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Barite deposition resulting from phototrophic sulfide-oxidizing bacterial activity

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Abstract—Barite ($BaSO_4$) deposits generally arise from mixing of soluble barium-containing fluids with sulfate-rich fluids. While the role of biological processes in modulating barium solubility has been shown, no studies have shown that the biological oxidation of sulfide to sulfate leads to barite deposition. Here we present an example of microbially mediated barite deposition in a continental setting. A spring in the Anadarko Basin of southwestern Oklahoma produces water containing abundant barium and sulfide. As emergent water travels down a stream to a nearby creek, sulfate concentration increases from 0.06 mM to 2.2 mM while Ba^{2+} concentration drops from 0.4 mM to less than 7 μM. Stable isotope analysis, microbial activity studies, and in situ experiments provide evidence that as sulfide-rich water flows down the stream, anaerobic, anoxygenic, phototrophic bacteria play a dominant role in oxidizing sulfide to sulfate. Sulfate then precipitates with Ba^{2+} producing barite as travertine, cements, crusts, and accumulations on microbial mats. Our studies suggest that phototrophic sulfide oxidation and concomitant sulfur cycling could prove to be important processes regulating the cycling of barium in continental sulfur-containing systems.

1. INTRODUCTION

Authigenic sea floor barite precipitation and diagenetic barite formation in the subsurface have been extensively studied due to their potential insight into oceanic paleoproductivity and economic importance, respectively. Barite deposits in these two environments have been well characterized, but there are few reports regarding the occurrence of recent surficial, continental barite deposits.

The role of biologic activity in aquatic barite deposition is well known. Barite accumulation on the floor of large water bodies has been proposed as an indicator of productivity by planktonic organisms (Finlay et al., 1983; Stroobants et al., 1991; Cattaldo et al., 1998; Schenau et al., 2001). Planktonic microorganisms may actively or passively accumulate barium (as Ba^{2+} or barite) (Gooday and Nott, 1982; Finlay et al., 1983; Wilcock et al., 1989; Bertram and Cowen, 1997; Cattaldo et al., 1998). As planktonic organisms accumulate barium and eventually die, they settle to bottom sediments. As the organisms decompose, barite saturated microenvironments develop and barite then precipitates (Varnavas, 1987; Stroobants et al., 1991; Stamatakis and Hein, 1993; Cattaldo et al., 1998; Naehr et al., 2000).

Another somewhat different seafloor system has been described in which massive barite deposits occur (up to 10 m in depth) (Greinert et al., 2002). In this system, referred to as a "Giant Cold Seep," sulfide and barium laden seep water mixes with oxygen and sulfate-rich sea water, resulting in barite precipitation (Cecile et al., 1983; Greinert et al., 2002). Both a decrease in sulfide concentration as seep water reaches surface sediments, and the presence of chemoautotrophic tube worms, suggests that sulfide may be acting as a substrate for chemolithotrophic bacterial formation of sulfate (Greinert et al., 2002).

Barite deposits are also found in terrestrial subsurface environments. Two general mechanisms have been proposed for their formation. In the first case, barium and sulfide laden brines mix with oxidizing meteoric water, resulting in abiotic oxidation of sulfide to sulfate which results in diagenetic barite formation (Plummer, 1971). Alternatively, barium laden brines may mix with sulfate-containing meteoric water, also resulting in barite formation (Kaiser, 1987; Williams-Jones et al., 1992). Although microbial processes have not been previously shown to be directly involved in sulfide oxidation and resultant barite formation in subsurface systems, stable isotope data has shown that sulfate or thiosulfate reducing bacteria may be involved in formation of sulfide and sulfite, respectively (Kaiser, 1987; Spirakis, 1991). These sulfur compounds can then be oxidized to form sulfate and subsequently barite.

These studies on both aquatic sediments and terrestrial subsurface sediments suggest that biologic activity plays an important role in modulating the solubility of barium. It is also clear that the redox cycling of sulfur (via biologic or abiotic mechanisms) strongly influences barium solubility. Microorganisms play an important role in the sulfur cycle via the reduction of sulfate and elemental sulfur to sulfide (Pfennig and Widdel, 1982; Trüper, 1984), the disproportionation of elemental sulfur and thiosulfate to sulfate and sulfide (Bak and Cypionka, 1987; Bak and Pfennig, 1987; Jørgensen, 1990), the oxidation of sulfide to elemental sulfur or sulfate, and the oxidation of sulfur to sulfate (Van Gemerden, 1983; Trüper, 1984; Brune, 1995; Friedrich, 1998). The role of sulfate reducing bacteria in barium cycling is already well established:

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Barite-SO_4^{2-} can be reduced to sulfide leading to the release of soluble Ba^{2+} (Bolze et al., 1974; Torres et al., 1996; Phillips et al., 2001; Karnachuk et al., 2002). Therefore, it stands to reason that sulfide oxidizing bacteria could also play an important role in barite formation. However, to our knowledge, no previous reports of the role of sulfur or sulfide oxidizing bacteria in this process exist. Here we report barite formation in a sulfide and sulfur-rich artesian spring. The oxidation of sulfide to sulfate (which precipitates with barium) in this spring is apparently catalyzed by the activity of anaerobic, anoxygenic, phototrophic bacteria.

2. MATERIALS AND METHODS

2.1. Sampling and Analytical Methods

For analysis of major ions (except sulfide) in spring water, samples were collected by syringe, filter-sterilized (0.22 μm filtered) and stored on ice before analysis. Nitrate, sulfate, and thiosulfate concentrations were determined using a Dionex ion chromatograph equipped with an AS4A column and conductivity detector (Dionex Instruments, CA). Ba, Ca, Fe, Si, and Sr concentrations were determined by flame atomic absorbance spectroscopy using Perkin-Elmer models 2380 and 5000 AA spectrophotometers (Perkin-Elmer, Inc., Shelton, CT). Samples for sulfide analysis were collected with a 10 mL pipette and added directly in equal volumes to anoxic zinc acetate (10% solution). Sulfide was quantified by the methylene blue assay (Cline et al., 1969). Alkalinity of the stream was determined by titration. Methane was determined in samples collected by completely filling 120 mL serum bottles and stoppering them directly in the field with no headspace. Samples were transported to the laboratory on ice and methane was analyzed within 4 h of collection. A N_2 bubble was added to each bottle, and the methane concentration in the bubble was quantified by gas chromatography. Oxygen concentrations in the stream were measured in the field by YSI 52 dissolved oxygen meter and YSI 5739 field probe. Stable isotope ratios were determined by mass spectroscopy (Coastal Science Laboratories, Austin, TX).

To quantify zero-valent sulfur, 1 L of spring water was collected, acidified with HCl to pH 1–2, and bubbled with oxygen free N_2 gas to volatilize sulfide. Acidification causes the precipitation of sulfane-S (polysulfides, polythionates) thiosulfate, and soluble S^0 (Burton and Machmer, 1968; Meyer, 1977; Fossing and Jørgensen, 1989), which were removed by filtration. Since no thiosulfate was detected in the spring water, precipitated sulfur was considered sulfane-S and soluble elemental sulfur, and will be referred to as zero-valent sulfur throughout the text (Van Gemerden and Mas, 1995). A known area of the filter was then placed in a serum bottle with a 12 $\times$ 75 mm test tube containing 2.5 mL anoxic zinc acetate solution (10%). Sulfur was converted to sulfide using a Cr(II) extraction procedure (Ulrich et al., 1997) modified to include dimethylformamide in the extraction mix (Hsieh and Chang, 1989). Volatilized sulfide was then trapped in the zinc acetate-containing test tube and measured spectrophotometrically as described above. The total amount of zero-valent sulfur present in 1 L could be extrapolated by calculating the zero-valent sulfur per area of filter, and the total zero-valent sulfur on the filter could be determined as the total zero-valent sulfur per l of water. Sulfide was extracted by purging it from the acidified spring water directly into traps containing 2 mol/L $AgNO_3$ for $\delta^{34}S$ analysis. The AgS precipitate was allowed to settle in the test tubes and dried before shipment to Coastal Science Laboratories (Austin, Texas) for $\delta^{34}S$ analysis by mass spectroscopy. Sulfate was precipitated from acidified spring water with excess $BaCl_2$ before $\delta^{34}S$ analysis.

Submerged cores were collected from a pool in the stream approximately 15 m from the source that contained extensive microbial mats (Fig. 1). The cores (including approximately 20 mL of stream water) were collected using an inverted 60 cc syringe modified by cutting off the flange at the plunger end. The open-ended syringes were pushed into the soft streambed sediment, and the top end was sealed with syringe needles plugged with rubber stoppers. The syringes were withdrawn from the streambed and the plunger was immediately replaced while the syringe was still submerged in the spring water. No headspace was allowed in the syringes. Cores were stored on ice for transport back to the lab before further processing. Samples for electron microscopic analysis were collected in 15 mL plastic tubes using a sterile spatula from mats in the spring near the confluence of the spring and the creek (Fig. 1). These samples were stored on ice for transport back to the laboratory for further processing.

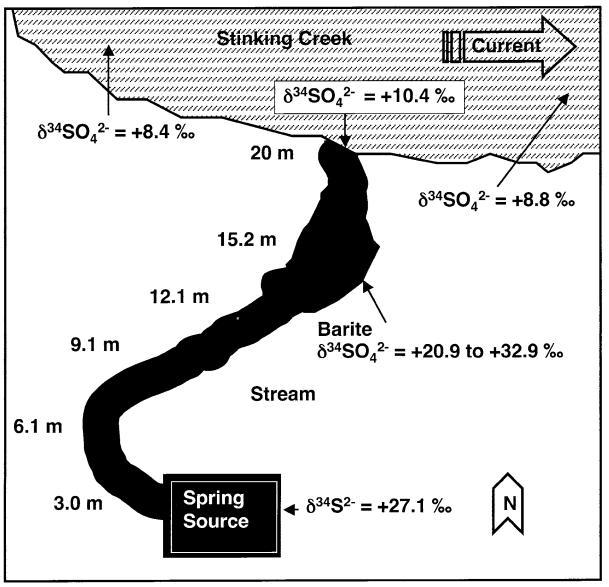

Fig. 1. Schematic diagram of study site illustrating the spring source, stream, and Stinking Creek with $\delta^{34}S$ values for sulfide or sulfate in the system.

2.2. Electron Microscopy and XRD

Mineral samples were dried, mounted on aluminum stubs, carbon coated, and observed in both a JEOL JSM-880 and ETEC Autoscan scanning electron microscopes for analysis. Biologic samples were fixed with 2% glutaraldehyde in 100 mM cacodylate buffer for 1 h at room temperature. They were subsequently dehydrated in ethanol, critical point dried, mounted on aluminum stubs and coated with gold/palladium for SEM analysis.

X-ray diffraction of powdered mineral samples was determined in an automated Rigaku diffractometer.

2.3. Sulfide Oxidation Activity Experiments

For sulfide oxidation experiments, $^{35}S^{2-}$ was produced by incubating $^{35}SO_4^{2-}$ with *Desulfovibrio desulfuricans* in SRB medium (Tanner, 1989) for 2 d. $^{35}S^{2-}$ was extracted by acidifying the culture with 6 N HCl and recovering the volatilized H_2S in a 0.5 mol/L NaOH trap (Ulrich et al., 1997). Trapped sulfide was added directly to the cores and caused no change in pH. Triplicate core incubations were performed in the dark (by wrapping core-containing syringes in foil) or in the light, under grow lamps (100 μmoles quanta/s/cm^2) at room temperature. Anaerobic incubations were performed with no headspace in the modified syringes, while aerobic incubations were performed with approximately 20 mL of air in the headspace. To determine evolution of $^{35}SO_4^{2-}$ in the core incubations, sulfide was removed by precipitation as ZnS (with 10% zinc acetate), and the supernatant was removed. Sulfate was separated from this supernatant by addition of 30 mM $BaCl_2$ and cold sulfate (as Na_2SO_4). Pellets were washed with 30 mM $BaCl_2$ and analyzed by liquid scintillation counting. Conversion of sulfide to sulfate was calculated by multiplying the ratio (μCi/mL $^{35}SO_4^{2-}$ as $BaSO_4$/initial $^{35}S^{2-}$; approximately 0.3 μCi/mL) by the initial sulfide concentration (approx. 10 mM). While isotopic exchange of ^{35}S may have occurred between the sulfide added and zero-valent sulfur species, it is unlikely that isotopic exchange occurred between

Table 1. Results of chemical modeling using PHREEQC for various minerals and gasses in Zodletone spring.

Phase	Saturation Index	Log(IAP)	Log(K)	Formula
Anhydrite	−3.14	−7.5	−4.36	$CaSO_4$
Aragonite	0.09	−8.24	−8.34	$CaCO_3$
Barite	1.23	−8.74	−9.97	$BaSO_4$
Calcite	0.24	−8.24	−8.48	$CaCO_3$
Celestite	−2.44	−9.07	−6.63	$SrSO_4$
CH_4(g)	0.1	−2.76	−2.86	CH_4
CO_2(g)	−1.5	−19.65	−18.15	CO_2
Dolomite	0.52	−16.57	−17.09	$CaMg(CO_3)_2$
FeS(ppt)	−2.13	−6.04	−3.92	FeS
Fluorite	0.16	−10.44	−10.6	CaF_2
Gypsum	−2.93	−7.51	−4.58	$CaSO_4{:}2H_2O$
O_2(g)	−3.22	−6.18	−2.96	O_2
Pyrite	8.82	−18.07	−26.89	FeS_2
Quartz	0.01	−3.97	−3.98	SiO_2
Strontianite	−0.54	−9.81	−9.27	$SrCO_3$
Sulfur	−1.56	−12.03	−10.47	S
Witherite	−0.92	−9.48	−8.56	$BaCO_3$

sulfide and the sulfate produced in the incubations (Fossing and Jørgensen, 1990a,b). Therefore, the production of $^{35}SO_4^{2-}$ can be attributed to the oxidation of reduced inorganic sulfur species, whether sulfide, polysulfides, polythionates, or elemental sulfur.

3. RESULTS

3.1. Site Description

The spring emerges near Zodletone Mountain in southwestern Oklahoma, at the boundary between the Cambro-Ordovician Slick Hills, a sequence of folded carbonate rocks uplifted and exposed in association with late Paleozoic compressional tectonics, and flat-lying Permian clastic and evaporite rocks (Younger, 1986; Campbell et al., 2000). At this site, barite is present along with calcite as abundant cement within Pleistocene stream alluvium, as well as in seasonal whitish streambed sediments. Spring source water is saturated with respect to methane (Table 1), and flow rates of water emanating from the spring have been maintained at 8 L/min since first described by Havens (1983). Spring water flows for ~20 m and discharges into a nearby creek (Fig. 1). It has been suggested (Younger, 1986) that the spring chemistry represents a mixture of deeper basinal brine and shallow groundwater. The brine is ejected from deep within the Anadarko basin along with petroleum, which occurs in seeps in the general vicinity. Spring water chemistry is anomalous compared to surrounding waters (Havens, 1983), containing 0.2 mol/L NaCl and minor amounts of fluorine and bromide as well as boron, strontium, barium (390 μM), sulfate (60 μM), and sulfide (8–10 mM). Results of chemical modeling using PHREEQC (Parkhurst, 1995) show that the emergent spring water is saturated with respect to quartz, fluorite, and aragonite, slightly supersaturated with respect to calcite, dolomite, and barite, and undersaturated with respect to witherite (barium carbonate) (Table 1). Dissolved oxygen was not detected in the spring, as the high sulfide concentration likely maintains anoxic conditions. Neither nitrate nor thiosulfate was detected in the spring. Sulfide concentration in the spring decreases from 8 mM to approximately 0.1 mM with distance from the source, while zero-valent sulfur concentration increases from 0.1 mM at the source to 1 mM at 9 m (Fig. 2). At approximately 15 m, sulfate concentration begins to increase, eventually reaching 2.2 mM shortly before confluence with the creek (Fig. 2). At the same time, Ba^{2+} concentration decreases dramatically (Fig. 2), presumably as a result of precipitation with sulfate as barite. Microbial mats are abundant throughout the spring. Creek water chemistry upstream of the confluence with the spring is typical of oxic surface water in the area.

Some green and purple sulfur bacteria have the ability to anaerobically oxidize sulfide to sulfate and to fix carbon dioxide phototrophically (Pfennig and Widdel, 1982; Van Gemerden, 1983; Trüper, 1984; Van Gemerden, 1993; Brune, 1995; Van Gemerden and Mas, 1995; Friedrich, 1998). Given the extensive mats of phototrophic organisms present at the site, we hypothesized that anaerobic, phototrophic oxidation of sulfide to sulfate is occurring in the spring.

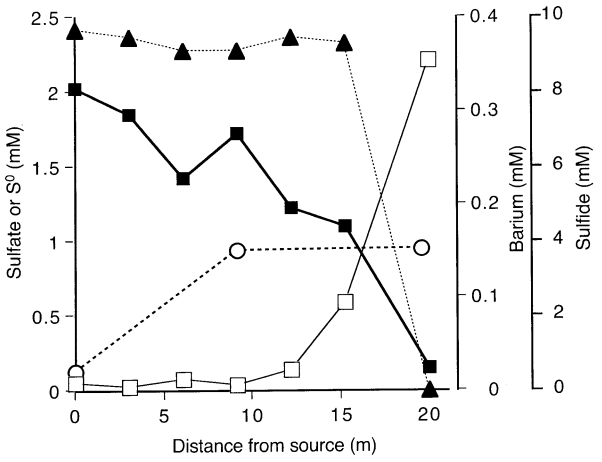

Fig. 2. Profile of dissolved ions over the length of Zodletone spring. Sulfate (open square), barium (solid triangle), sulfide (solid square), and zero-valent sulfur (open circle) concentrations are expressed with respect to distance from the source.

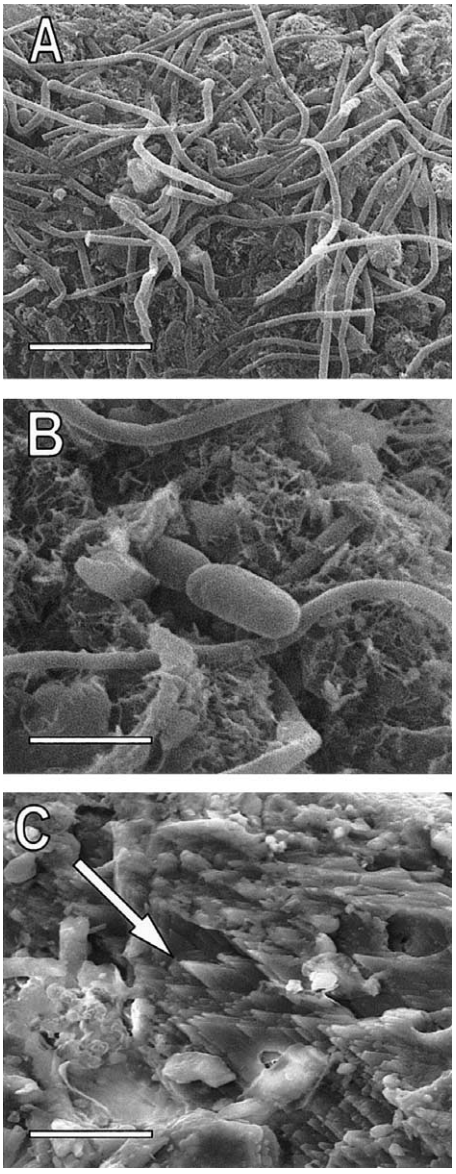

Fig. 3. (A and B) Scanning electron micrograph of bacteria in mats found near spring source. Note the abundance of filamentous organisms (A) as well as the presence of short rod-shaped organisms on a solid substrate (B). (C) Scanning electron micrograph of nail-head calcite (arrow). Calcium is the major constituent in this region based by X-ray analysis, but sulfur and barium are also present. Samples collected from microbial mats and associated mineral crusts along the bank of Stinking Creek. (Bars = 8 μM (A), 2.7 μM (B), or 12.7 μM (C)).

3.2. Characterization of Minerals Associated with Microbial Mats

Electron microscopy of encrusted mat samples revealed the presence of filamentous (Fig. 3a) and rod-shaped (Fig. 3b) microorganisms attached to mineral surfaces. Minerals associated with the mats were identified as calcite and barite. Calcite was identified by X-ray mapping and confirmed by powder X-ray diffraction analysis (data not shown). Barite was identified by powder X-ray diffraction. The calcite associated with the microbial mats was predominantly of the scalenohedral, or "nail-head" form (Fig. 3c).

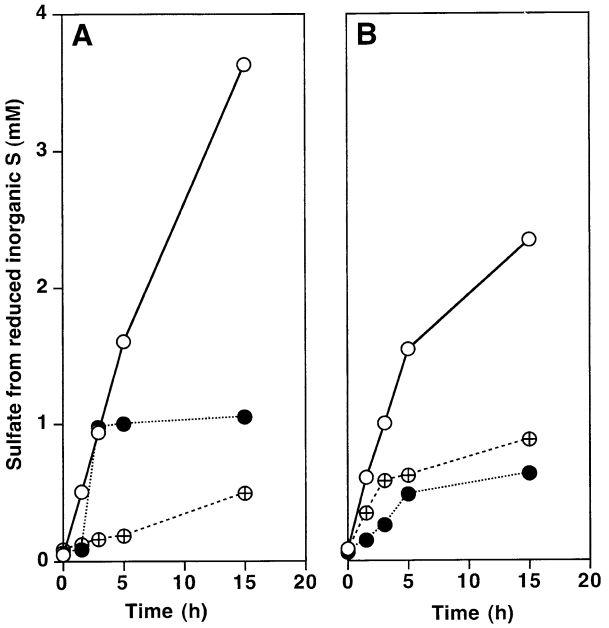

Fig. 4. Production of sulfate from reduced inorganic sulfur in sediment cores collected from a pool approximately 15 m downstream from the spring source. Graphs represent the oxidation of reduced inorganic S to SO_4^{2-} (as indicated by the production of $^{35}SO_4^{2-}$ upon addition of a $^{35}S^{2-}$ tracer) in light-incubated cores (open circles), dark-incubated cores (solid circles), or heat-inactivated sediments (circle with cross). (A) Anaerobic incubations. (B) Aerobic incubations.

3.3. Stable Isotope Analysis

$\delta^{34}S$ was determined for sulfide in the spring, sulfate in the creek and in barite mineral crusts (Fig. 1). Sulfide at the spring source had a $\delta^{34}S$ of +27.1‰. Barite-SO_4^{2-} was similarly heavy with $\delta^{34}S$ ranging from +20.9 to +32.9‰, compared to +8.4‰ for sulfate upstream of the confluence of the spring with the creek (Fig. 1). This suggested that barite-SO_4^{2-} originated as the heavy sulfide in the spring and is not derived from the much lighter sulfate in surrounding surface waters. Furthermore, the soluble sulfate at the confluence of the spring and creek and downstream was heavier than that upstream (Fig. 1), suggesting mixing of heavy sulfate from the spring and lighter sulfate in creek water.

3.4. Sulfide Oxidizing Activity in Core Incubations

Cores were collected from the spring and incubated with $^{35}S^{2-}$, anaerobically or with a headspace of ambient air under light and dark conditions to determine the role of phototrophic bacteria in sulfide oxidation. Aqueous subsamples were analyzed for the production of $^{35}SO_4^{2-}$. Minimal oxidation of sulfide occurred in both oxic and anoxic heat-killed controls (Fig. 4), indicating that oxidation of sulfide to sulfate is not due primarily to abiotic processes, most notably the reaction of sulfide with oxygen. Accumulation of 0.5–1 mM sulfate from sulfide was observed in aerobic or anaerobic, dark incubations

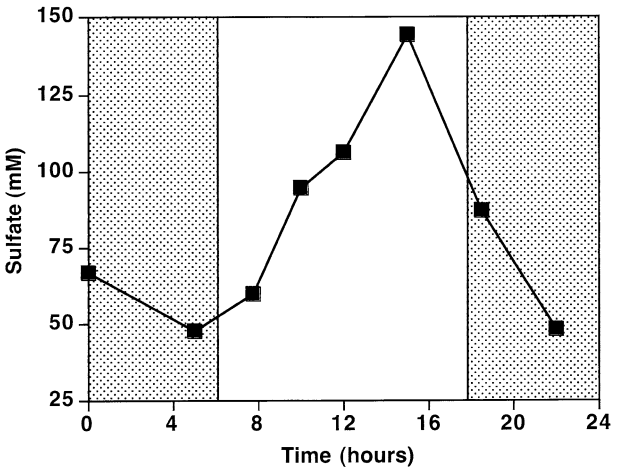

Fig. 5. Diel variation in dissolved sulfate concentration (square) over a 24 h period. Unshaded regions correspond to daylight hours.

(Fig. 4). More importantly, in light incubations, 2.5 and 4 mM sulfate was produced from sulfide in aerobic and anaerobic incubations, respectively. These results suggest that oxidation of spring sulfide to sulfate is mediated primarily by phototrophic bacterial activity and that aerobic chemolithotrophic sulfur oxidizing bacteria do not play a major role in sulfate production. The cores incubated in the light, which were black at the beginning of the incubation, were extensively bleached, indicating oxidation of solid-phase sulfide.

3.5. Diel Fluctuations in Sulfate Concentration

To determine the role of phototrophic bacterial activity in sulfate production in situ, diel variations in sulfate concentration were monitored in the spring over a 24 h period at the same pool from which the cores were collected. Sulfate concentration increased from 48 μM to 144 μM during daylight hours, peaking at 3:00 PM before decreasing to 48 μM after sunset (Fig. 5). These results confirm our laboratory experiments showing that sulfate is generated primarily as a result of anoxygenic, phototrophic bacterial activity.

4. DISCUSSION

Extensive mineral deposits identified as primarily barite and calcite along with microbial mats were observed at Zodletone spring. After sulfide-rich water emerges from the spring source, sulfate concentration increases as sulfide and soluble barium concentrations decrease. Stable isotope analysis suggested that the barite-SO_4^{2-} was derived from isotopically heavy sulfide which emerges at the spring source. The heavy sulfur in spring sulfide can be attributed to extensive depletion of lighter sulfur from the subsurface sulfur source by an earlier microbial reduction, followed by removal of lighter sulfide. Alternatively, the heavy sulfur may be derived from closed-system reduction of local Cambro-Ordovician evaporite beds known to be enriched in ^{34}S (+25 to +29‰) (Claypool et al., 1980). The higher $\delta^{34}SO_4^{2-}$ (+10.4‰) at the spring-creek confluence than upcreek (+8.4‰) also suggested that isotopically heavy sulfide in the spring was being oxidized to sulfate which mixed with creek water and lead to isotopically heavier sulfate. The isotopic signature of upcreek sulfate is consistent with sulfate in nearby Permian evaporite beds (Denison et al., 1998), the likely source for creek sulfate. These data suggest that sulfide emerging from the spring is oxidized to sulfate over the course of the spring leading to precipitation of barium as barite.

Authigenesis of minerals including carbonates, sulfides, and phosphates is often associated with phototrophic bacterial activity (Goncharova et al., 1993; Zavarzin, 1994; Reid et al., 2000; Stolz, 2000). The presence of microbial mats and microorganisms associated with barite and calcite minerals in Zodletone spring lead us to hypothesize that bacterial activity was responsible for the oxidation of sulfide to sulfate and subsequent deposition of barite. Greater amounts of sulfide were converted to sulfate in anaerobic light sediment core incubations than in aerobic, light incubations, dark incubations (aerobic or anaerobic) or heat killed incubations (aerobic or anaerobic). These results suggest that the oxidation of sulfide to sulfate in the spring is not likely due to abiotic oxidation of sulfide by oxygen or by aerobic, chemotrophic oxidation of sulfide. Sulfide oxidation to sulfate in this system is due to the activity of phototrophic microorganisms, and occurs under the anoxic conditions that are maintained in the spring. Further evidence that the production of sulfate is mainly due to phototrophic bacterial activity is shown by the diel fluctuations of sulfate concentration in situ.

While the evidence we present suggests that sulfate is a result of phototrophic activity, based on these results, we are unable to determine if anoxygenic phototrophic bacteria are exclusively responsible for the production of sulfate. All bacterial activities in microbial mats occur at greater rates during daylight hours (Van Gemerden, 1993). While we did not detect dissolved oxygen in the spring water, Cyanobacteria may produce oxygen within the mats which could be used as an electron acceptor for chemotrophic sulfide or sulfur oxidation to sulfate. This is unlikely to be occurring, as sulfide inhibits oxygenic, cyanobacterial photosynthesis, sometimes at concentrations as low as 0.1–0.2 mM (Van Gemerden, 1993), and many Cyanobacteria switch to anoxygenic photosynthesis (sulfide oxidation) at high sulfide concentrations (Van Gemerden, 1993). With the high sulfide concentrations present in Zodletone spring, it is unlikely that Cyanobacteria would be performing oxygenic photosynthesis.

A geochemically similar spring to Zodletone spring was microscopically characterized by Douglas and Douglas (2001). Like Zodletone spring, this spring was anoxic, contained abundant sulfide (3.8 mM), and was not thermal (9°C). Interestingly, they measured low concentrations of barium (3.2 μM-6.2 μM) in spring water and in microbial mat pore water, but did not indicate the presence of barite minerals. Cyanobacteria which were believed to be carrying out anoxygenic photosynthesis, and purple and green sulfur bacteria were found in this spring (Douglas and Douglas, 2001). Indeed, work performed at Zodletone spring by Elshahed et al. (2003) revealed the presence of green and purple sulfur bacteria, green nonsulfur bacteria, and Cyanobacteria, all of which are capable of phototrophic sulfide oxidation to zero-valent sulfur and/or sulfate. (Pfennig and Widdel, 1982; Van Gemerden, 1986; Brune, 1995; Van Gemerden and Mas, 1995)

The increase in spring water zero-valent sulfur concentration

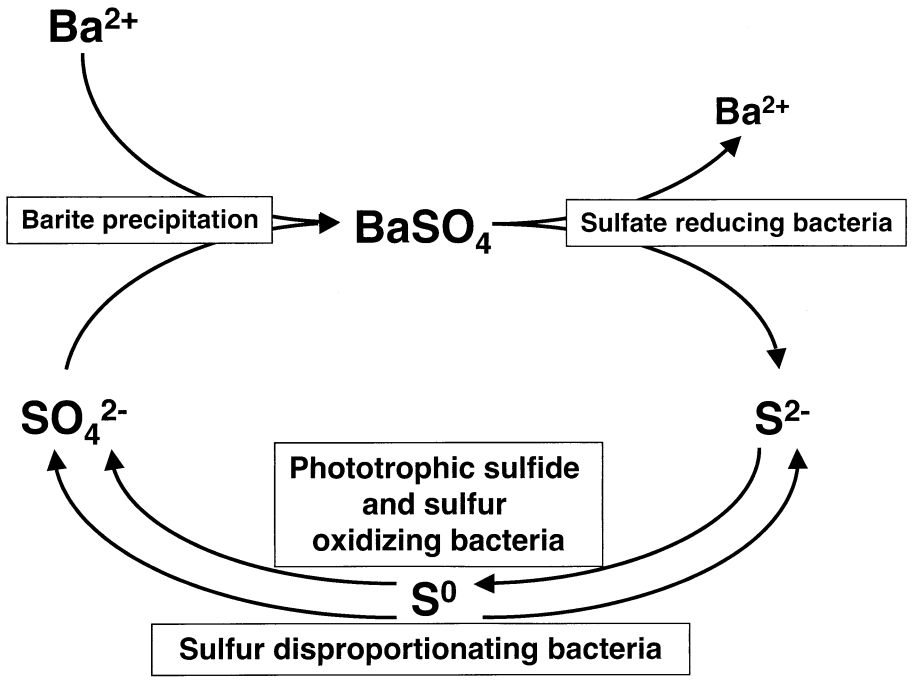

Fig. 6. Bacterially mediated sulfur cycling reactions modulate the solubility of barite in Zodletone spring. Soluble barium can be released from barite by sulfate reducing bacteria and then reprecipitated as barite by bacterial processes that generate sulfate, which include: sulfide and sulfur oxidation by phototrophic bacteria and the disproportionation of zero-valent sulfur or thiosulfate to sulfide and sulfate. (Modified from Trüper, 1984, to reflect the interaction of biologic sulfur cycling and barium solubility in Zodletone spring).

with distance from the spring source suggests that zero-valent sulfur is an intermediate in sulfide oxidation to sulfate at Zodletone spring. Zero-valent sulfur may be further oxidized to sulfate in spring water by anoxygenic phototrophic bacteria (Van Gemerden and Mas, 1995), or may be disproportionate to sulfate and sulfide (Bak and Cypionka, 1987; Bak and Pfennig, 1987; Jørgensen, 1990; Janssen et al., 1996; Finster et al., 1998). In either case, sulfate is a product of the activity of these organisms, and the production of the partially oxidized sulfur species is a result of anoxygenic phototrophic bacterial activity. In the latter scenario barite-SO_4^{2-} is also ultimately derived from phototrophic activity.

Sulfate-reduction activity has been detected at the site and is associated with the phototropic mats (Elshahed et al., 2003). It is well known that sulfate reducing bacteria are able to grow on solid phase sulfates such as barite albeit at lower rates (Bolze et al., 1974; Phillips et al., 2001; Karnachuk et al., 2002) and are therefore often responsible for Ba^{2+} mobilization from barite (Torres et al., 1996; Greinert et al., 2002). While sulfate reduction is occurring in Zodletone spring, the observed increase in sulfate concentration in the spring suggests that sulfide oxidation to sulfate is occurring at a greater rate than sulfate reduction, and therefore, much of the barite that may be mobilized by sulfate reducing activity may have subsequently precipitated in the presence of high sulfate concentrations.

This study underscores the importance of sulfur cycling microorganisms in modulating the solubility of barite. Figure 6 illustrates the proposed role for microbial sulfur cycling in modulating barium solubility in Zodletone spring. Once barium is mobilized (often as a result of sulfate reduction activity; Bolze et al., 1974; Torres et al., 1996; Phillips et al., 2001; Karnachuk et al., 2002), anoxygenic phototrophic sulfide oxidizing bacteria (i.e., purple and green sulfur bacteria) in surficial systems may produce conditions for barite precipitation. While the precipitation of soluble barium with sulfate is ultimately an abiotic reaction, it is the result of bacterial sulfate production. Further, sulfur-disproportionating bacteria may also catalyze the precipitation of barite, by producing sulfate and sulfide from zero-valent sulfur or thiosulfate. While the site we describe here is surficial and anoxic, the mechanism we describe for barite precipitation may be applicable to other systems.

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