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A GEOBIOLOGICAL APPROACH TO UNDERSTANDING DOLOMITE FORMATION AT DEEP SPRINGS LAKE, CA
Faculty: *DAVID JONES*, Amherst College, *JASON TOR*, Hampshire College,
Students: *KYRA BRISSON*, Hampshire College, *KYLE METCALFE*, Pomona College, *MICHELLE PARDIS*, Williams College, *CECILIA PESSOA*, Amherst College, *HANNAH PLON*, Wesleyan Univ., *KERRY STREIFF*, Whitman College

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Keck Geology Consortium: Projects 2013-2014
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A GEOBIOLOGICAL APPROACH TO UNDERSTANDING DOLOMITE FORMATION AT DEEP SPRINGS LAKE, CA
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KERRY R. STREIFF, Whitman College
Research Advisor: Kirsten Nicolaysen

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MAGNESIUM ISOTOPE RECORDS ASSOCIATED WITH DOLOMITE FORMATION IN A MODERN LAKE

CECILIA PESSOA, Amherst College
Research Advisor: David S. Jones

INTRODUCTION

Since dolomite was discovered over 200 years ago this enigmatic mineral has been studied in the field and laboratory and yet, little consensus has been reached over "the dolomite problem": dolomite is abundant in the geologic record, but despite modern environments that are supersaturated it precipitates in few locations and is nearly impossible to produce in labs (Graf and Goldsmith 1956; Vasconcelos and McKenzie 1997). Fewer continental locations than marine settings have been studied (De Deckker and Last 1989) and little is known about how magnesium isotope ratios (δ^{26}Mg) are affected during dolomite formation. The occurrence of dolomite in the sediments of Deep Springs Lake (DSL), an alkaline playa lake in eastern California, provides an opportunity to study magnesium isotope systematics associated with modern dolomite formation. This project provides new data on magnesium isotope fractionation associated with low-temperature dolomite formation in a lacustrine continental setting through the analysis of the sediments and pore water of DSL.

Profiles of δ^{26}Mg coupled with [Ca^{2+}], and [Mg^{2+}] in the lake sediment and pore waters provide a new perspective on where and how dolomite is precipitating in DSL. The availability of magnesium ions is a limiting factor for dolomite production at DSL (Meister et al. 2011), and variations in the ion concentrations and the Mg/Ca ratio with depth and at various locations on the lake bottom can indicate influential factors at play. The fractionation of magnesium isotopes in the sediment is telling because carbonate minerals preferentially take up ^{24}Mg while clay minerals incorporate the heavier isotopes ^{25}Mg and ^{26}Mg (Higgins and Schrag 2010). The data collected and analyzed in this study give insight into the roles of microbial activity at depth in the subsurface, the differences between spring sites and lake bottom locations, and important geochemical and mineralogical horizons in the sediment of Deep Springs Lake.

SITE DESCRIPTION

Deeps Springs Lake lies in California's Inyo County east of the Sierra Nevada mountain range. It is in the northeastern trending Deep Springs Valley between the White and Inyo Mountains bounded by faults (Peterson, Bien, and Berner 1963). This ephemeral alkaline lake is at an elevation of about 1500 m and is 2.7 km across. The lake can be divided into zones based on the dominant mineralogy of the overlying evaporite crusts. The crusts form an uneven surface marked by desiccation cracks and teepee structures. The thick and sticky underlying mud is dark green-grey. The lake bottom is extremely flat except for the remains of an artificial levee, which now stands only along the eastern side.

DSL is recharged by seasonal melt water from a drainage area of 200 mi^2 in the surrounding mountains (Jones 1965). The lake is also fed by a network of springs discharging into the lakebed. The annual precipitation averages 5 inches on the valley floor to 15 inches at the basin divide (Jones 1965).

To the north and east are granodioritic intrusive bodies while older sedimentary strata lie south and west (Jones 1965). The sedimentary rocks are composed of quartzite, sandstone, siltstone, shale, limestone,

dolomite sandstone, and dolomitized limestone (Jones 1965; Nelson 1962; 1966). The bulk of rocks in the mountains around the northeastern end of the valley are monzonite plutons (Nelson 1966; McKee and Nelson 1967). The recent deposits are Quaternary alluvial fans and lakebeds; alluvium on the valley floor is at least 600 ft deep and lacustrine deposits extend to a depth of 30 ft and reach 5 miles north of the current playa (Jones 1965).

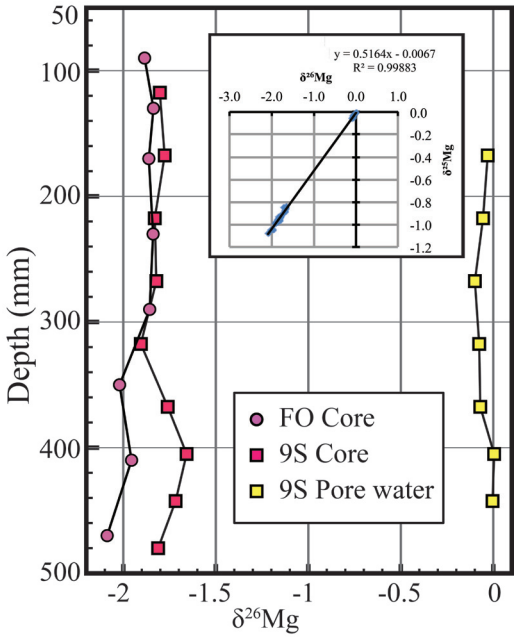

Figure 1. The $\delta^{26}Mg$ of both 9S and FO cores, and 9S pore water. Inset shows $\delta^{25}Mg$ against $\delta^{26}Mg$.

METHODS

The lack of standing water during the field season in June 2013 revealed numerous small springs on the northern side of the Deep Springs Lake saltpan, and field efforts were focused on that area. Temperature, pH, and salinity measurements were taken at each spring studied as well as the photographs, dimensions, and GPS coordinates. Spring water and peeper-collected pore water were filtered, stored in centrifuge tubes, and kept on ice. Whole and sub-sampled push cores of sediment were taken from two lakebed sites and five sites adjacent to springs using meter-long tubes of 2 or 3 inches in diameter. Pore water was collected by field-deployed peepers at one spring, 9 Spring (9S), and one non-spring lake bottom site, Muddy Site (MS), and by centrifugation of sub-sampled sediment cores, Far Out (FO).

In the lab, sediment was washed in de-ionized water, dried, homogenized, and weighed before dissolution in 2% trace metal grade acetic acid. Major and trace element concentrations for water and sediment samples were determined through inductively coupled plasma optical emission spectrometry (ICP-OES) at Amherst College. Magnesium for isotopic analysis was separated by ion chromatography (IC) and isotopic ratios measured by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) at Princeton University.

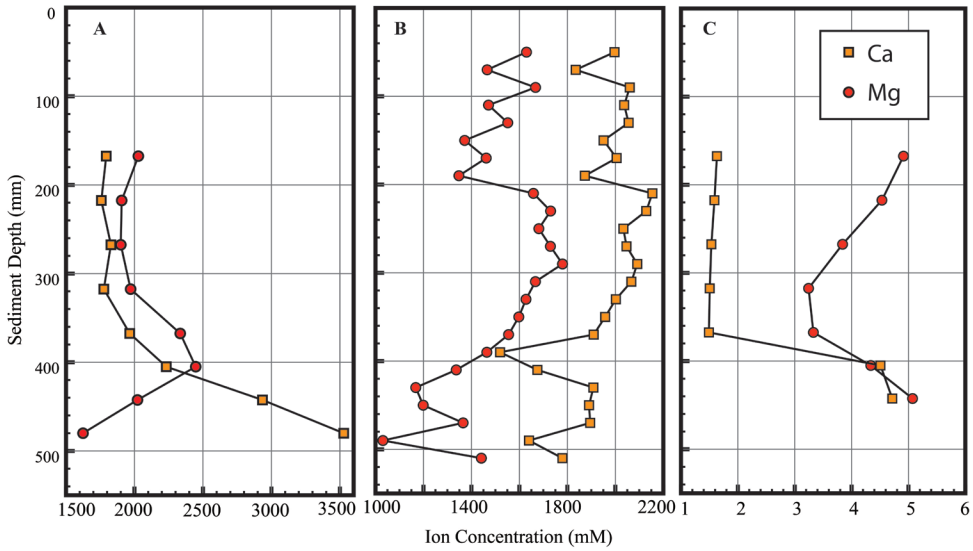

Figure 2. The magnesium and calcium concentrations for (A) 9S core, (B) FO core, and (C) 9S pore water (Plon 2014).

RESULTS

The Mg stable isotope data show that there is very little variation in isotopic composition with depth in dolomite at FO and 9S, and little variation in the 9S pore water (Fig. 1). Dolomite from both cores has δ^{26}Mg values of about -1.8‰ and the 9S pore water is about 0.0‰. The precision of the δ^{26}Mg measurements is ±0.08‰. The correlation coefficient for the isotopic ratios is $R^2 = 0.998$ and the regression line slope is 0.516 (Fig. 1). The paired pore water-dolomite δ^{26}Mg data yield a fractionation factor of 1.8‰ between the pore water and sediment at 9S. The MS pore water was too saline and the $[Mg^{2+}]$ too low for the successful separation of magnesium through ion chromatography such that isotopic analysis was not possible.

Significant changes in $[Ca^{2+}]$, $[Mg^{2+}]$, and Mg/Ca occur at a depth of 30-40 cm below the exposed DSL sediment surface at 9S and FO (Figs. 2-3). In the 9S core the concentration of ions follow each other closely, with magnesium higher than calcium, until 40 cm depth where they diverge sharply and calcium becomes much more concentrated than magnesium. In the 9S pore water the concentrations are much lower, never above 5 mM of either magnesium or calcium, but magnesium is at least four times as concentrated as calcium until 37 cm (Fig. 2). FO pore water magnesium and calcium concentrations were below the detection limit.

FO and 9S cores have Mg/Ca ratios 1 ± 0.3 until a depth of 30-40 cm where there is a dramatic decrease in both; this is pronounced in the spring-associated 9S core (Fig. 3). In contrast, the Mg/Ca ratio of the pore water at 9S starts at a high of 6.9 and decreases gradually to 4.4 before plummeting to ~1 (Fig. 3). At 9S, this shift at depth corresponds to a nearly 50% decrease in the percentage of dolomite and an accompanying increase in aragonite the carbonate portion of the sediment (Fig. 4). While the 9S Mg/Ca ratio remains somewhat constant before dropping significantly at 40 cm of depth, the FO site has smaller variations beginning at the top of the core and a much smaller drop in the Mg/Ca ratio at that depth.

DISCUSSION

Down core trends in δ^{26}Mg show strong homogeneity; the 9S pore water varies <0.1‰ and the FO and 9S sediment cores only up to 0.25‰ (Fig. 1). The slight variations are not significant because the range of values is on the same order as the uncertainty of these measurements. This result contrasts strongly with studies which report pore water variations up to 2‰ in marine sediments (Higgins and Schrag 2010) due to authigenic dolomite precipitation in the sediment. The δ^{26}Mg values at DSL are nearly uniform with depth and the different sites, spring-related and non-spring, show little variation between them, suggesting dolomite precipitation from geochemically homogeneous water.

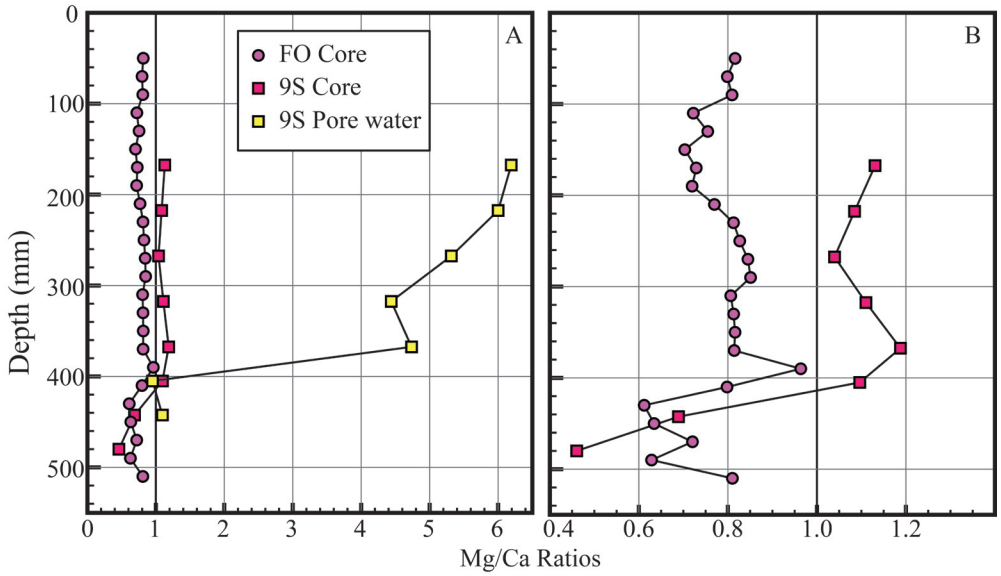

Figure 3. (A) The Mg/Ca molar ratios of 9S pore water (Plon 2014) and 9S and FO cores. (B) Detail of the two cores that shows the drop at 400 mm depth.

The Mg isotope fractionation factor of ~1.8‰ between 9S pore water and dolomite is consistent with the precipitation of dolomite found in studies of marine dolomite authigenesis (Higgins and Schrag 2010). While the down core δ^{26}Mg trends differ, the fractionation factor of the continental lake DSL and marine cores are the same, suggesting that both sites are producing dolomite through the same process.

The data show that there is no isotopic evidence for dolomite precipitation within the sediment of DSL where anaerobic microbial activity is highest: at anoxic depths in the sediment or near springs. These results challenge findings that emphasize the importance of microbial metabolism in the production of dolomite (Vasconcelos and McKenzie 1997). Sulfate-reducing bacteria are present in the anoxic depths of carbonate mud, but the homogeneity of δ^{26}Mg at all depths measured in cores and pore water indicate that sulfate reducing bacteria are not altering conditions in the sediment to facilitate the precipitation of dolomite (Vasconcelos and McKenzie 1997). If dolomite were forming in the sediment from the pore water, and facilitated by anaerobic microbial activity, the pore water δ^{26}Mg would decrease significantly below the oxidized layer of sediment. In addition, the fractionation factor would not be so consistent because precipitation in the sediment would alter the δ^{26}Mg of pore water. This study provides independent evidence from δ^{26}Mg trends supporting the hypothesis that dolomite precipitates in the DSL water rather than within the sediment (Meister et al. 2011).

Changes in the calcium and magnesium ion concentrations, the Mg/Ca ratios, and percentage of dolomite in the carbonate portion of sediment identify the 30-40 cm zone as a significant depth in the DSL sediment. This is possibly the interface between the lake water and ground water that is feeding the springs. However, it is also possibly a change in mineralogy related to past changes in the lake chemistry that occurred as those sediments precipitated from the lake water. Sampling cores farther towards the center of the lake would give insight into this phenomenon. The shift remaining at a constant depth would suggest an interface between

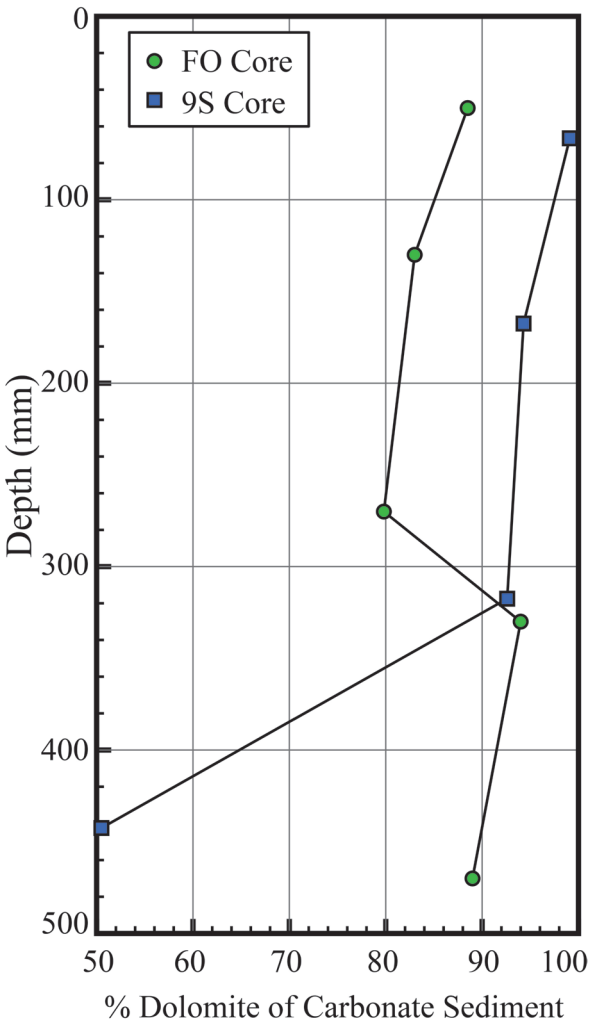

Figure 4. The percentage of dolomite in the carbonate sediment (dolomite, calcite, and aragonite) (Plon 2014).

lake and ground water. However, the center of the lake has standing water more than the edges and would produce more sediment than peripheral areas, therefore, if the shift were to gradually deepen this would indicate a change in the lake's chemistry at some point in the past that affected the mineralogy. The sedimentation rate for DSL has been estimated at 1 mm per 1-30 yrs based on ^{14}C dating of dolomite crystals of different sizes (Peterson, et al., 1963); for a depth of 30-40 cm that gives an age range of 300 - 12,000 yrs. Should this shift prove to be a relic of a past change in lake water chemistry, further dating work would prove valuable to narrow the range of when it happened.

The δ^{26}Mg results reported here should be augmented

and repeated by studying more sites. Measuring the magnesium isotopic ratios of other cores and pore water previously collected will strengthen this result. It would be especially helpful to collect cores and pore water from locations closer to the center of the lake. The most important additional data will be the δ^{26}Mg of the lake water itself, which will require sampling in late winter or spring when the lake is full.

CONCLUSIONS

The data collected from Deep Springs Lake and analyzed in this project support the following conclusions about the nature of the magnesium isotope cycle and the production of dolomite at the lake.

1. The δ^{26}Mg measured in the sediments and pore water of DSL are nearly constant with depth. These values vary <0.1‰ in the pore water and only up to 0.25‰ in the cores.

2. There is no difference observed between the spring-related and non-spring sites studied. The proximity to areas of exceptionally high microbial activity below the sediment-water interface doesn't impact the δ^{26}Mg of sediments.

3. The magnesium isotope fractionation factor measured is ~-1.8‰ for this continental lacustrine setting. This is the same as is found in marine settings, suggesting that there are similar processes occurring in marine and continental settings of dolomite precipitation.

4. There is an interface observed at a depth of 30-40 cm where changes in the magnesium and calcium concentration, Mg/Ca ratio, and percent of dolomite in the carbonate sediment appear at both spring and non-spring sites and in both pore waters and sediments.

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