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Barium and barite dynamics in Antarctic streams

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ABSTRACT

Most natural waters are undersaturated with respect to barite ($BaSO_4$), and while much work has focused on the processes of microbially mediated barite precipitation in undersaturated solutions, particularly in marine environments, little documentation exists on the changes in barite saturation in stream waters. We examined ephemeral glacial meltwater streams in the McMurdo Dry Valleys, Antarctica, that undergo large variations in streamflow and temperature on both a diel and seasonal basis. We measured dissolved Ba in stream water in downstream transects and on a diel cycle, total Ba in stream sediments, algal mats, and lake sediments. Ba concentrations decreased downstream in all four transects, and mineral saturation modeling indicates these waters go from supersaturated to undersaturated with respect to barite in very short distances. Ba is concentrated in stream benthic algal mats at a factor less than observed in marine systems. Both seasonal and diel changes in stream water temperature affect the solubility of barite near glacial sources. Our work shows that both changing stream temperature and the presence of algal materials likely play significant roles in controlling Ba concentrations in polar streams.

INTRODUCTION

In high-latitude and high-altitude regions, streamflow is primarily controlled by temperature, which in turn controls ephemeral streams that may only flow for a few weeks to months per year. During high-latitude summers, sun angle has a great influence on flow, such that streamflow can vary as much on a diel basis as it does throughout the flow season (McKnight et al., 1999; Cozzetto et al., 2006). Generally, the saturation state of minerals in streams, especially binary salts, have been determined based on samples collected a few times during the flow season. Yet, recent diel studies on streams and rivers have demonstrated that changes in key physical and biogeochemical parameters affecting mineral solubility, such as pH and temperature, can change dramatically though a 24 h cycle (Gammons et al., 2005; Parker et al., 2007).

Most natural waters are undersaturated with respect to barite ($BaSO_4$), as the mixing of barium-rich and sulfate-rich waters are usually needed to produce the mineral via *in situ* precipitation (Griffith and Paytan, 2012). Much work has focused on the microbial mediation of barite precipitation in undersaturated ocean waters, as it is used as tool to reconstruct the seawater chemistry at the time of precipitation (Gonzalez-Muñoz et al., 2012). Little work has described Ba and barite dynamics in natural river systems or low-ionic-strength waters. The global mean riverine concentration of Ba is low, at 74 nmol L^{-1}, and even lower values of 22–29 nmol L^{-1} are associated with old cratonic-based watersheds (Gaillardet et al., 2014). Higher Ba concentrations have been documented in northern polar and alpine rivers such as the Mackenzie River in Canada, ranging from 140 to 575 nmol L^{-1} (Guay and Falkner, 1998), and the Yuma River System in the Himalaya, ranging from 17 to 871 nmol L^{-1} (Dalai et al., 2002).

We present Ba data from six streams in the McMurdo Dry Valleys (MDV), Antarctica. The MDV are a polar desert with low mean annual temperature, they form the largest ice-free region on the continent, and contain a number of ephemeral streams that flow 4–12 weeks per year (McKnight et al., 1999). Evaporation and sublimation play a role in controlling the solubility of binary salts such as $CaCO_3$, $CaSO_4{\cdot}H_2O$, NaCl, and others in ephemeral aquatic environments (Keys and Williams, 1981; Dickinson and Rosen, 2003; Bisson et al., 2015; Toner et al., 2013). Work in Svalbard, Norway, on proglacial meltwater streams similar to those in the MDV, has demonstrated that evaporation and cryoconcentration can precipitate, and later re-dissolve, Mg^{2+} and Ca^{2+} sulfate salts at higher flows (Cooper et al., 2002). Yet, little work has been directed at understanding the behavior of Ba and $BaSO_4$ in polar environments.

We collected stream water samples along downstream transects of meltwater streams in the MDV, and calculated the saturation index of barite in these systems under differing temperature regimes in order to better understand the temporal dynamics of barite. Additionally, we measured Ba concentrations in sediments and algal mats collected in stream channels and a terminal lake to establish their role in the overall interactions between barite precipitation/dissolution in the system.

METHODS

Stream water samples were collected from six MDV streams. Downstream transects were collected from Commonwealth Stream, Wales Stream, and Von Guerard Stream in Taylor Valley (TV), and from Miers Stream and Adams Stream in Miers Valley, and diel samples were collected from Andersen Creek and Von Guerard Stream in TV. (Fig. 1). Samples were filtered within 24 h of collection, and major anion (Cl^-, SO_4^{2-}) and cation (Na^+, K^+, Ca^{2+}, Mg^{2+}) concentrations were analyzed using ion chromatography (Welch et al., 2010). The relative standard deviations (RSDs) based on replicates of check standards were better than 2%. Bicarbonate concentrations were calculated as the difference between the major cation and anion equivalents (Lyons et al., 2011), a method found to be accurate within ~10% in these streams (Welch et al., 2010). Ba concentrations were analyzed using a Thermo Finnigan Element 2 inductively coupled plasma–sector-field–mass spectrometer (ICP-SF-MS). The RSD based on replicate check standards was 3%.

Streambed sediments were collected from the stream channels of Commonwealth Stream, Von Guerard Stream, and Lost Seal Stream, in eastern TV (Fig. 1). Streambed sediments were not available from Miers Valley streams, and our data may not be representative of that region. Sediments were analyzed for Ba concentrations by X-ray fluorescence (XRF) spectrometry.

Stream cyanobacterial mats (*Nostoc* spp) were collected from Von Guerard Stream and Bowles Stream, both on the south side of Lake Fryxell in TV. Algal mats were collected at three locations along a downstream transect from Bowles Stream (near glacier, at mid-reach, and at the mouth at Lake Fryxell), and one location in the middle reaches of Von Guerard Stream. Samples were kept frozen in the field, then freeze-dried upon return to the laboratory at McMurdo Station, and later fully digested in 2.5:1 HNO_3:H_2O_2 solution and analyzed for Ba using ICP–optical emission spectrometry (ICP-OES). The RSD of the Ba measurements, based on multiple analyses of replicate check standards, was 1%. Replicate subsamples of algae were digested and analyzed separately from three samples, and had an average standard deviation of 2.8 μg g^{-1}. Aliquots

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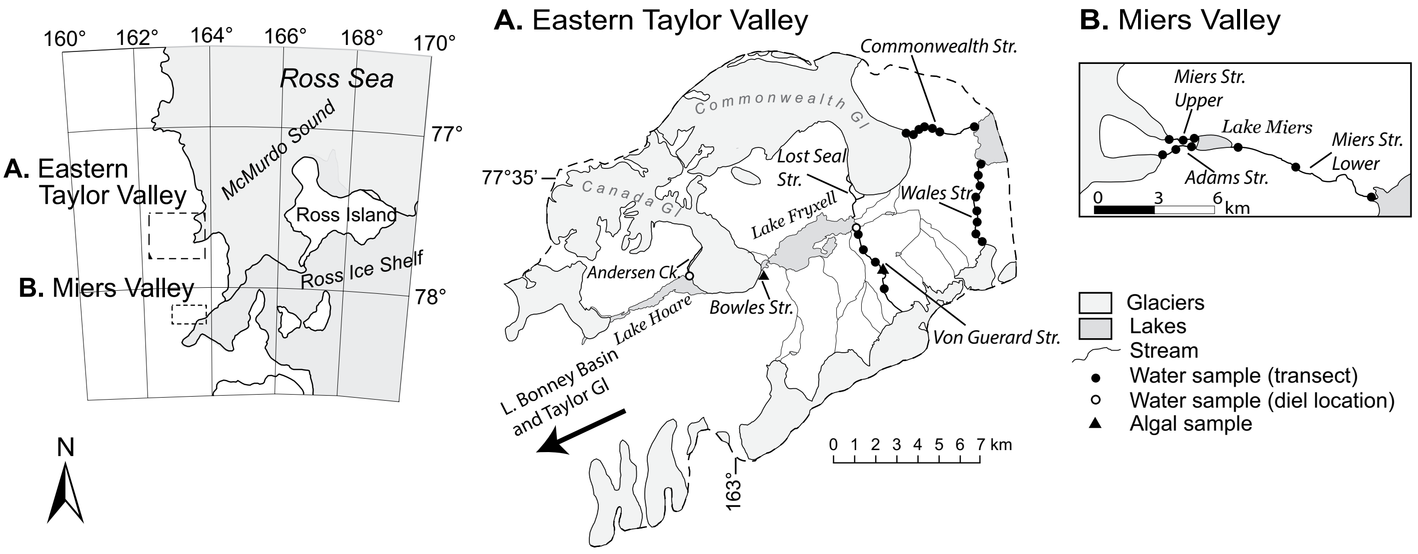

Figure 1. Map of the McMurdo Dry Valleys, Antarctica, with sampling locations. Gl—glacier; Ck.—creek; Str.—stream.

of sediment and algal mat samples were air dried, placed on carbon tape on an aluminum stub, and coated with Au-Pd before analysis using an FEI Quanta FEG 250 field emission scanning electron microscope (SEM) equipped with a Bruker energy dispersive spectroscopy detector (EDX).

Finally, five sediment samples from the top 16 cm of a core collected from the bottom Lake Hoare (Berger and Doran, 2001), a terminal closed-basin lake in TV, were homogenized, subsampled, and analyzed using XRF. Subsamples of the Lake Hoare core were also leached with 1M H_3PO_4 to solubilize any $CaCO_3$ present (Froelich, 1980), and the leachate analyzed for Ba using ICP-OES. The sediments followed the sequential leaching steps described by Froelich (1980), but only the $CaCO_3$ fraction is reported.

Barite saturation indices were calculated for stream waters using PHREEQC (U.S. Geological Survey, https://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/) at the range of temperatures that have been previously measured in TV streams (Cozzetto et al., 2006).

RESULTS

Barium concentrations in these Antarctic streams range from 29 nmol L^{-1} to ~3000 nmol L^{-1}, with a mean of 287 nmol L^{-1} and a median of 132 nmol L^{-1} (Table DR1 in the GSA Data Repository[1]), higher than the global mean of 74 nmol L^{-1} (Gaillardet et al., 2014). Ba concentrations of samples from diel sampling at the outlets of Andersen Creek and Von Guerard Stream ranged from 76 to 301 nmol L^{-1} and from 29 to 102 nmol L^{-1}, respectively. In all of the stream transects sampled, the Ba concentrations decreased with increasing distance from the glacial headwaters, which stands in contrast to other weathering products such as H_4SiO_4, Li, and K, which increase downstream (Table DR1) as a result of chemical weathering in the hyporheic zone (Gooseff et al., 2002). One exception was Commonwealth Stream, where the Ba concentration increased from 58 to 183 nmol L^{-1} in the last sample collected closest to the ocean (Table DR1). However, this sample was not collected from the channelized streams, but rather from a broad deltaic region where the rock:water ratio is much higher than in the rest of the stream. H_4SiO_4 concentrations also increase by more than a factor of two, suggesting increased weathering of silicate minerals rather than evaporation, as the sample falls on the local meteoric water line (Gooseff et al., 2006).

The mean of six stream sediments analyzed for Ba was 697 ± 177 μg g^{-1}, and the five Lake Hoare sediments yielded a mean of 592 ± 34 μg g^{-1} (Table 1), comparable to the average upper continental crust value of 624 μg g^{-1} (Rudnick and Gao, 2003). The mean Lake Hoare sediment leachate that targeted $CaCO_3$ phases was 1.55 ± 0.08 μg g^{-1}. The mean Ba concentration in the algal mats was 29 ± 6 μg g^{-1} (Table 2).

TABLE 1. TOTAL Ba CONCENTRATIONS IN SEDIMENTS

Sample	Ba (μg g^{-1})	H_3PO_4 leachate Ba (μg g^{-1})
Lake		
Lake Hoare 0–2 cm	614	1.56
Lake Hoare 2–4 cm	607	1.49
Lake Hoare 6–8 cm	558	1.55
Lake Hoare 10–12 cm	576	1.63
Lake Hoare 14–16 cm	605	1.53
Streambed		
Commonwealth	529	
Von Guerard (1)	667	
Von Guerard (2)	870	
Lost Seal (1)	812	
Lost Seal (2)	672	
Lost Seal (3)	632	
Upper Continental Crust*	624	

Note: Numbers following streambed location indicate replicate samples.
*From Rudnick and Gao (2003).

TABLE 2. TOTAL BA CONCENTRATIONS IN ALGAL MATS (*nostoc spp*)

Stream	Location	Ba (μg g^{-1})
Bowles	upstream	33
Bowles	mid-reach (1)	31
Bowles	mid-reach (2)	37
Bowles	mouth (1)	24
Bowles	mouth (2)	24
Von Guerard	mid-reach (1)	23
Von Guerard	mid-reach (2)	27
Von Guerard	mid-reach (3)	31

Note: Numbers following location indicate replicate samples.

[1]GSA Data Repository item 2018302, Figure DR1 (images of barite in sediments and algal mat) and Table DR1 (stream water geochemistry of downstream transects and stream water geochemistry of diel sampling), is available online at http://www.geosociety.org/datarepository/2018/ or on request from editing@geosociety.org.

DISCUSSION

The steady decreases in Ba concentrations in the downstream transects suggest that Ba is either acquired in supraglacial streams or from proglacial material, then subsequently removed by in-stream processes. Previous studies in the MDV have shown that variations in glacial meltwater chemistry, including major and trace elements, are controlled by both aerosols in snow deposition and wind-blow salt and dust (Lyons et al., 2003; Fortner et al., 2005, 2011). Easily-solubilized eolian material and cryoconite holes on glacier surfaces have been identified as sources of trace elements to MDV streams (Bagshaw et al., 2007; Fortner et al., 2011).

Barite can be precipitated in dilute solutions as a result of biologic activity when Ba and/or SO_4^{2-} is enriched due to the decomposition of organic matter (Ganeshram et al., 2003; Bates et al., 2017). Cyanobacteria have been found to accumulate Ba in intracellular carbonates (Cam et al., 2016), and both freshwater and marine algae have been documented to concentrate Ba at factors of 200 to 200,000 (Mann and Fyfe, 1984; Fisher et al., 1991). Using the mean Ba concentration in the streams (338 nmol L^{-1}) and the algal mats (29 µg g^{-1}), we calculate a mean concentration factor of ~625. Marine bacteria have been shown to metabolically mediate the biomineralization of barite (Bonny and Jones, 2007; Gonzalez-Muñoz et al., 2012), and algal mats from nearby Lake Vanda and the Onyx River in Wright Valley (just to the north of TV) have nanometer-sized barite crystals on the surface of their cell walls (Tazaki et al., 1997), and when the algae die, the barite is preserved. Using SEM with EDX, we observed barite in streambed sediments and algal mats from streams in eastern TV that ranges in size and morphology from nanometer-sized grains to micron-sized angular crystals, to euhedral crystals that can be tens of microns (Fig. DR1). Subhedral and anhedral microcrystals of barite form in the laboratory from highly supersaturated solutions (Bonny and Jones, 2007), while rhombic and related geometric forms grow more slowly at lower supersaturated concentrations (Bertram and Cowen, 1997). In marine sediments, Ba has been observed in various phases, with the majority in the opal + aluminosilicate and "residual" phases (Gonneea and Paytan, 2006). We are unable to distinguish the major carrier phase for Ba in the stream and lakes sediments at this time, but in the lakes, carbonate minerals play a minor role, and in the streams, algal mats only represent 6% or less of the total sedimentary Ba. Although there are abundant diatoms in the stream algal mats, we are currently unable to discern their role in Ba biogeochemistry. However, no relationship was found between dissolved Ba and H_4SiO_4 concentration in the streams.

Our modeling results demonstrate that the saturation index of barite decreases downstream. Figure 2 shows that in the Miers/Adams Stream system and in Wales Stream, the waters are supersaturated with respect to barite near the glacial source and become undersaturated downstream.

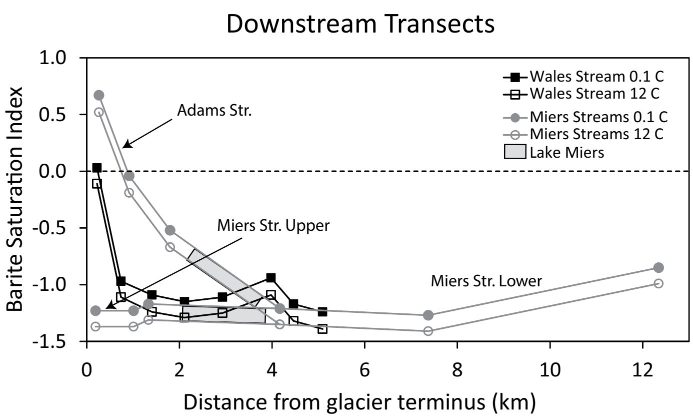

Figure 2. Saturation indices for downstream transects at Wales and Miers Streams (Str.), Antarctica, at pH 7. Adams and Miers Streams both flow into Lake Miers, and the outlet downstream of Lake Miers is also called Miers Stream (see Figure 1).

While the Miers/Adams Stream system includes Lake Miers and mixing along its length, the decrease in saturation index occurs primarily upstream of this area. Figure 2 also demonstrates the importance of temperature on barite behavior. At the higher temperatures observed in MDV streams, barite becomes more undersaturated. Stream temperatures vary between 0 and 15 °C, depending on time of day and time of year—on clear sunny days, the stream channels and hyporheic zones can absorb energy due to their low albedo, and then conduct this heat directly to the stream waters (Cozzetto et al., 2006). One can envision the potential for rapid, daily recycling of barite, where it precipitates during colder and/or higher flow times of the day, and dissolves at warmer times, and possibly also at baseflow conditions when the water-rock ratio of the channel is lower (i.e., more conduction per volume of water).

Natural waters achieve equilibrium with barite from both undersaturated and supersaturated conditions over a wide range of water compositions and temperatures (Zhen-Wu et al., 2016). These authors state that their experiments demonstrate that "aqueous solution-barite equilibrium is broadly achieved in nature," (Zhen-Wu et al., 2016, p. 207) suggesting that the precipitation–dissolution scenario presented here is realistic, and that variations in temperature on multiple temporal scales in these Antarctic streams drive the geochemical dynamics of Ba through barite solubility changes. In addition, evaporation and sublimation of water and snow in both the streams and hyporheic zones of the streams can strongly aid in concentrating solutes, thus aiding the precipitation of relatively insoluble salts, such as barite. Previous work in the MDV has demonstrated the importance of these processes in accumulating salts on the landscape in general (Keys and Williams, 1981; Bisson et al., 2015; Toner et al., 2013), and aquatic-terrestrial interfaces in particular (Gooseff et al., 2002).

The role of organic matter in controlling Ba dynamics in these streams is currently difficult to assess. As noted above, the algal mats in the streams concentrate Ba at an intermediate factor compared to other aquatic environments. For example, marine phytoplankton have Ba concentrations of approximately double that observed by us (Martin and Knauer, 1973). The barite we observed (Fig. DR1) could be "bio aggregates" produced by algal growth (Stroobants et al., 1991) or be crystals produced simply from inorganic reactions as discussed above. Future work will be needed to answer this question.

CONCLUSIONS

We investigated the dynamics of Ba and barite in the ephemeral streams in the McMurdo Dry Valleys, Antarctica, and found that Ba concentrations decrease steadily in downstream transects, and that seasonal and diel changes in stream water temperature probably play a role in the solubility of barite near the glacier source, and therefore the concentration of dissolved Ba in these systems. Barite saturation decreases along the streams' flow paths, sometimes transitioning from supersaturated near the glacier source to undersaturated further downstream. Algal mats collected from streams indicate a mean Ba concentration factor of ~625 relative to stream water. Ba concentrations in streambed and lake sediments are slightly lower than average upper continental crust, and a small percentage of the total Ba is associated with organic matter. Our work demonstrates a dynamism of this aquatic system with respect to Ba biogeochemistry, and suggests that changing stream temperatures, and the presence of algal materials in streams, may play important roles in the solubility of barite and therefore Ba concentrations in polar streams.

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