



Celestine in a sulfidic spring barite deposit - A potential biomarker?



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ABSTRACT

We have documented the presence of celestine (SrSO_4) within sediment accumulating at an artesian sulfidic spring (Zodletone Spring, Oklahoma) dominated by barite (BaSO_4) precipitation associated with microbiological activity. The distribution and speciation of Sr in solid phases was determined by synchrotron-based micro-X-ray fluorescence spectroscopy and micro-X-ray diffraction, and particle morphology and texture was determined using electron microscopy. In all the natural sulfidic spring samples and lithified tufa sample, celestine was detected in fine-grained micron-scale Sr-rich phases but not in euhedral, Sr-poor grains. In parallel laboratory-based precipitation experiments, celestine was not observed even when solutions contained high Sr/Ba. Thermodynamic predictions alone do not account for the presence of micron-scale celestine in the sulfidic spring, and they do not account for the differences in Sr presence and distribution in naturally-occurring versus synthetic grains. While the mechanism is unclear, based on this evidence we hypothesize that the combination of bacterial surfaces and microenvironments within the crusts and microbial mats creates a synergistic effect where Sr is preferentially exchanged over Ba between the overlying stream water and the pore water within the mats allowing celestine to precipitate. Ultimately, our results point to an important role of biological activity for preferential Sr uptake. The presence of micron-scale celestine in ancient barite deposits can therefore potentially be used as a biomarker for conditions similar to modern sulfidic springs.

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1. Introduction

Barite (BaSO_4) precipitates in the natural environment today in a variety of settings, some clearly associated with biological activity. Examples of biologically associated processes that induce barite mineralization include organic matter decomposition in marine settings (e.g., (Dehairs et al., 1980; Dymond et al., 1992)) with marine bacteria possibly providing appropriate microenvironments for barite precipitation (Torres-Crespo et al., 2015), sulfide oxidation by bacteria in sulfidic springs and cold seeps adding sulfate to barium-rich waters (Senko et al., 2004; Stevens et al., 2015), and barium accumulation in diatom extracellular polymeric substances within the continental interior (Bonny and Jones, 2007b). In low barite saturation state environments typical of most aqueous systems, the microenvironments created by microbial biomass or sediment surfaces appear to be essential for

heterogeneous precipitation of barite (e.g., Stevens et al., 2015; Torres-Crespo et al., 2015; Widanagamage et al., 2015). As such, microbiological activities can potentially play two roles in barite deposition: (1) give rise to barite supersaturated microenvironments in otherwise undersaturated fluids, and (2) produce sulfate in the absence of O_2 (e.g., phototrophic sulfide oxidation) and/or at rates exceeding those of the abiotic oxidation of sulfide by O_2 (e.g., chemolithotrophic sulfide oxidation). This clear association of barite formation with biological activity has been previously suggested to provide evidence for the presence of biological activity in ancient rocks (e.g., (Jewell, 2000; Martín-Algarra, 2000; Bonny et al., 2008; Sanz-Montero et al., 2009)). However, the use of barite as a biomarker is complicated by the many varied precipitation processes including abiotic precipitation which can occur when Ba-rich waters mix with sulfate-rich waters or Ba-rich sulfidic waters become oxidized, for example in specific mineral springs or marine hydrothermal or cold seep systems (e.g., (Hanor, 2000; Bonny and Jones, 2007a)).

Barite also precipitates in solid solution with celestine (SrSO_4), although there is a clear bimodal elemental distribution within these phases: most barite contains <7 mol% SrSO_4 and most celestine contains <4 mol% BaSO_4 (Hanor, 1968; Prieto et al., 1993; Prieto et al., 1997). Recent work has suggested that sulfate precipitation, in porous media

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where heterogeneous nucleation and growth occurs, results in the formation of relatively pure barite and celestine with little solid solution forming (Poonoosamy et al., 2016). Both minerals have low solubilities, but barite is far less soluble than celestine. Thus Ba^{2+} is much more strongly partitioned into the solid phase over Sr^{2+} . In addition, the partition coefficient of Sr in barite is low (Hanor, 2000). Therefore, it is expected that when barite saturation is reached in a natural system, barite will precipitate out of solution with relatively low concentrations of Sr. Celestine could precipitate if Sr/Ba ratios in solution evolved to favor precipitation of celestine over barite. However, this would only occur based on thermodynamic considerations in the absence of Ba concentrations in the bulk fluid sufficient to precipitate barite, or if other processes are in play that induce incorporation of Sr into the solid phases during barite precipitation. Furthermore, both minerals remain resistant to dissolution in the rock record unless sulfate-reducing conditions develop.

The incorporation of Sr in barite has been useful as a recorder of solution chemistry and mode of precipitation in recent and geologic samples. Radiogenic Sr determination ($^{87}\text{Sr}/^{86}\text{Sr}$) can differentiate the source of Sr, whether it is contemporaneous seawater, hydrothermal/magmatic in origin, or from diagenetic alteration of preexisting rocks, all of which can be considered to be related to the genesis of the fluids from which the mineral precipitates (Burke et al., 1982). The stable isotopic ratio of Sr ($^{88}\text{Sr}/^{86}\text{Sr}$) in barite is related to both the source of Sr and mode of precipitation (Widanagamage et al., 2014, 2015). It has also been shown that the stable Sr isotopic ratio of a precipitated solid is dependent on the mineralogy, as distinct isotopic differences (i.e., fractionations) between Sr in barite and Sr in celestine were determined using Density Functional Theory modeling (Widanagamage et al., 2014).

Previous work by our group (Widanagamage et al., 2015) has indicated the potential importance of heterogeneous and complex micro-scale environments in controlling the fate and transport of Sr during sulfate precipitation. Evidence for the presence of celestine in addition to Sr-bearing barite at the micron scale suggested that the formation of celestine may exert a strong control on the apparent stable Sr isotope fractionation of a bulk sample from the continental setting if present in sufficient quantities. However, the extent of the celestine precipitation as a function of changing water chemistry through a spring discharge system and the potential important role of biologically-driven precipitation remain unclear.

In the current work, we aim to understand the microcrystalline mineralogy of solids precipitated in a natural environment in order to best interpret their trace element chemistry and isotopic compositions. In particular, the association with microbiological activity or structures in a natural system could impart heterogeneity in the minerals precipitated not predicted by thermodynamics or solution chemistry. Although the morphology, texture and bulk Sr compositional variations in barites are known for environments where precipitation appears to be dominated by abiotic processes (e.g. (Paytan et al., 2002; Averyt and Paytan, 2003; Van Beek et al., 2003; Averyt and Paytan, 2007)), it is unclear how these variables are affected by biological activity in heterogeneous micro-environments at the sub-micron-scale.

In this paper, we systematically document the sub-micron-scale heterogeneity of Sr incorporation and mineralogy of natural and experimental samples using electron microscopy and synchrotron-based micro-X-ray fluorescence mapping and micro-X-ray diffraction. We compare Sr uptake by natural and synthetic barite to determine if local, biologically induced precipitation of sulfates in microenvironments can result in micron-scale celestine.

2. Methods and material

2.1. Field site description

Samples were collected from an artesian sulfidic spring (Zodletone Spring at the southern perimeter of the Anadarko Basin in southwestern

Oklahoma, Fig. 1) where barite precipitates today. The large spring, surrounded by concrete walls, lies in a tennis-court-sized area of bare soil (Younger, 1986), feeds a small brooklet (drainage ~20 m long) that winds down towards Saddle Mountain Creek entering it as a small cataract (~1.5 m high). The thickness of the deposit is not known, but it appears to have accumulated over time from indurated tufa from previous spring discharge points and channels. Bulk water and solid chemistry have been previously investigated (Younger, 1986; Senko et al., 2004; Widanagamage et al., 2015). The chemistry of the spring water reflects a mixture of deeper basinal brines with some shallow groundwater (Younger, 1986). Barite is found with calcite and quartz within the Pleistocene stream alluvium, as well as in seasonal whitish streambed sediments (Younger, 1986; Senko et al., 2004). These minerals are all saturated in the waters as are fluorite, aragonite, and dolomite, however witherite (BaCO_3) and celestine (SrSO_4) are not (Senko et al., 2004; Widanagamage et al., 2015).

Three samples were investigated from (1) the crust on the spring wall, (2) the end of the drainage (small cataract), and (3) Saddle Mt. Creek bed (<30 cm water depth). These three sites were chosen where barite is currently found because one site is the location where the spring emanates at the surface and the other two sites are downstream of the first location and represent change in hydro-geomorphic and geochemical conditions (Table S1). Barite was concentrated using a modified sequential acid leaching procedure to separate refractory minerals, such as barite from the bulk sediment prior to analysis (Widanagamage et al., 2015). A lithified (indurated) hand sample was also collected nearby (<50 m away from the current spring location) and analyzed without any additional processing.

Little work has been done to characterize microbial communities and activities within Saddle Mt. Creek [also referred to as "Stinking Creek" in the literature (Senko et al., 2004; Luo et al., 2005)] or the area where the spring water discharges into the creek, but both the spring source and microbial mats/mineral deposits along the stream have been well characterized (Elshahed et al., 2003; Luo et al., 2005; Youssef et al., 2010; Spain et al., 2015). Microbial communities associated with the spring source and mats in the stream have been shown to be similar, and dominated by phylotypes attributable to sulfur metabolizing lineages (Elshahed et al., 2003; Luo et al., 2005; Spain et al., 2015). A notable difference between the spring source and mats in the stream (or drainage) is that mats contained a higher relative abundance of Cyanobacteria and Chloroflexi, which are likely mediating anoxygenic, phototrophic sulfide oxidation (Elshahed et al., 2003; Bühring et al., 2011). Indeed, evidence of anoxygenic phototrophic sulfide oxidation has been repeatedly observed throughout the Zodletone Spring system, and given the anoxia reported in the system, it is unlikely that sulfide oxidation by O_2 (whether abiotic or microbially-mediated) substantially contributes to sulfide oxidation (Elshahed et al., 2003; Senko et al., 2004; Luo et al., 2005; Bühring et al., 2011; Spain et al., 2015). As such, all sulfate produced in the system is likely biogenic (Senko et al., 2004). The anoxic conditions in the system are further illustrated by the observation of maximal sulfate reducing bacterial activity noted at the water-mat interface (Elshahed et al., 2003). Taken together, these observations indicate that microbiological activities are largely driven by anaerobic sulfur metabolism, including phototrophic and chemotrophic sulfide oxidation, sulfur disproportionation, and sulfate/sulfur reduction (Elshahed et al., 2003, 2004; Senko et al., 2004; Spain et al., 2015), and that the generation of sulfate is via anoxygenic phototrophic microbial activities.

2.2. Synthetic barite precipitation

Three samples of experimentally synthesized barite samples precipitated from a Ba and Sr-rich solution by adding sulfate under controlled conditions in the laboratory (Widanagamage et al., 2014) were prepared as thin sections for the current study as described in Section 2.3. The range of chemistry of the experimental solutions was generally similar to the spring and creek, except Ba and Sr concentrations

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