestine). In order to better understand the geochemistry of barite deposits, future work is necessary to study the controls on radiogenic and stable Sr-isotope signatures of barite in the context of the temporally and spatially dynamic nature of the continental setting.

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1. Introduction

Barite (BaSO₄) is a widely distributed, highly stable mineral in continental magmatic, metamorphic, and sedimentary rocks. Typically, barium rich fluid mixes with sulfate rich fluid resulting in barite precipitation (Hanor, 2000; Griffith and Paytan, 2012). Barite can precipitate in natural settings due to processes associated with biological activity (e.g., Senko et al., 2004; Bonny and Jones, 2007b). For example, sulfide oxidizing bacteria in sulfur-rich springs are thought to play a major role supplying sulfate to Ba-rich waters in modern continental settings (Senko et al., 2004). In addition diatoms are thought to accumulate barium ions (Ba²⁺) in extracellular polymeric substances (EPS) inducing barite precipitation where sulfate is present (e.g., Bonny and Jones, 2007b). Few geochemical studies of barite precipitated in modern continental settings exist, but they could help in better understanding the

genesis of ancient barite deposits, and potentially be used to establish biological activities in ancient rocks (e.g., Jewell, 2000; Huston and Logan, 2004; Bottrell and Newton, 2006; Bonny and Jones, 2008b; Sanz-Montero et al., 2009) and address questions surrounding the geochemistry of barite formation in extraterrestrial materials (e.g., Burt et al., 2004).

Barite has high affinity to incorporate strontium (Sr) in its crystal structure (7000 to 10,000 ppm Sr; Averyt et al., 2003; Monnin and Cividini, 2006) since Sr is chemically similar to Ba, which makes barite an important archive of both radiogenic and stable Sr-isotope compositions. The ratio of radiogenic ^{87}Sr to non-radiogenic ^{86}Sr can be used to determine the source(s) of the solution(s) from which barite precipitated (Reesman, 1968; Maynard et al., 1995) including differentiating paleotectonic settings of sediment-hosted, stratiform barite deposits (e.g., Jewell, 2000; Clark et al., 2004) and reconstructing contemporaneous seawater composition using marine barite (e.g., Goldberg et al., 1969; Paytan et al., 1993). For these studies, the stable Sr-isotope ratio ($^{88}Sr/^{86}Sr$) is assumed to be constant and used as an internal

normalization ratio to correct for instrumental mass fractionation, which by definition erases the signature of natural mass dependent Sr-isotope fractionation in the measured sample.

Recent work using external corrections for mass fractionation effects during measurement of Sr-isotopes by mass spectrometry have revealed significant mass dependent Sr-isotope variations ($\delta^{88/86}$Sr reported and measured relative to standard SRM 987) in many types of natural samples such as soils, rocks, plants, rivers, rain, seawater, marine carbonates, and hydrothermal fluids (Fietzke and Eisenhauer, 2006; Ohno and Hirata, 2007; Halicz et al., 2008; Ruggeberg et al., 2008; Krabbenhöft et al., 2009, 2010; De Souza et al., 2010; Knudson et al., 2010; Böhm et al., 2012; Ma et al., 2013; Raddatz et al., 2013; Stevenson et al., 2014; Vollstaedt et al., 2014; Pearce et al., 2015). Results from abiotic barite precipitation experiments have shown that barite preferentially incorporates the light isotopes of Sr during precipitation from solution, in agreement with previous work on stable metal isotopes in barite and other solids (e.g., calcium stable isotopes) and Density Functional Theory modeling calculations (Widanagamage et al., 2014). The experimental work also reveals that Sr-isotope fractionation is likely controlled by chemical kinetic effects primarily because at higher temperatures barite was more fractionated from the solution opposite to what equilibrium conditions would predict. Barite saturation state was also found to influence Sr-isotope fractionation (Widanagamage et al., 2014). This initial published work demonstrated that stable Sr-isotope ratios in barite are variable and could be useful in revealing conditions during precipitation such as abiotic processes including changes in temperature and/or solution chemistry and processes associated with biological activity if unique isotopic fractionation factors can be identified. Using unique isotopic signatures to distinguish between abiotic and microbially mediated barite is important for establishing evidence of biological activities in ancient rocks and ensuring accurate interpretations of geochemical data from barite.

In this study, we aim to identify the controlling factors of stable mass dependent Sr-isotope fractionation during natural barite precipitation in modern continental settings to gain insight into various biologically mediated barite precipitation processes and to compare these results with previously published experiments that evaluated Sr-isotope fractionation in abiotic barite (Widanagamage et al., 2014). The combined use of elemental ratios (Sr/Ba) and radiogenic and stable mass dependent Sr-isotope compositions of barite will be investigated as a new set of geochemical tools to identify the mode of barite mineralization in the continental setting. Further, we will explore the possibility of sub-micron-scale heterogeneity of Sr incorporation in the solid samples and comment on its potential influence on the measured bulk elemental and isotopic measurements.

2. Study sites

Three sulfidic, warm artesian springs in the United States were sampled in order to study the stable Sr-isotope fractionation in barite precipitated in association with biological activity: 1) Zodletone Spring, Oklahoma, 2) Stinking Spring, Utah and 3) Doughty Springs, Colorado (Fig. 1).

Zodletone Spring (Oklahoma) feeds a small tributary brook (~20 m long), which flows into the southern bank of Saddle Mountain Creek in the Anadarko Basin. Barite was previously found along with other minerals such as calcite and quartz within Pleistocene stream alluvium, as well as in seasonal whitish streambed sediments (Younger, 1986; Senko et al., 2004). Anaerobic, anoxygenic phototrophic bacteria at the site oxidize sulfide to sulfate, which is thought to induce barite precipitation (Senko et al., 2004).

Stinking Spring (Utah) emerges through the normal faulted Mississippian Lodgepole Limestone Formation, which outcrops as cliffs and ledges north of the Great Salt Lake near the base of Little Mountain in the Wasatch Mountain Range (Klauk and Budding, 1984; Blacket and Wakefield, 2004; Bonny and Jones, 2007b). Thick microbial mats associated with diatoms, cyanobacteria, and sulfate reducing bacteria occur along the flow path (Bonny and Jones, 2007b). These mats are lithified by calcite precipitated from the spring water forming porous calcite deposits (tufas) that trap and preserve diatom frustules. Microcrystalline barite is found in association with diatom frustules, but not soft bodied microbes (Bonny and Jones, 2007b). It is thought that at this site diatoms bioaccumulate barium in their tissues and adsorb barium in diatom extracellular polymeric substances (EPS) inducing precipitation of primary barite (Bonny and Jones, 2007b).

Doughty Springs (Colorado) are located in the Lower Cretaceous Dakota Sandstone Formation emanating from fractures in the cliff and cauldrons in the ground on the northern bank of the North Fork of the Gunnison River in Delta County (Headden, 1905; Cunningham et al., 1996). Mineral precipitation, presumably calcite (but aragonite or barytocalcite could be present), along with barite and elemental sulfur forms a large travertine terrace, which is periodically undercut by the river (Younger, 1986). Barite is found associated with surface organic matter and seen as replacing vascular plant material along with acicular calcite and in surface crusts so that it has been described as an alteration product (Younger, 1986). Barium accumulation from the water by protozoans and algae is also thought to explain the high amount of barite precipitating in the travertine despite the low barium concentrations in the water; however solely abiotic processes have not been ruled out (Younger, 1986).

3. Methods

3.1. Water chemistry

3.1.1. In situ

Field work was conducted at all sites in summer 2011. Water temperature, pH, oxidation reduction potential (ORP), conductivity, and dissolved oxygen (DO) were measured in situ along the spring paths using a portable YSI Professional Plus multiparameter meter. Sulfide concentration and alkalinity were measured immediately at the field site using colorimetry (HACH method 8131) and titration (HACH method 8203) respectively. Duplicate samples reproduced within 11.3% and 1.8% RSD for sulfide and alkalinity respectively.

3.1.2. Anions

Filtered water samples were collected for chloride (Cl^-) and sulfate (SO_4^{2-}) analyses. An additional set of water samples were collected to analyze thiosulfate ($S_2O_3^{2-}$) concentrations and were treated with ~2 mL of $ZnCl_2$ to precipitate ZnS and prevent oxidation of sulfide to thiosulfate prior to analysis following Cunningham et al. (1996). Samples were stored on ice in the dark prior to analysis in the lab at Kent State University. Sulfate, thiosulfate, and chloride concentrations were determined using a Dionex (DX-600) ion chromatograph (IC) system. Samples were diluted with ultrapure water prior to analysis. External precision is <5% (RSD) for the IC method confirmed on duplicate analyses (n = 2) of intermediate Cl^-, SO_4^{2-}, and $S_2O_3^{2-}$ standards during the analytical run, resulting in RSD for Cl^-, SO_4^{2-} and $S_2O_3^{2-}$ of 2.3%, 0.2% and 0.1% respectively. Field duplicates (3 duplicated samples) resulted in a larger range of RSD values of <0.1% to 3.7% for Cl^-; 3.6% to 34.0% for SO_4^{2-} and 0.02% to 16.8% for $S_2O_3^{2-}$. A sample split in the lab yielded RSD for Cl^-, SO_4^{2-} and $S_2O_3^{2-}$ of 0.5%, 4.2% and 3.7% respectively.

3.1.3. Cations

Water samples were collected by syringe, filter-sterilized (0.22 μm) and acidified using trace metal grade nitric acid for cation analysis. Ba, Sr, K, Na, Ca, Mg, Fe, and Al concentrations were determined by a Perkin Elmer 3300DV inductively coupled plasma emission spectrometer (ICP-OES) at Kent State University. Bulk, mixed standard solutions were prepared with certified ICP standard solutions. Based on replicate analyses (n = 3) of an intermediate concentration standard during the analytical run the external precision for all cations is better than 2.5% (RSD). Field