PROCEEDINGS OF THE TWENTY-SEVENTH ANNUAL KECK RESEARCH SYMPOSIUM IN GEOLOGY

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Keck Geology Consortium: Projects 2013-2014 Short Contributions— Geobiology of Dolomite Formation Project

A GEOBIOLOGICAL APPROACH TO UNDERSTANDING DOLOMITE FORMATION AT DEEP SPRINGS LAKE, CA

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JASON M. TOR, Hampshire College

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KERRY R. STREIFF, Whitman College Research Advisor: Kirsten Nicolaysen

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EXPLORING MEDIATION OF DOLOMITE PRECIPITATION USING STABLE CARBON AND OXYGEN ISOTOPES, DEEP SPRINGS LAKE, CA

KERRY R. STREIFF, Whitman College **Research Advisor:** Kirsten Nicolaysen

ABSTRACT

Modern dolomite (CaMg(CO₂)₂) precipitation is extremely limited and occurs in few locales, despite oversaturation in many environments. The significant quantity of dolomite present in Deep Springs Lake, CA provides an opportunity to test the hypothesis that bacteria surmount the barriers that normally prevents dolomite precipitation. Analysis of stable carbon and oxygen isotope ratios of modern sediment in five cores obtained near springs in the lake test the hypothesis that biological activity induces dolomite formation. The δ^{13} C average value from bulk carbonate sediment at all studied locations (3.8%) is consistent with equilibration with atmospheric CO₂. This dolomite could not have precipitated from inorganic carbon dissolved in pore water adjacent to a methane-rich spring, which has greatly enriched average δ^{13} C values (9.4%). For an environment in equilibrium, the inorganic precipitation of carbonates would normally create enriched δ^{13} C values in comparison to the pore water. For spring site 9S#11, the offset between carbon isotopes of carbonate and organic carbon in sediment cores ($\Delta^{13}C = \delta^{13}C_{\text{carbonate}} - \delta^{13}C_{\text{organic}}$) was homogeneous throughout the depth profile and averaged 26.9‰. Both lines of evidence suggest that dolomite precipitation in Deep Springs Lake does not rely upon bacterial mediation.

INTRODUCTION

Understanding modern microbiological contributions to carbonate precipitation is advantageous for identifying signatures of early life on Earth and may aid in detection of biological activity on other planets. Several recently conducted studies, including Meister *et al.* (2011), Wacey *et al.* (2007), and Botz & von der Borch (1984), have utilized stable isotope ratios to aid in understanding the mechanism of modern dolomite formation, testing hypotheses of biological mediation versus an ion super-saturation model. By analyzing carbon-13 and oxygen-18 isotope fractionation, this study investigated the potential associated effects of sulfate-reducing bacteria and methanogens on dolomite precipitation from sites clustered around the northern limits of Deep Springs Lake.

METHODS

Sediment Preparation

In June 2013, sediment cores were taken from the viscous mud below the saltpan of Deep Springs Lake ~1 m laterally away from each spring using ~5 cm and ~6.5 cm diameter polyurethane tubes. The cores, taken from four sites (MS, 9S, SS, FO), were sampled at regular depths that matched the depths of sampled pore water. To prevent the formation of salt crystals from pore water, the samples were washed with deionized (DI) water in triplicate before they were dried in an oven (70°C) overnight (~12 hours) and finely powdered.

Isotope Measurements

The δ^{13} C and δ^{18} O ratios were determined on the washed and dried aliquots of dried an homogenized sediment. Thirty-four sample tubes, including 6 Washington State University (WSU)-Carbonate

Standards, 2 NBS-19 Standards, 5 doubled samples and a blank, were placed in the Finnigan GasBench II mass spectrometer and kept at a constant temperature of 26°C. The samples were flushed with pure helium (~5 min per tube) and 0.1 mL of 100% phosphoric acid was added.

In order to measure δ^{13} C and Total Organic Carbon (TOC) content from the organic matter, the washed and dried sediment was dissolved, leaving an insoluble residue. Enough 3 M hydrochloric acid was added to ~3.0 g of powdered sediment for the total quantity within each vial to reach 35 mL. To measure TOC, ~5.0 mg of the insoluble residue was measured on a high precision Sartorius microbalance and placed into tin capsules (5 x 9 mm). Samples were burned in excess of oxygen and an elemental analyzer at Wesleyan University then analyzed the resulting CO₂ and N₂ gases emitted. Using the masses of carbon and initial sediment weights, the TOC was calculated. To measure δ^{13} C of organic matter, approximately 5.0 mg of the insoluble residue was weighed into tin cups, gently compacted and loaded into Oregon State University's (OSU) Costech Zero Blank Autosampler with isotopic lab standards. The residue was then flash combusted at above 1000°C using a Carlo Erba NA1500 elemental analyzer and analyzed through use of a DeltaPlusXL isotope ratio mass spectrometer.

RESULTS

Total Organic Carbon

For these samples, TOC (Fig. 1) varies between 0.2 and 1.3 wt % and in three cores appears to increase with depth. Core FO#4, located centrally in the lake, remains relatively homogenous with depth but exhibits a much higher value overall (average ~1.2 wt %). At the lake margin, TOC in cores SS#9 and MS#2, the non-spring site, more than doubles by the last point recorded at depths of 26 cm and 47 cm respectively. Core 9S#11 shows that sediment adjacent to the spring with the largest output of surface water has very consistent TOC content until ~40 cm below the surface where an excursion to higher organic content exists.

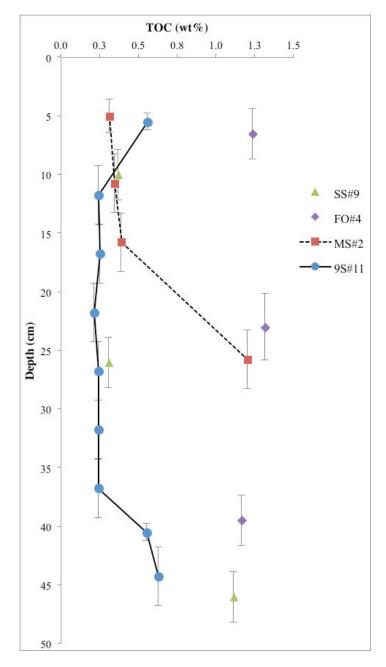


Figure 1. Down-core profile of Total Organic Carbon (TOC) content of bulk soft sediment from Deep Springs Lake sites SS#9, FO#4, MS#2 and 9S#11. A dashed line identifies a non-spring site, MS #2, whereas a solid line indicates 9S#11, the most complete core for a spring site. Differences in the reproducibility of each carbon and oxygen measurement are smaller than symbol size on this and subsequent plots. Vertical error bars show the sampling interval from which each sediment plug was obtained.

Carbon and Oxygen Isotopes

The δ^{13} C and δ^{18} O values for matter (Fig. 2) in bulk carbonate sediment (dolomite and aragonite) display consistent values and both plots trend slightly less positive values with increasing depth for all four

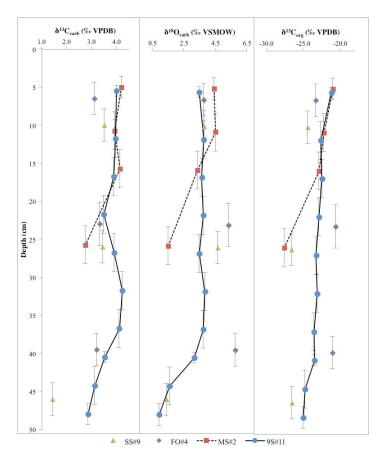


Figure 2. Down-core profiles of $\delta^{13}C_{carbonate}$, $\delta^{18}O_{carbonate}$ & $\delta^{13}C_{organic}$ in bulk sediment from Deep Springs Lake sites SS#9, FO#4, MS#2 and 9S#11.

cores. The δ^{13} C values vary between +1.4 and +4.3% whereas the δ^{18} O values vary between +0.9 and +5.8%. For both isotopic tracers, spring site 9S#11 stays relatively homogenous at +4 and +3‰ respectively until ~40 cm below the surface when isotopic compositions drop rather dramatically to +2.5 and +0.5% respectively. Both plots also show that the isotopic compositions for site MS#2, a more centrally located, non-spring site compared to 9S#11, sharply decrease at ~25 cm below the surface. The δ^{13} C values for organic matter (Fig. 2) in bulk sediment range from -21 to -28‰ throughout the profile. The values for core 9S#11 remain relatively consistent and illustrate a minor steady depletion with depth. As seen in the carbonate data, core MS#2, a non-spring site, exhibits a distinct deviation towards more negative values at ~25 cm below the crust.

The Δ^{13} C values (Fig. 3), the isotope fractionation between the carbonate and organic matter, vary

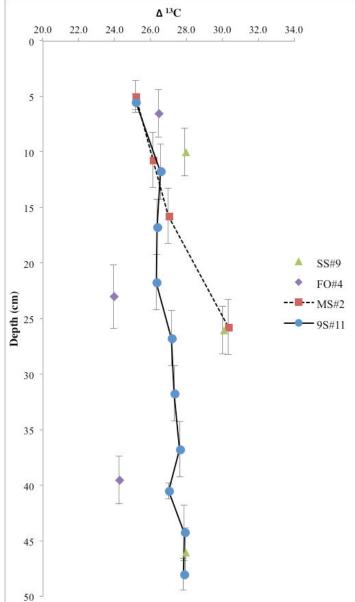


Figure 3. Down-core profile of $\Delta^{13}C$ ($\delta^{13}C_{carbonate}$ - $\delta^{13}C_{organie}$) in bulk sediment from Deep Springs Lake sites SS#9, FO#4, MS#2 and 9S#11.

between 23 and 31% throughout the profiles. Core 9S#11 exhibits a monotonic increase in the isotopic difference with depth while the other cores demonstrate a slightly more irregular distribution. MS#2 shows a much larger consistent change in depth than any other the other core sites. At shallow depths (~5 - 20 cm) all of the sites display similar isotopic data values (Figs. 2 and 3).

DISCUSSION & CONCLUSIONS

Botz and van der Borch (1984) proposed that dolomite would form in fresh water lakes under conditions of extreme super saturation and high Mg content. Meister and others (2011) in their previous investigation Deep Springs Lake mapped out a number of carbonate minerals, including both aragonite and dolomite. There are two different equilibriums present in this system: the atmosphere with DIC and DIC with the carbonates. A more negative δ^{13} C value indicates a larger amount of 12 C, the lighter carbon isotope. 13 C is

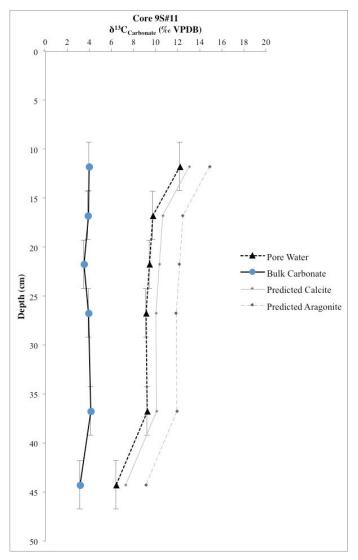


Figure 4. Down-core profile comparing $\delta^{13}C_{carbonate}$ values from the bulk sediment and Dissolved Inorganic Carbon (DIC) in pore water from Deep Springs Lake spring site 9S#11. Pore water data from Plon, 2014, this volume. Gray lines forecast expected $\delta^{13}C$ carbonate values for a system in equilibrium with the $\delta^{13}C$ of the DIC in the pore water (Rubinson & Clayton, 1969). The dramatic difference in predicted and measured carbonate carbon isotopic compositions precludes inorganic precipitation as the sole mechanism for carbonate formation.

heavier than 12 C and forms slightly stronger chemical bonds. In addition, diffusion of 13 CO $_2$ is slower than that of 12 CO $_2$ because of the associated difference in mass (O'Leary, 1988). If inorganic precipitation of carbonate minerals from pore water is the dominant dolomite forming process, then the δ^{13} C $_{carbonate}$ should be isotopically heavier than the pore water that formed it. Wacey and others (2007) proposed that microbial metabolism could explain the isotopic compositions of dolomitic sediments from lakes in South Australia.

Field evidence for intense microbial activity at spring site 9S#11 includes bubbles of methane gas, indicating methanogenesis at depth. In methanogenesis, bacteria intake organic matter and produce one reduced species (methane, CH₄) with isotopically depleted δ^{13} C and one oxidized species (CO₂) with isotopically enriched δ^{13} C. At 9S#11 the δ^{13} C of the pore water DIC maintains an enriched average value of 9.4% although it becomes slightly depleted with depth (Plon, 2014, this volume), whereas the $\delta^{13}C_{\text{carbonate}}$ remains uniform with an average value of 3.8% (Fig. 4). In contrast, the predicted values for carbonate inorganically precipitated from this DIC (in gray) are based upon carbon fractionation factors from Rubinson & Clayton (1969) for a system in equilibrium. These data are inconsistent with dolomite precipitating from the porewater DIC that is associated with methanogenesis.

The δ^{13} C and δ^{18} O values from the carbonates of spring site 9S#11 (Fig. 2) and the TOC (Fig. 1) remain relatively uniform except for an excursion beginning at ~35 cm depth. Aragonite (CaCO₂) exhibits an orthorhombic crystal lattice, whereas dolomite (MgCa(CO₂)₂) is hexagonal. The differences in these lattices and the bond strength with carbon causes fractionation between 12C and 13C resulting in a fractionation factor for aragonite that >1% more depleted than dolomite (Meister et al., 2011). The excursion of δ^{13} C & δ^{18} O values toward the base of the 9S#11 core, and possibly the excursions at depths of ~25 cm in two other cores, supports an inference that the different fractionation factors for different minerals explains this phenomenon. We observe a discernible increase in aragonite at the depth where isotopic depletion begins to occur.

Consistency with depth for site 9S#11 is particularly apparent throughout all isotope data plots although

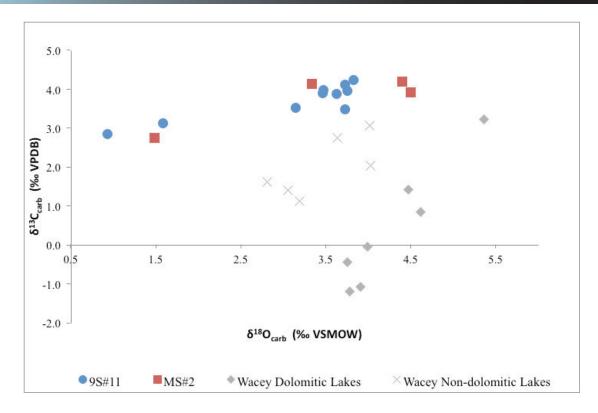


Figure 5. Cross-plot of $\delta^{18}O_{carbonate}$ and $\delta^{13}C_{carbonate}$ from bulk carbonate sediment in Deep Springs Lake (9S#11 & MS#2) and from the dolomitic and non-dolomitic Coorong Lakes in South Australia. Note that the lakes plot in distinctly different areas from each other and from Deep Springs Lake values.

it is striking in the values including organic matter because there are many components that would cause increased variation. A wide range of fractionation factors is expected depending on ambient CO₃ concentrations, although the largely negative δ^{13} C values from the organic matter (Fig. 2) and subsequent elevated Δ^{13} C values (Fig. 3) are associated with the presence of additional biological factors. The average δ^{13} C organic matter value of -23.2% (Fig. 2), and average fractionation factor of 26.9% (Fig. 3) is similar to recorded isotopic analyses of Rubisco in C₃ plants (Popp et al., 1998). These data suggest the organic matter was fixed through standard photosynthetic processes involving lake bicarbonate for the carbonate source. Either high CO, and/or low growth rate conditions present in Deep Spring Lake at the time of dolomite precipitation are liable to be effects of the hypersaline environment.

With the assumption that the organic matter is fixed from the dissolved inorganic carbon (DIC) during surface precipitation, the difference between $\delta^{13}C_{\text{carb}}$ and $\delta^{13}C_{\text{org}}$ should be relatively constant if the $\delta^{13}C_{\text{carb}}$ is set at the surface rather than within the sediment. This is the case for 9S#11 (Fig. 3), providing further support for surface precipitation rather than microbially mediated precipitation in the sediment. The plot of δ^{13} C in the organic matter (Fig. 2) becomes slightly isotopically depleted with depth but does not show the sharp excursion present in the neighboring carbonate plots. Also, the $\delta^{13}C_{\mbox{\tiny carb}}$ values are not depleted, which would be the case if the carbon source for dolomite precipitation was respired organic material produced during a biological process such as sulfate reduction. Sulfate reduction produces isotopically depleted bicarbonate for the DIC and since these dolomites appear to have precipitated from DIC in equilibrium with the atmosphere, it is unlikely that dolomite from Deep Springs Lake formed as a byproduct of sulfate reducing bacteria.

Figure 5 is a cross-plot showing δ^{13} C values (plotted against δ^{18} O) for carbonate lake sediments. The δ^{13} C data collected from Deep Springs Lake spring

site 9S#11 and non-spring site MS#2 range from 2.9 to 4.2‰ while values from the Coorong Region of South Australia plot more negatively. Also, $\delta^{13}C$ values for Coorong dolomitic lake sediments range from -1.2 to +3.2‰ whereas non-dolomitic lake sediments are more positive and condensed between +1.1 and +3.1‰ (Wacey et al., 2007). The reason that dolomitic sites in Deep Springs Lake plot with more enriched $\delta^{13}C$ values may simply be due to meteoric differences in location sites. If so, spring and non-spring locations near Deep Springs Lake that do not contain dolomite would present even more enrichment and would be plotted above the data from this exploration.

In summary, it appears unlikely that the DIC at 9S#11 spring is in equilibrium with the atmosphere and may have been influenced by methanogens. The $\delta^{13}C_{\text{carbonate}}$ & $\delta^{18}O_{\text{carbonate}}$ data indicate that the carbonate precipitated from DIC in equilibrium with the atmosphere and not from the DIC produced by respiration of organic matter. Therefore, it is dubious to infer that dolomite precipitation is solely mediated by anaerobic microbial metabolisms.

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REFERENCES

- Botz, R.W. & von der Borch, C.C. (1984) Stable isotope study of carbonate sediments from the Coorong Area, South Australia. *Sedimentology* 31:837–849.
- Harkness, D.D. & Wilson, H.W. (1979) Scottish universities research and reactor centre radiocarbon measurements III. *Radiocarbon* 21:203-256.
- Meister, P., Reyes, C., Beaumont, W., Rincon, M., Collins, L., Berelson, W., Stott, L., Corsetti, F. & Nealson, K.H. (2011) Calcium and magnesium-limited dolomite precipitation at Deep Springs Lake, California. *Sedimentology* 58:1810-1830.

- Popp *et al.* (1998) Effect of phytoplankton cell geometry on carbon isotope fractionation. *Geochim. Cosmochim. Acta* 62, 69-77.
- Rubinson, M. & Clayton, R.N. (1969) Carbon-13 fractionation between aragonite and calcite. *Geochimica et Cosmochimica Acta*, 33, 8:997-1002.
- Wacey, D., Wright, D.T. & Boyce, A.J. (2007) A stable isotope study of microbial dolomite formation in the Coorong Region, South Australia. *Elsevier: Chemical Geology* 244:155-174.