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IMPLICATIONS OF SULFATE REDUCTION ON DOLOMITE FORMATION AT DEEP SPRINGS LAKE, CALIFORNIA

MICHELLE PARADIS, Williams College
Research Advisor: Dr. Phoebe A. Cohen

INTRODUCTION

The presence and metabolic activity of sulfate-reducing bacteria (SRB) have both been invoked to explain why dolomite is being precipitated in certain hypersaline, alkaline, evaporative environments. Comparing dolomitic and non-dolomitic ephemeral lakes in the Coorong regions of Australia, for example, Wright and Wacey (2005) noted that the dolomitic lakes show a greater seasonal increase in alkalinity and have a significantly higher SRB count.

Several mechanisms are invoked to explain the potential importance of sulfate-reduction in dolomite precipitation (van Lith, 2003). First, magnesium commonly occurs in the ion pair Mg-SO$_4^{2-}$ (Fig. 1a). SRB, by using up sulfate for their metabolism, might increase the effective concentration of free Mg$^{2+}$. Second, magnesium-bearing extracellular polymeric substance (EPS) is secreted by many microbes, including SRB, and might create a microenvironment suitable for dolomite nucleation. Third, the process of cation adsorption, in which Ca$^{2+}$ and Mg$^{2+}$ ions are concentrated on bacterial cell surfaces, where bicarbonate is also produced, provides a carbonate nucleation point (Fig. 1b).

GEOLOGIC SETTING

At the time when Jones (1965) classified the lake hydrology, the lake received river water inputs from nearby creek systems. However, due to artificial water collection in the surrounding area, this source of inflow has been nearly eliminated (Meister et al., 2011). Water is supplied to the lake almost exclusively from three groups of springs in the valley, from direct rainwater inflow, and from springs within the area of the lake. At peak, the lake covers an area of approximately 4 km$^2$, though at the time of this study in July 2013, the water table was 0-20 cm below the surface in areas of interest. The carbonate mud that makes up the playa is composed primarily of authigenic dolomite, although the exact composition varies laterally and with depth (Jones, 1965). The uppermost 0-3 cm of sediment is an evaporitic crust, which can form by capillary efflorescence or whenever...
evaporation exceeds inflow (Jones, 1965). Ions in rainwater and in groundwater supplied by dissolution of feldspars and other minerals are left behind during evaporation to form the crust (Eugster, 1980). Immediately beneath the crust, the carbonate mud is oxidized and tan; at depths ranging from 10 to about 25 cm the transition to anoxia is marked by grey/green mud, richer in organic matter.

GOALS

The purpose of this study is to characterize sulfur geochemistry in three sub-settings of Deep Springs Lake: spring water, porewater, and carbonate mud. If sulfate reduction is actively taking place in the sediment, sulfate levels in pore water should decrease nonlinearly with depth (van Lith et al., 2002). Isotope analysis can help constrain this metabolic activity, as the lighter $^{32}$S is metabolically favored over $^{34}$S, creating a $^{34}$S enrichment in residual sulfate when sulfate reduction occurs. Concentration and isotope data for spring water sulfur also are collected. This allows for comparison between springs and also between springs and nearby sediments. The carbonate associated sulfate (CAS) isotope ratios ($\delta^{34}$S$_{CAS}$) are measured. During the formation of calcium carbonates, a small fraction of the carbonate ion sites in the lattices are taken up by sulfate ions. These sulfate ions preserve the $\delta^{34}$S values of the sulfate ions incorporated into the carbonate lattices (Gill et al., 2008).

FIELD METHODS

Two-inch diameter intact sediment push cores were taken at Muddy Site (MS), Nine Site (9S), located near a spring, and Far Out Site (FO) from the top 40-50 cm of sediment to provide sediment for CAS extraction. At FO, a 50 cm long, 4-inch diameter push core was taken. Sediment was extruded from the core and separated into centrifuge tubes for porewater extraction in the lab.

At MS and 9S, 40 cm long “peepers” were used to collect porewater (Teasdale et al, 1995). The peepers consist of two polycarbonate sections divided into seventeen 3 cm long wells. These wells were filled with deionized water, and were separated from the surrounding sediment by a piece of dialysis paper, so that dissolved ions could diffuse across the dialysis membrane, but no water could transfer between wells. The peepers were allowed to equilibrate with the porewater for four days, after which the water was collected.

At each of the springs, 35 ml of water was taken up with a sterile syringe and passed through a 0.22 micron Sterivex filter into a centrifuge tube to remove everything but dissolved ions and microbes. The centrifuge tubes were immediately placed on ice and were kept refrigerated throughout lab work to inhibit microbial activity.

LAB METHODS

To extract sulfate from the spring water and porewater collected from the peepers, 2-4 ml of the filtered water was mixed with 2 ml of oversaturated barium chloride ($\text{BaCl}_2$) solution. The porewater from FO was extracted from the sediment core by centrifuging the sediment and filtering through a 0.22 micron Sterivex filter. The $\text{BaCl}_2$ solution reacted with dissolved $\text{SO}_4$ to form barium sulfate ($\text{BaSO}_4$), a white precipitate. The precipitates were centrifuged and washed three times in deionized water. After drying, the precipitates were weighed and sent for isotope analysis at Washington University in St. Louis, which was performed using a Costech ECS 4010 elemental analyzer and a Thermo Finnigan Delta V Plus mass spectrometer. Isotope values are in ‰ relative to the Vienna Canyon Diablo Troilite, and are reproducible to 0.3‰.

From the MS and 9S intact sediment cores, sediment was taken at depths corresponding with each of the porewater peeper wells. To assess whether there was major lateral variation between these sites and FO, four sediment samples were also taken from the FO core. All sediment samples were dried and ground with a mortar and pestle. The sediment samples underwent a NaCl wash to remove SO4 not contained in the carbonate lattice through formation of Na$_2$SO$_4$ (Wotte et al., 2012). The samples were then rinsed three times in deionized water. To dissolve the carbonate fraction of the sediment, 6M HCl was added to the sediment. Addition of 3 g of SnCl$_2$ helped to
reduce sulfide oxidation. The solutions were vacuum-filtered before supersaturated BaCl₂ was added. The BaSO₄ that precipitated was treated the same way as that which had precipitated from the spring water and porewater.

RESULTS

Porewater ICP data

ICP analysis (Plon, this volume) demonstrated that at MS and FO, porewater [Mg²⁺] and [Ca²⁺] are both between 0 and 2 parts per million (ppm), while at 9S they reach 114 ppm and 55 ppm respectively. These ion concentrations at 9S decrease slowly with depth until the trend abruptly shifts to a rapid increase at about 40 cm depth (Fig. 2).

Porewater [SO₄²⁻] and δ⁳⁴S data

Porewater [SO₄²⁻] ranges from 1.0 parts per thousand (ppt) to 3.7 ppt at 9S and from 28.6 to 42.4 ppt at MS (Fig. 3a-b). At both sites, concentration decreases with depth until about 40 cm, at which point it increases significantly. At FO, [SO₄²⁻] is both higher and more variable than at the other two sites, ranging from 49.1-89.3 ppt (Fig. 3c).

Variation in δ³⁴S ranges most widely at 9S, increasing from 21.7 to 25.5‰. Above 40 cm, δ³⁴S appears to vary almost directly with [SO₄²⁻]; at that point downward [SO₄²⁻] rapidly increases while δ³⁴S decreases (Fig. 3d). Values of δ³⁴S at MS fall between 24.1 and 24.9‰, similar to upper-range values at 9S. It appears that there is little correlation between

Figure 2: [Mg²⁺] and [Ca²⁺] ICP data at a) 9S and b) MS. Note that the x-axes on the two graphs are different.

Figure 3: Porewater [SO₄²⁻] and δ³⁴S values: a) 9S [SO₄²⁻]; b) MS [SO₄²⁻]; c) FO [SO₄²⁻]; d) 9S δ³⁴S; e) MS δ³⁴S; f) FO δ³⁴S
δ^{34}S and [SO\textsubscript{4}^{2-}] except at depths below 36 cm, where [SO\textsubscript{4}^{2-}] increases and δ^{34}S abruptly begins to decrease (Fig. 3e). Values and trend of δ^{34}S at FO are similar to those at MS (Fig. 3f).

**Sediment [SO\textsubscript{4}^{2-}] and δ^{34}S_{CAS}**

At both MS and 9S, δ^{34}S_{CAS} decreases with depth (Fig. 4a-b). [SO\textsubscript{4}^{2-}] in these sediments does not appear to follow a clear trend, though at 9S there is evidence for a positive correlation with δ^{34}S_{CAS} (Fig. 4c-d). At FO, a complete CAS profile was not taken. For the sake of comparison however, three sulfate samples from this site were analyzed and yielded δ^{34}S_{CAS} values between 25.6 and 34.0‰, higher than values at the other sites.

**Spring water [SO\textsubscript{4}^{2-}] and δ^{34}S data**

Higher [SO\textsubscript{4}^{2-}] is generally associated with higher overall salinity (Fig. 5) [SO42-] at Nine Spring is similar to values for porewater sulfate at depths between 12 and 37 cm, though the spring water is isotopically enriched with a δ^{34}S value of 30.5‰. Spring water sulfate at all sites has δ^{34}S values ranging from 24.1 to 35.1‰. There is a weak negative correlation between these values and spring salinity.

**DISCUSSION**

Meister et al. (2011), on the basis of finding <2 ppm Mg\textsuperscript{2+} and Ca\textsuperscript{2+} in porewater at depth, suggested that supersaturation with respect to dolomite does not persist below the water-sediment interface, which is capped by an impermeable evaporite layer. ICP data used in this study, however, indicate that at least at 9S, where there was no mineral crust, Mg\textsuperscript{2+} and Ca\textsuperscript{2+} ions were found well below the sediment surface, and in fact their concentrations peaked at 35-40 cm below the surface. This apparent discrepancy suggests that there may be two separate masses of water influencing the porewater chemistry: meteoric water moving downward and upward moving groundwater containing ions from the breakdown of clays at depth. Had the water table level at the time of sampling been at a steady state, the difference in ion concentration at
9S and MS would likely be reflected in mineralogy. Given the fair amount of uniformity among carbonate concentrations at these sites however, it appears that on average the water sources and their movement through the sediment are the same. The mineralogy at FO is systematically different from the other two sites because it is closer to the basin center and therefore under meteoric water for longer each year.

Since SRB are generally anaerobic and preferentially metabolize \(^{32}\)S over \(^{34}\)S, their presence can be inferred from a positive trend in \(^{34}\)S of the residual sulfate downward through the oxic-anoxic interface, consistent with actual porewater \(^{34}\)S values at 9S (Fig. 3). There are two alternative explanations that could explain the observed trend, however.

First, the gradient between isotopically heavy and light sulfate could be an artifact of the intermixing of two different water sources. However, porewater \([\text{SO}_4^{2-}]\) at 9S is consistently within 0.5 ppt of the spring water \([\text{SO}_4^{2-}]\) at the site if the uppermost and lowermost depths sampled are omitted. This omission does not substantially affect the trend in \(^{34}\)S. If the porewater at MS, where \([\text{SO}_4^{2-}]\) values are an order of magnitude or more higher, can be considered of predominantly meteoric water composition, and the 9S spring water is representative of groundwater, then it should follow that a substantial mixing of the two would result in higher \([\text{SO}_4^{2-}]\) in the 9S porewater than was observed. It seems unlikely, therefore, that the trend in \(^{34}\)S results from the incorporation of meteoric water into the groundwater.

Second, increasing \(^{34}\)S could indicate that groundwater sulfate becomes \(^{34}\)S-depleted as it moves toward the surface. This can happen when \(^{34}\)S-depleted H2S, a byproduct of sulfate reduction, is oxidized to elemental sulfur and then back to sulfate by sulfur-oxidizing bacteria near the sediment surface. That the MS and FO porewater \(^{34}\)S values all fall in the 24 to 26‰ range would in this scenario reflect a lack of upward flowing groundwater from anoxic to oxic zones in the sediment at these locations. This possibility makes it difficult to discern the relative importance of sulfate reduction and sulfide oxidation in creating the observed porewater \(^{34}\)S gradients.

While the porewater \(^{34}\)S values can serve as a record of bacterial metabolism at the time of sampling, \(^{34}\)S\(_{\text{CAS}}\) values are more indicative of long-term trends. The sharp \(^{34}\)S-enrichment below 27 cm at 9S (Fig. 4) could suggest a systematic isotopic fractionation for different carbonates minerals, as generally there is a greater ratio of aragonite to dolomite with depth (Plon, this volume). The MS data exhibits the same trend in \(^{34}\)S\(_{\text{CAS}}\) though to a less dramatic extent, and could support this hypothesis. However, the trend might also reflect a major change in the hydrology or bacterial populations in the lake basin associated with the loss of creek inputs due to artificial water collection in the surrounding area within the last 50 years.

CONCLUSIONS

Porewater sulfate concentration and isotope data indicate that there is limited evidence for the activity of SRB associated with anoxia in the sediment of Deep Springs Lake. While increasing \(^{34}\)S values with depth at all three sites can be used to substantiate this claim, however, the observed trends could alternatively suggest the intermixing of multiple water sources, or, more likely, the occurrence of sulfide oxidation as spring water moves from anoxic to oxic regions of sediment. Values of \(^{34}\)S\(_{\text{CAS}}\) demonstrate a long-term trend in isotope fractionation as sulfate was incorporated into carbonate lattices. A trend toward \(^{34}\)S\(_{\text{CAS}}\)-depletion below 27 cm could be related to differential isotopic fractionation into dolomite versus aragonite.

As the evidence for sulfate reduction is obscured by other variables, it is not possible to draw conclusions about SRB mediation of dolomite precipitation from this study alone. Bacterially mediated carbonate precipitation experiments using bacteria collected from the lake might give more insight into this question.

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REFERENCES


