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 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.

Key Words: stable strontium isotopes; continental barite; biologically mediated; artesian spring

1. Introduction

Barite (BaSO_4) 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 (Ba^{2+}) 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 (7,000 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 ($^{88}\text{Sr}/^{86}\text{Sr}$) 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 ($\delta^{88/86}\text{Sr}$ 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; De Souza et al., 2010; Knudson et al., 2010; Krabbenhöft 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 and 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 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 (Klausk 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 are 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-}) analysis. An additional set of water samples were collected to analyze thiosulfate ($\text{S}_2\text{O}_3^{2-}$) 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 $\text{S}_2\text{O}_3^{2-}$ standards during the analytical run, resulting in RSD for Cl^- , SO_4^{2-} and $\text{S}_2\text{O}_3^{2-}$ 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-} ; 0.02% to 16.8% to for $\text{S}_2\text{O}_3^{2-}$. A sample split in the lab yielded RSD for Cl^- , SO_4^{2-} and $\text{S}_2\text{O}_3^{2-}$ 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 duplicates showed variations in duplicate measurements of 0.0% to 13.2% (RSD) expect for very low concentrations of Ba in Colorado (Table 1).

3.1.4. Saturation calculations

Water chemistry data from each sampling location were used to calculate saturation indices of potential minerals using Visual MINTEQ 3.0 (Gustafsson, 2007). Saturation index (S.I.) is defined as the difference between the log of the ion activity product (IAP) and the log of the solubility product (K_{sp}) or $\log(IAP) - \log(K_{sp})$.

3.2. Barite elemental ratios

Sediment samples were collected from the spring source to the end of the discharge at all sites. Barite was separated from these bulk sediment samples using a severe digestion process to dissolve all other solid phases except barite following Griffith et al. (2008), including ashing to remove organics. Samples were examined under a FEI Quanta 200 Environmental Scanning Electron Microscope (ESEM) with EDS attachment to ensure the purity of barite was >80% in the residue prior to elemental and isotopic analysis. Barite samples (~3 mg) were dissolved 4-5 days in a 7 mL mixture of 10 mM ethylenediaminetetraacetic acid (EDTA) solution adjusted to pH >13 using potassium hydroxide (~4.14 g KOH in 2 L of 10 mM EDTA) following Averyt et al. (2003). Sr and Ba concentrations of the solutions were measured using an ICP-OES Perkin Elmer 3300DV with cross flow nebulizer and Scott-type spray chamber at Kent State University immediately after dissolution. Based on replicate analyses ($n = 3$) of the low standard during the

analytical run, the external precision for Sr and Ba were better than 2% (RSD) and reproducible within 4% for Sr/Ba.

3.3. Isotopic analysis

3.3.1. Sample preparation

Strontium isotopic analyses were done on the water and barite (sediment) samples collected from each study site. Purified barite samples were dissolved in cation exchange resin (MCI Gel, CK08P) following the method outlined in Griffith et al. (2008) and used in Widanagamage et al. (2014). Strontium was isolated from other cations in the natural waters and dissolved barite solutions using extraction chromatography with Sr Spec resin (50-100 µm mesh, Eichrom Industries, Lisle, IL, U.S.A.) at the University of South Carolina (USC) following Scher et al. (2014).

Many multiples of the required mass of Sr for isotopic analysis was loaded onto the columns (~1 µg of Sr) to minimize the relative contribution of contaminant Sr. The Sr blank determined on the barite separation and Sr-spec column procedure is <0.1% of the processed barite samples for the entire procedure, and mass balance calculations indicate that no correction for a blank was necessary in this study.

3.3.2. Mass spectrometry

Strontium isotope ratios were measured on a Neptune Plus Multicollector-Inductively Coupled Plasma Mass Spectrometer (MC-ICPMS) in the Center for Elemental Mass Spectrometry (CEMS) at USC. The multicollector allows for simultaneous detection of masses, providing precise and reliable isotopic ratio data for both radiogenic and stable isotopic measurements of Sr. Mass discrimination within the instrument is large (for Sr isotopes ~2.5% u⁻¹) and is corrected using internal and external corrections following Scher et al. (2014).

Conventional internal correction was done assuming non-radiogenic $^{86}\text{Sr}/^{88}\text{Sr}$ ratio = 0.1194 to calculate radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (Neir, 1938). All masses of Sr were collected (84, 86, 87, and 88). Samples and standards were doped with 20 ppb Zr for the external mass bias correction, and masses 90 and 91 (i.e., ^{90}Zr and ^{91}Zr) were measured. Isobaric interferences of krypton (Kr) on masses 84 and 86 and rubidium (Rb) on mass 87 arise from trace quantities of Kr in the argon supply and from Rb in low but detectable quantities resulting from incomplete separation from Sr during cation chromatography. Masses 82, 83, and 85 (i.e., ^{82}Kr , ^{83}Kr , ^{85}Rb) were measured to correct for these interferences. Isobaric interference corrections were made assuming natural isotope ratios of Kr and Rb (i.e., $^{83}\text{Kr}/^{84}\text{Kr} = 0.20175$; $^{83}\text{Kr}/^{86}\text{Kr} = 0.66474$; $^{85}\text{Rb}/^{87}\text{Rb} = 2.59231$) and correcting these ratios for mass bias using an exponential law with $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ as the reference ratio. A sample standard bracketing technique was used in order to further constrain mass bias during analyses, which improved the reproducibility of the measurements (e.g., Kramchaminov et al., 2012; Scher et al., 2014).

Using the sample introduction system described in Scher et al. (2014) (nickel sample cone, nickel skimmer (H) cone, cyclonic Scott-type spray chamber), sensitivity for Sr was 125-150 V/ppm Sr resulting in a sample size of 80-100 ng of Sr for a complete analysis. The mean and standard deviation of the isotope ratios were calculated from one block consisting of 20 cycles of 8 s integrations. Prior to each analysis on-peak blanks were measured on the acid used to dilute the samples and blank corrections were applied to the raw intensities. Blank corrections were negligible, amounting to <0.01% for masses 86, 87, 88, 90, and 91. Replicate analysis of SRM 987 yielded $^{87}\text{Sr}/^{86}\text{Sr}$ equal to 0.710285 ± 0.000020 (2SD, n=113) for the analytical session. All of the $^{87}\text{Sr}/^{86}\text{Sr}$ values reported here have been normalized to SRM 987 $^{87}\text{Sr}/^{86}\text{Sr} = 0.710248$ (McArthur, 1994). A sample of seawater collected during the GEOTRACES Intercalibration

cruise was used as a consistency standard for the method and replicate analysis yielded 0.709171 ± 0.000017 (2SD, n=11) for $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{88/86}\text{Sr} = 0.37\text{‰} \pm 0.08$ (2SD, n=11) equivalent to published seawater Sr-isotope data (e.g., Krabbenhöft et al., 2009).

3.4. Scanning electron microscopy

Samples intended for scanning electron microscopy (SEM) were collected in the field using sterile spatulas, and immediately fixed with a solution of glutaraldehyde (1%) and site water. Samples were stored on ice in the dark during their return to Kent State University. After air drying, samples were mounted (wet) on carbon tabs on the aluminum stubs and examined using a FEI (FEI Company, Hillsboro, OR) Quanta 200 Environmental Scanning Electron Microscope (ESEM) fitted with an EDAX (EDAX Inc., Draper, UT) energy dispersive X-ray spectroscopy (EDS) system.

3.5. Synchrotron x-ray microprobe analysis

Thin sections were prepared of natural and synthetic barite grains embedded into epoxy and mounted by Spectrum Petrographics, Inc. (Vancouver, WA). Standard thin sections (30 μm thick) were mounted onto high-purity quartz-glass slides. X-ray microprobe analysis was performed at beamline 13-IDE (Newville et al., 1999) at the Advanced Photon Source (APS) and included micro-X-ray fluorescence ($\mu\text{-XRF}$) mapping and micro-X-ray diffraction ($\mu\text{-XRD}$). The synchrotron x-ray beam size used for the $\mu\text{-XRF}$ images was $1.5 \mu\text{m} \times 1.5 \mu\text{m}$ at full width half-maximum using a Pt-coated Kirkpatrick-Baez (K-B) focusing optics system (XRadia). X-ray fluorescence data was collected using a four-element Si Vortex Detector (SSI). Monochromatic x-rays were selected using a water cooled Si(111) $\phi = 90$ double crystal monochromator. Maps were collected at 20 keV and data were collected at $1 \mu\text{m}$ pixel size and 25 ms dwell time per point for the following elements: K, Rb, Sr, Ba, Cu, Zn, and Fe. Fluorescence maps were

analyzed using the software package Larch (Newville et al., 2013). Fluorescence counts were normalized to the measured intensity of the incident energy of the x-ray beam (I_0) for each energy map across each line; I_0 did not change (within 1%) over each map area and for each energy. Micro-XRD patterns were collected on selected areas in transmission geometry using an area CCD camera with the incident beam energy set at 20 keV ($\lambda = 0.6200 \text{ \AA}$). The resulting images were processed with FIT2D (Hammersley, 1997). The sample-to-detector distance and geometric corrections were calculated using CeO_2 as a standard. After these corrections were applied, the 2D images were integrated radially to yield 1D diffraction patterns that could then be analyzed using standard techniques. Background subtraction, including removal of the scattering from the glass slide, and phase identification were performed using JADE 6.5 (Materials Data Inc., Livermore, CA).

4. Results

4.1. Natural water and barite geochemistry

Barite precipitation occurs at all three sites under different geochemical conditions. During sample collection, the source waters of the springs ranged in temperature from 16.5°C (Colorado – Middle Springs) to 44.2°C (Stinking Spring, Utah). The source (spring) waters are classified as sodium-chloride type in Oklahoma and Utah, and sodium-bicarbonate to sodium-chloride type in Colorado (following Back, 1966) with conductivity measurements as high as 62 mS/cm in Utah and as low as $\sim 5 \text{ mS/cm}$ in Colorado (Table 1).

The sampling locations have barium-rich (up to 0.419 mM), sulfide-rich (up to 4.28 mM) waters with Sr/Ba ratios ranging from 0.63 mol/mol (Oklahoma) to 19.29 mol/mol (Colorado), see Table 1. In all cases, the water is sulfidic and suboxic with increasing oxygen and sulfate concentrations from the spring source along the flowpath where oxidation of sulfide to

thiosulfate and sulfate occurs (Fig. 1). At all sites barite (as well as calcite, aragonite, and dolomite) is supersaturated in the waters while celestine (SrSO_4) is not (Tables 1, A1). One exception exists (CO/B1), with the lowest Ba^{2+} concentration ($< 1 \mu\text{M}$) and, therefore, barite undersaturation. The highest saturation index (S.I.) for barite is 1.86 in Stinking Creek, Oklahoma with the highest SO_4^{2-} concentration (3.738 mM). However, barite saturation index is not significantly related to SO_4^{2-} when considering all the water samples ($R^2 = 0.092$; $n = 26$). Barite saturation index does significantly ($p < 0.05$) positively correlate to total molar concentration of S (as sulfide, thiosulfate and sulfate) in solution, concentrations of Ba^{2+} and sulfide, and pH ($R^2 = 0.741, 0.445, 0.430, 0.359$ respectively).

Sufficient barite for isotopic and elemental analysis was only found in 16 sediment samples from the 26 sampling locations. Barite crystals range from 1 to 20 μm in size and form euhedral to anhedral crystals in the shape of rosettes, needle-like elongated crystals, asters, as well as other shapes shown in Fig. 2. Diatoms, biological streamers and filamentous bacterial structures were associated with mineral phases at the three sites, described in more detail in the discussions.

Barite Sr/Ba ratios range from 23.7 to 77.9 mmol/mol ($n = 16$), but are not significantly correlated with Sr/Ba ratios in solution ($R^2 = 0.131$; $p > 0.05$). However, Sr/Ba in barite is significantly (positively) related to Sr concentration in solution ($R^2 = 0.799$; $p = 0.0001$; Fig. A1). Barite Sr/Ba is also significantly correlated ($p < 0.05$) with water temperature, ionic strength and conductivity ($R^2 = 0.542, 0.783, \text{ and } 0.494$ respectively), but not the calculated saturation index of barite or any other measured solution parameter.

A large range of stable Sr-isotope compositions was measured in the barite samples (-0.43 to +0.16‰) and natural waters (-0.04 to +0.50‰) as shown in Fig. 3. The waters measured

in this study have the highest and lowest $\delta^{88/86}\text{Sr}$ values measured thus far in natural waters (Fig. 3). The barite samples analyzed are among the lowest $\delta^{88/86}\text{Sr}$ values measured in natural solid samples. Colorado waters and Utah samples show large ranges of $\delta^{88/86}\text{Sr}$ values compared to Oklahoma samples.

Barite $\delta^{88/86}\text{Sr}$ is significantly related ($p < 0.05$) to the Sr/Ba measured of the same barite samples ($R^2 = 0.347$; $p = 0.0164$), but is not significantly related ($p > 0.05$) to water $\delta^{88/86}\text{Sr}$ measured at the same location for this study when considering all three sites together ($R^2 = 0.225$; $p = 0.0636$). Water $\delta^{88/86}\text{Sr}$ is not significantly related to any measured water parameter except the $^{87}\text{Sr}/^{86}\text{Sr}$ value of the water ($R^2 = 0.485$; $p = 0.0027$) and the total molar sulfur in solution ($R^2 = 0.384$; $p = 0.0105$), a trend that is forced by the very high isotopic and total sulfur values of the three Oklahoma samples.

Barite has lower $\delta^{88/86}\text{Sr}$ values than the analyzed solution at the same sampling location in all samples, except one location from Colorado (CO/ME) whose water and barite $\delta^{88/86}\text{Sr}$ values are within error the same. This suggests that barite preferentially incorporates the light isotopes of Sr during precipitation from solution in agreement with previously published data (Widanagamage et al., 2014). Apparent stable Sr-isotope fractionation ($\Delta^{88/86}\text{Sr} = \delta^{88/86}\text{Sr}_{\text{barite}} - \delta^{88/86}\text{Sr}_{\text{water}}$) varies from +0.07 to -0.64‰ ($\pm 0.07\%$; average propagated 2SD; Fig. 4). When considering all sample locations together, there is no significant relationship ($p < 0.05$) between Sr-isotope fractionation and any measured water parameter. A significant negative relationship is seen between apparent stable Sr-isotope fractionation and the measured barite Sr/Ba ratio ($R^2 = 0.392$; $p = 0.0095$).

Radiogenic Sr-isotope measurements ($^{87}\text{Sr}/^{86}\text{Sr}$) in these same barite and water samples were significantly correlated when considering all sites together ($R^2 = 0.999$; $p < 0.0001$). The

measured barite and water $^{87}\text{Sr}/^{86}\text{Sr}$ values were all more radiogenic than surface sedimentary units suggesting deep radiogenic sources of Sr in the spring waters (Table 1). Each spring has unique $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, which are generally reflected in the $^{87}\text{Sr}/^{86}\text{Sr}$ values of the barite. However, barite $^{87}\text{Sr}/^{86}\text{Sr}$ is significantly less radiogenic than the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the water collected at the same sampling location at each site except OK/S1.

4.2. Sr speciation and distribution in natural barite

μ-XRF; μ-XRF analysis provides micron-scale spatial distribution of major, minor, and trace elements. Higher intensities in the μ-XRF image correspond to higher concentration of that particular element (Fig. 5). Micro-XRF analysis of the OK/S6 thin section sample indicated that Ba was evenly distributed within the barite grains, consistent with the presence of the barium sulfate mineral barite (Fig. 5c). In contrast, Sr was heterogeneously distributed within the barite grains (Fig. 5b). Sr spatial distribution appeared to be divided into two populations: (1) low Sr concentrations spatially correlated with Ba, and (2) Sr ‘hotspots’ that were randomly distributed within the barite grains. The dominant Sr-bearing phase(s) associated with these two pools of Sr was probed by micro-XRD, described below. Element maps of additional elements including iron (Fe), potassium (K), and titanium (Ti) indicated that these elements are not spatially correlated with Ba (Fig. 5d). These elements are likely present within silicate and/or oxide minerals that are incorporated within the barite grains, and therefore were not dissolved by the acid digestion procedure used to separate and concentrate barite for isotopic and elemental analysis.

μ-XRD; Micro-XRD analysis was used to determine the dominant Sr-bearing phase(s) in the two pools of Sr observed in the micro-XRF maps (Fig. 6). The micro-XRD patterns were

dominated by barite peaks. Given the presence of Sr identified in the μ -XRF maps, these grains are likely a Sr-bearing barite (OK/S6 b, c, d, e, j; Fig. 6). Previous work has shown that barite containing up to 0.007 weight percent Sr in barite has a diffraction pattern that is nearly identical to Sr free (pure) barite (Antao, 2012), and hence we cannot differentiate between these two phases. In contrast, some micro-XRD patterns collected showed both barite and celestine (SrSO_4) peaks (OK/S6 a, f, g, h, i; Fig. 6). In cases where the d-spacing value of a given diffraction peak overlaps between barite and celestine (e.g., $d = 2.75, 3.3$, and $3.45 \text{ \AA}$), the peak is identified as barite as it is assumed to be the overall dominant mineral phase present. Unique celestine peaks are typically identified based on the presence of diffraction peaks at d-spacing values near $3.0, 3.2$, and $3.8 \text{ \AA}$ (Jacobson et al., 1998). The presence of celestine was spatially correlated with regions in the micro-XRF maps associated with Sr hot-spots and low concentration zones. Although celestine is likely associated with the Sr hot-spots, it is important to note that these fine-scale regions overlap and cannot be differentiated here.

These results provide evidence that Sr uptake during barite precipitation is dominated by two pathways: (1) co-precipitation with barite, and (2) precipitation as a secondary sulfate phase (celestine). Although the warm spring solutions are oversaturated with respect to barite, they are under-saturated with respect to celestine. Hence, the presence of micron-scale celestine incorporated within the barite grains is a surprising and novel finding, and the mechanism for celestine formation and the implications for Sr-isotope fractionation will be discussed below.

5. Discussion

5.1. Precipitation of barite in a continental setting

Subaerial barite precipitation on the continents is rare. Only a small number of modern spring sites have been shown to precipitate barite in a continental setting (e.g., Headden, 1905;

Okamoto, 1911; Younger, 1986; Bonny and Jones, 2003; Elshahed et al., 2003; Senko et al., 2004; Bonny and Jones, 2007a, b, 2008a, b). Two potential mechanisms for barite formation in a continental setting are (1) Ba and sulfide-rich brine reaches surface oxidizing conditions or mixes with oxidizing meteoric water resulting in sulfur oxidation and barite formation (Senko et al., 2004) and (2) Ba-rich brine mixes with sulfate containing meteoric water to precipitate barite. In these brines, Ba is released during alteration of silicate, carbonate, and sulfate minerals (Hanor, 2000). Sulfate is supplied either from an oxidized solution (like meteoric water) or from abiotic or biological oxidation of sulfur in sulfidic solutions. All three of the studied sites precipitate barite from relatively deep-sourced Ba-rich sulfidic spring waters, highlighting the importance of sulfur oxidation within the waters as a process for barite formation.

Precipitation of barite in the sulfidic, low barite saturation environment characteristic of the three studied sites requires not only input of sulfate (via sulfur oxidation, e.g., Senko et al., 2004), but also a mechanism to concentrate Ba^{2+} via adsorption on mineral faces and/or within microbial biomass (Bonny and Jones, 2007b). Concentration of Ba^{2+} to mediate barite precipitation is also evident in the marine environment today. Marine (pelagic) barite is thought to precipitate in largely under-saturated seawater within microenvironments created by decaying organic material enriched in Ba (Paytan and Griffith, 2007 and references therein). Barium is concentrated in these microenvironments, inducing marine barite precipitation in mostly under-saturated seawater.

Biologically mediated Ba^{2+} accumulation is thought to be important in establishing localized barite supersaturation, and thereby passively induce “biomediated” barite precipitation and/or actively “biomineralize” barite (Bonny and Jones, 2007a). Microbial surfaces are generally negatively charged due to the presence of carboxyl and phosphoryl groups in the outer

cell membrane, EPS sheaths, or other layers (Beveridge et al., 1983; Fortin et al., 1998; Bonny and Jones, 2007a). At the Utah study site, diatoms are thought to accumulate Ba^{2+} on their cell surfaces or within EPS (Bonny and Jones, 2007b). Additional divalent cations such as strontium (Sr^{2+}) could also be incorporated in the microbial biomass and create Sr-rich microenvironments. ESEM images from the biological samples collected from all three sites show the presence of microbial biomass (e.g., bacterial filaments, diatoms, see Fig. 2) associated with barite crystals.

In laboratory experiments without microbial biomass, a high initial barite saturation index (~2.9) was required to spontaneously precipitate barite directly from a Ba-rich solution by addition of a sulfate-rich solution (i.e., homogeneous nucleation and precipitation) (Widanagamage et al., 2014). However in the field sites studied, barite is precipitated in solutions with barite saturation index $\ll 1$. We hypothesize that heterogeneous nucleation and crystal growth could play a larger role in barite precipitation in these low barite saturation state natural environments than in high saturation state environments like the laboratory experiments. It is clear that the presence of microbes, organic substances, or other minerals plays a major role in barite precipitation at all three sites in this study supporting this hypothesis that heterogeneous nucleation and crystal growth is an important process. This mechanism is also likely important for barite formation in other settings such as marine hydrothermal environments or the ocean water column (e.g., Sanz-Montero et al., 2009; González-Muñoz et al., 2012).

Diverse barite crystal morphology is seen in the study sites in the continental setting. Solution chemistry, ion diffusion rate and crystal growth rate play a role in barite crystal morphology during precipitation (Widanagamage et al., 2014). Unlike laboratory conditions, these parameters change frequently within the continental setting both temporally and spatially (e.g., wet and dry seasons, degassing of deep sourced fluids, turbulent mixing) creating diverse

crystal morphology. In contrast, marine (pelagic) barite shows uniform crystal size and shape suggesting a considerably less variable environment of nucleation and crystal growth for marine barite (Paytan et al., 2002).

Specific crystallinity and morphology of barite crystals have been linked to precipitation environment in the continental setting. For example, Bonny and Jones (2007a) identified euhedral platy barite crystals as having precipitated at liquid-liquid interfaces and high ionic strength solutions, while stellate barite formed at water-air interfaces in barite supersaturated solutions. Bonny and Jones (2008a) differentiated barite crystals grown directly from solution or nucleated on mineral surfaces (like calcite) as euhedral, tabular and rhombic while barite precipitated on microbial cell surfaces and in microbial EPS as subhedral and anhedral microcrystals. Our results agree with these previous observations, but the diversity of morphologies within each site suggests that identifying a unique barite precipitation environment based on crystal morphology is probably an oversimplification of the complex processes occurring in most continental settings (Bonny and Jones, 2008b; Widanagamage et al., 2014).

Solution chemistry, such as presence of humic substances and other organic compounds, divalent cations other than Ba^{2+} , and saturation state are also thought to influence crystal growth and morphology (e.g., Hennessy and Graham, 2002; Smith et al., 2004) and should be considered when studying barite precipitation in the continental setting. For example, spontaneous barite precipitation from solution can be prevented by the presence of humic substances or other organic compounds, which could be attributed to crystal-growth inhibition due to adsorption of organic compounds to the growing crystal surfaces (Smith et al., 2004). Future work could explore these potential relationships at the studied sites in more detail as no clear relationships

between crystal morphology and chemistry were observed within the data set collected for this study.

5.2. Incorporation of Sr in continental barite

5.2.1. Bulk Sr content of barite

Strontium is incorporated into barite recovered from each field site. The barite sample with the highest amount of Sr was at UT/S6 in the middle terrace at Stinking Spring, UT with a value of 77.54 mmol/mol (Sr/Ba). The second highest was the crust on Zedletone Spring, Oklahoma (OK/S6) with a value of 75.9 mmol/mol (Sr/Ba). The lowest Sr contents were all from Doughty Springs, CO, which has Sr concentrations in the waters almost an order of magnitude lower than the other sites in UT and OK (Table 1). The overall Sr content in continental barite is more similar to natural marine barite samples (~30 mmol/mol; Averyt and Paytan, 2003) than the high temperature (40°C) experiments reported in Widanagamage et al. (2014), which had the highest Sr content of all the experiments yielding values up to 800 mmol/mol for barite precipitated from 5 mol/mol Sr/Ba solution.

In the natural samples measured in this study, the concentration of Sr in barite appears to be related to Sr content in the waters, but not Sr/Ba ratios, temperature or saturation state unlike barite precipitated in the laboratory. Variable physicochemical and biological conditions within microenvironments where barite precipitates likely control the partitioning of Sr within the growing barite crystals. The importance of Ba accumulation on organic material and within EPS is apparent from the clear association of barite crystals and microbial biomass (Fig. 2), and the lack of a significant relationship between solution and barite chemistry (e.g., Sr/Ba ratios), which is theoretically expected and predicted from experimental data.

5.2.2. Micron-scale Sr heterogeneity

At the micron-scale, Sr content is heterogeneously distributed within the barite microcrystals for the one natural sample examined (OK/S6) and likely for the other natural samples. Furthermore, celestine is present in the natural sample (Fig. 5) despite being undersaturated in the waters (Table 1). Carbonates enrich Sr relative to Ba with weight ratios in excess of 1000 and are thought to influence the precipitation and occurrence of celestine in the geologic record (Hanor, 2000). On the micron-scale, carbonate precipitation and dissolution could serve as a mechanism to create heterogeneous nucleation environments resulting in precipitation of celestine nucleating on the carbonate. Carbonate minerals are observed in the SEM images of unprocessed sediment samples (Fig. 2) as all sites are supersaturated with respect to calcite, aragonite and dolomite. Altogether, the presence of celestine supports the hypothesis that many of the barite crystals precipitating in the continental setting nucleate heterogeneously and their growth is influenced by formation of microenvironments within the larger depositional setting. These microenvironments are highly dynamic being influenced by changes in physical and chemical parameters due to the hydrologic setting and possibly more importantly by the organisms that live there.

5.2.3. Source of Sr in barite

Radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of barite should indicate the source of Sr in the precipitated barite (Paytan et al., 2002). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios measured in the barite samples were similar but not identical to the measured spring and discharge water $^{87}\text{Sr}/^{86}\text{Sr}$ ratios at the same sampling locations. All barite $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were significantly less radiogenic than the water $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (except OK/S1). For example, in Oklahoma, barite from the creek ($^{87}\text{Sr}/^{86}\text{Sr} = 0.710127$) is significantly less radiogenic than creek water ($^{87}\text{Sr}/^{86}\text{Sr} = 0.710208$) and spring water ($^{87}\text{Sr}/^{86}\text{Sr} = 0.710276$). This implies that the source of Sr in the barite was from a mixture of the spring

waters and a less radiogenic component. One explanation is that radiogenic spring water may mix with less radiogenic meteoric water to various degrees throughout the year in the creek. This could lead to barite precipitates that presumably precipitate throughout the year being less radiogenic than the water collected during the summer when rainfall was exceptionally low. Meteoric water is likely less radiogenic than the Zodletone Spring water since underlying Cambro-Ordovician carbonate rocks have lower $^{87}\text{Sr}/^{86}\text{Sr}$ ($^{87}\text{Sr}/^{86}\text{Sr} = 0.70890$ to 0.70919 ; Land and Elmore, 1995) values than the spring water ($^{87}\text{Sr}/^{86}\text{Sr} = 0.710276$). The creek water ($^{87}\text{Sr}/^{86}\text{Sr} = 0.710208$) was also less radiogenic than the spring water during the summer field work supporting this hypothesis. At times when rainfall is low, the water is probably more radiogenic than at other times when meteoric water dilutes the radiogenic spring water to a greater extent.

In Utah and Colorado, barite was similarly less radiogenic than the waters collected. Mixing of radiogenic spring water with less radiogenic Sr sources or meteoric water may also explain the differences at these sites. Altogether this suggests variable sources of Sr to the precipitating barite, both spatially and temporally, and an integrated barite geochemical signature for the sediment sampling methods used in this study. Sampling of water throughout the year (i.e., at different seasons) is required at each site to understand fully if spatial variations in water chemistry throughout the year could explain the measured barite values.

5.3. Processes controlling stable Sr-isotope fractionation in continental barite

The apparent Sr-isotope fractionation seen in this study (Fig. 4) is generally similar in magnitude to both that measured in experiments that are kinetically influenced, and calculated theoretically under equilibrium conditions (Widanagamage et al., 2014). There does not appear to be a unique, biologically influenced Sr-isotope fractionation in the natural samples measured in this study. However the controls on the Sr-isotope fractionations seen in the experiments (i.e.,

saturation state and temperature influencing Sr distribution coefficients and Sr-isotope fractionation) are not controlling the Sr-isotope fractionations measured in the natural samples. Several processes (e.g., mineralogy, equilibrium temperature effects, precipitation rate or kinetic effects influenced by saturation state or microbial biomass) could influence Sr-isotope partitioning between phases and will be explored in the sections that follow.

5.3.1. Mineralogy control

The barite crystals (solid phase) had the lowest $\delta^{88/86}\text{Sr}$ values of any of the samples measured in this study, although some water samples had lower $\delta^{88/86}\text{Sr}$ values than other barites precipitated at field sites that had higher water $\delta^{88/86}\text{Sr}$ values (Fig. 3). It has been shown both experimentally and theoretically that barite precipitated from solution enriches the light Sr-isotopes preferentially (Widanagamage et al., 2014). In equilibrium calculations that approximate Sr-isotope fractionation between solution and solid mineral phases, barite is the isotopically lightest phase modeled (Schauble and Griffith, 2011; Widanagamage et al., 2014). Strontianite (SrCO_3) shows little to no fractionation of stable Sr-isotopes from ‘solution’, and celestine (SrSO_4) is between strontianite and barite (Widanagamage et al., 2014).

Diffraction data shows that the dominant Sr-bearing phase in the sample tested is Sr-bearing barite. However, celestine peaks were identified at some spots in the sample changing the local Sr coordination environment and likely the partitioning of Sr-isotopes. This is because different Sr-bearing phases have different fractionation factors suggested by the calculated theoretical equilibrium fractionation factors (Schauble and Griffith, 2011; Widanagamage et al., 2014) and data collected to date (Fig. 3). Changes in local coordination environment, due to the presence of multiple Sr-bearing phases within the samples, will affect the bulk Sr-isotope signature and apparent isotope fractionation between solid and solution if the Sr-isotope

fractionations are very different between the phases and a significant amount of Sr is in more than one phase. This is expected to be the case for samples with barite and celestine as described below.

The isotopic difference due to equilibrium effects between celestine and barite (at 25°C) is approximately 0.20‰, with celestine being less fractionated from solution than barite (Widanagamage et al., 2014). Using this estimate, the minimum amount of celestine (SrSO_4) that would result in a measurable difference (of at least 0.7‰) in the isotopic composition of the bulk sample relative to a ‘true’ barite value is only 4 mol % celestine (assuming pure celestine as one end member and barite with 7.6 mol % Sr – the value measured in OK/S6 sample as the other end member). However celestine is likely not pure and probably contains Ba (and other cations) since it forms in solid solution with barite (Hanor, 2000). So this is an estimate of the minimum amount of celestine that would affect the bulk Sr-isotope measurement. Nonetheless, this back-of-the-envelope calculation suggests that celestine, if present, should influence bulk Sr-isotope measurements if the Sr-isotope fractionation is very different from barite as suggested by equilibrium theoretical calculations.

5.3.2. *Physicochemical controls*

Equilibrium temperature isotope effects indicate reduced Sr-isotope fractionation at higher temperatures, while kinetic isotope effects would result in larger Sr-isotope fractionation at higher temperatures if this increase in temperature affects crystal growth [see discussion in Widanagamage et al. (2014)]. However, water temperatures measured during field work were not significantly related to apparent Sr-isotope fractionation. There is no relationship between temperature and saturation state but there appears to be a relationship between temperature and barite Sr/Ba. However the locations of samples from high temperature waters are from field sites

that have high water Sr concentrations, and this is likely the cause of the higher Sr/Ba ratios in barite and not the increased temperature. It should be noted, however, that Sr/Ba ratios in water are not related to Sr/Ba in barite suggesting that microenvironments have Sr/Ba ratios different from the waters, and these microenvironments likely control barite Sr/Ba ratios. No measured physical or chemical parameter is significantly correlated with barite Sr/Ba, except at Middle Spring (Doughty Springs, Colorado), which has a significant relationship between barite Sr/Ba and sulfate concentrations. Furthermore a significant relationship exists between temperature and $\delta^{88/86}\text{Sr}$ of barite but it is not as strong as the correlation between temperature and barite Sr/Ba suggesting that if temperature is important in partitioning of Sr in barite it is not controlling Sr-isotope fractionation.

During controlled experiments, barite saturation state was found to influence the partitioning of Sr in barite and the Sr-isotope fractionation, indicating a kinetic control on Sr-isotope fractionation from supersaturated solutions (Widanagamage et al., 2014). However, in this study, barite (or celestine) saturation state was not related to measured barite Sr/Ba ratios or Sr-isotope compositions and thus does not control the Sr-isotope composition. The barite saturation state in the natural waters was much lower than that for the abiotic laboratory experiments, which probably limits its homogeneous precipitation from solution (which is the hypothesized mode of precipitation in the controlled experiments). This supports the hypothesis that Ba is concentrated in microenvironments within organic material or on mineral surfaces effectively raising the saturation state of barite locally, and resulting in barite precipitation in natural waters.

Sr/Ba in barite is inversely related to $\delta^{88/86}\text{Sr}$ in barite (and apparent Sr-isotope fractionation), but there is no clear physical or chemical control across all field sites (Fig. 7).

This correlation is opposite to the relationship expected if the higher Sr/Ba ratios in the bulk samples were related to increases in the amount of celestine in the sample (which should be theoretically less fractionated from solution than barite). Instead, we suggest that Sr partitioning in barite is related to conditions within the microenvironments where we hypothesize barite precipitates in natural waters. There is a large spread in apparent Sr-isotope fractionation values versus barite Sr/Ba ratios (Fig. 7) supporting the hypothesis that in the natural continental setting the microenvironments where barite precipitates are highly variable.

5.3.2. Biochemical controls

Barite precipitation in association with biological material is hypothesized to be an important process at all three of the study sites in the continental setting. Few studies have been done to investigate the potential influence of bio-induced mineralization on isotope fractionation of similar alkaline earth metal isotope systems. Magnesium (Mg) isotope fractionation during hydrous Mg carbonate precipitation in a lacustrine system has been investigated in detail both in the lab and in the field (Shirokova et al., 2013). Although cyanobacterial photosynthesis was deemed to be necessary to induce mineralization by increasing solution pH, increasing fluid saturation state, and potentially providing nucleation sites, the presence of biofilms and other heterotrophic bacteria had an insignificant effect on the overall Mg-isotope fractionation factor compared to trends observed in laboratory results (Shirokova et al., 2013 and references therein). Results presented in this paper suggest a similar conclusion can be drawn for Sr-isotope fractionation during bio-induced mineralization of barite - that the presence of biological material although critical for precipitation of barite in the natural system have an insignificant effect on the overall Sr-isotope fractionation factor compared to trends in isotopic fractionation seen in abiotic experiments in the lab.

6. Conclusions

Continental barite examined in this study was significantly depleted in the heavy stable isotopes of Sr relative to the water from which it precipitated, with an apparent Sr-isotope fractionation between barite and solution ranging from $\Delta^{88/86}\text{Sr} = \sim 0.0$ to -0.6‰ under various conditions. This apparent Sr-isotope fractionation was generally similar in magnitude and direction to both measured synthetic barite samples and calculated values for equilibrium conditions (Widanagamage et al., 2014). Neither temperature nor saturation state controlled Sr partitioning or apparent stable Sr-isotope fractionation during barite precipitation for all three sites. Relationships between water and barite chemistry measured in this study are not apparent suggesting that barite does not precipitate directly from solution (i.e., homogeneously), but heterogeneously on microbial biomass or mineral surfaces. We hypothesize that microbial biomass in the natural continental setting creates microenvironments which changes the physicochemical parameters, thus locally influencing stable Sr-isotope incorporation during barite precipitation. Negatively charged microbial surfaces are likely important in concentrating Ba (and Sr) in continental settings where barite saturation state is low, but nonetheless barite precipitation occurs. Future work is necessary to carefully study the dynamics of the microenvironments in order to understand the factors influencing stable Sr isotope fractionation during barite precipitation in low saturation state environments. Furthermore, evidence for the presence of celestine in addition to Sr-bearing barite at the micron scale suggests that formation of celestine will also exert a strong control on apparent stable Sr-isotope fractionation in the continental setting if present in sufficient quantities.

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Figure Captions

Figure 1. Study site sample locations in the United States with mineral precipitation at/near spring and drainage path. Flow direction indicated with blue arrows. T = temperature in degree Celsius (°C). DO = dissolved oxygen concentration in mg/L.

Figure 2. Scanning electron microscope backscatter images of sediment collected in this study. Zodletone Spring, Oklahoma: A. Spring sediment (unprocessed) sample with bacterial filaments (circled) around silicate sediment grain showing the association with barite (white) crystals in what appears to be EPS; B. Another image from same unprocessed, preserved sample (OK/S6) showing rounded barite (white) crystals; C. Concentration of barite crystals grown in a circular pattern from unprocessed, preserved sediment sample at the end of the drainage path (OK/S1); D. Intergrown tabular barite (white) crystals in a chemically processed sample at the same location as C; E. Subhedral platy and euhedral to rounded barite (white) crystals chemically separated (processed) from sediments sampled in Saddle Mountain Creek (OK/S7). Stinking Spring, Utah: F. Massive barite (white) replacement of what appears to be biological material and anhedral barite (UT/S5); G. Barite (white) crystals associated with bacterial filaments (UT/S6); H. Barite (white) replacement of a diatom alongside anhedral barite (UT/S7); I. Needles and asters of barite (white) from a processed sample (UT/S7). Doughty Springs, Colorado: J. Large (~20 µm) rosettes and tabular barite crystals in an unprocessed, preserved sample from the Middle Springs (CO/ME); K. Barite asters and needles within a mix of organics, sulfur and calcite grains in an unprocessed, preserved sample from Drinking Spring (CO/D2); L. Rounded crystals and needles of barite infilling or replacing structure in Bathtub Spring (CO/B1).

Figure 3. Natural samples from marine and continental Earth systems analyzed for stable Sr-isotope compositions. Blue bar indicates value for modern seawater reported in previously published studies. Igneous and metamorphic rocks from Ohno and Hirata (2007), De Souza et al. (2010), and Pearce et al. (2015); hydrothermal fluids from Krabbenhöft et al. (2010) and Pearce et al. (2015); continental barite (solid gray) and associated waters (solid black) from this study; modern rivers, alpine water, rain and snow from De Souza et al. (2010), Krabbenhöft et al. (2010), De Souza et al. (2010); terrestrial plants, speleothem calcite, loess, continental dust, groundwater, and terra rossa soil from Halicz et al (2008), De Souza et al. (2010), and Pearce et al. (2015); terrestrial bones from Knudson et al. (2009); sclerosponges from Fietzke et al. (2008); brachiopods from Vollstaedt et al. (2014); planktonic foraminifer from Krabbenhöft et al. (2010) and Böhm et al. (2012); halimeda, coccoliths and continental shelf taxa from Krabbenhöft et al. (2010); cold water corals from Ruggeberg et al. (2008), Raddatz et al. (2013); and tropical corals from Fietzke and Eisenhauer (2006), Halicz et al. (2008), and Krabbenhöft et al. (2010).

Figure 4. Stable Sr-isotope composition for natural continental barite samples and associated waters at Stinking Spring, Utah (gray triangles), Doughty Springs, Colorado (solid squares), Zodletone Spring and Stinking Creek, Oklahoma (open diamonds) relative to SRM 987. Apparent fractionation factor lines in permil ($\Delta^{88/86}\text{Sr} = \delta^{88/86}\text{Sr}_{\text{barite}} - \delta^{88/86}\text{Sr}_{\text{water}}$) are drawn for reference. Light gray data from experimental results of Widanagamage et al. (2014). Error bars are 2SD of replicate analyses on the MC-ICPMS.

Figure 5. Reflected light image (A) with 100 μm scale bar, and $\mu\text{-XRF}$ maps (at the same scale) of sample OK/S6 (processed barite sediment). The map shows the intensity of Sr (B)

distribution within barite (brighter yellow areas represent higher Sr concentrations), Ba (C), and Fe (D). Maximum normalized intensity values shown in top right corner on each μ -XRF image. μ -XRF maps were normalized by incident X-ray beam intensity (I_0).

Figure 6. Micro-XRD patterns for spots a through j identified in Fig. 6 for OK/S6 (processed barite sediment). Barite (b) and celestine (c) dominated the majority of the identified peaks. Unlabeled peaks are dominated by feldspar, quartz, and dolomite, which were added to the epoxy during thin section preparation for increased structural integrity. Reference lines for barite (Jacobson et al., 1998) and celestine (Jacobson et al., 1998) are also shown.

Figure 7. (A) Sr/Ba ratios (mmol/mol) vs. stable Sr-isotope composition measured in natural continental barite samples, and (B) vs. apparent Sr-isotope fractionation ($\Delta^{88/86}\text{Sr} = \delta^{88/86}\text{Sr}_{\text{barite}} - \delta^{88/86}\text{Sr}_{\text{water}}$) relative to SRM 987. Stinking Spring, Utah (gray triangles), Doughty Springs, Colorado (Middle Springs = solid squares; Drinking Spring = open squares; Bathtub Spring = gray square), Zodletone Spring and Stinking Creek, Oklahoma (open diamonds). Error bars are 2SD of replicate analyses on the MC-ICPMS.

Figure 1

FIGURES

a. Zodletone Spring, Oklahoma

b. Stinking Spring, Utah

c. Doughty Springs, Colorado

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Supplementary Figure A1.

Sr concentration (mM) in waters vs. Sr/Ba (mmol/mol) in barite. Stinking Spring, Utah (gray triangles), Doughty Springs, Colorado (Middle Springs = solid squares; Drinking Spring = open squares; Bathtub Spring = gray square), Zodletone Spring and Stinking Creek, Oklahoma (open diamonds).

Table 1
Click here to download Table: Table 1.xlsx

Sample ID	Distance (m) from the source	Temperature °C	Conductivity μS/cm	DO mg/L	pH	Sr mM	Ba mM
OK/S6	0	20.5	16,635	0.50	7.32	0.259	0.409
OK/S5	15	20.9	16,586	1.58	7.44	0.264	0.416
OK/S4	27	21.1	16,115	2.02	7.31	0.263	0.418
OK/S3	39	21.3	16,738	2.54	7.43	0.261	0.418
OK/S3 field duplicate		21.9	16,873	2.70	7.38	0.268	0.418
OK/S2	46	21.4	16,539	4.80	7.40	0.266	0.415
OK/S1	52	21.4	16,067	5.17	7.71	0.267	0.419
OK/S7	67	33.6	177	1.60	7.92	0.186	0.015
UT/S1	0	44.2	62,505	0.74	6.56	0.345	0.071
UT/S1 lab duplicate			62,505			0.340	0.073
UT/S2	16	43.6	61,767	1.05	6.68	0.311	0.066
UT/S3	32	42.1	60,675	0.64	6.79	0.323	0.068
UT/S4	40	41.6	60,480	0.19	6.84	0.308	0.066
UT/S5	47	39.1	58,374	3.13	6.79	0.320	0.068
UT/S6	57	37.2	57,120	3.87	6.84	0.311	0.071
UT/S7	68	34.4	15,560	6.72	7.44	0.327	0.073
UT/S8	83	35.1	53,783	7.70	7.48	0.353	0.077
CO/MW	0	16.5	4,600	0.97	6.30	0.034	0.005
CO/M	0	18.1	4,785	2.95	6.62	0.035	0.006
CO/M lab duplicate						0.036	0.006
CO/ME	3	18.4	4,834	3.12	6.61	0.036	0.008
CO/ME1	5	18.4	4,817	4.48	6.71	0.035	0.006
CO/ME2	10	19.5	4,866	5.34	7.03	0.036	0.007
CO/ME3	18	21.5	4,890	4.44	7.41	0.037	0.006
CO/ME4	22	24.2	5,338	3.75	7.62	0.036	0.002
CO/D1	0	16.5	4,349	3.20	6.51	0.028	0.000
CO/D2	2.4	16.5	4,370	3.30	6.75	0.036	0.002
CO/D2 field duplicate		17.3	4,325	3.34	6.78	0.037	0.004
CO/B1	0	16.6	4,438	1.57	7.43	0.035	0.002
CO/B2	4	20.4	4,755	5.50	7.65	0.034	0.002

^aS.I. =Saturation index calculated using Visual Minteq 3.0

^bn = Number of stable Sr isotope measurements

^c2SD = 2 standard deviation based on replicates of stable isotope measurements

^dpropagated error = sqrt[(2SD of $\delta^{88/86}\text{Sr SrNO}_3$)² + (2SD of $\delta^{88/86}\text{Sr barite}$)²]

n/a = not applicable