

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

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Mt. Holyoke College, South Hadley, MA

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**EVALUATING EXTREME WEATHER RESPONSE IN CONNECTICUT RIVER FLOODPLAIN ENVIRONMENT:**

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

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**POTENTIAL EFFECTS OF WATER-LEVEL CHANGES ON ON ISLAND ECOSYSTEMS: A GIS SPATIOTEMPORAL ANALYSIS OF SHORELINE CONFIGURATION**

Faculty: *KIM DIVER*, Wesleyan Univ.

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**PÃHOEHOE LAVA ON MARS AND THE EARTH: A COMPARATIVE STUDY OF INFLATED AND DISRUPTED FLOWS**

Faculty: *ANDREW DE WET*, Franklin & Marshall College, *CHRIS HAMILTON*, Univ. Maryland, *JACOB BLEACHER*, NASA, GSFC, *BRENT GARRY*, NASA-GSFC

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**THE GEOMORPHIC FOOTPRINT OF MEGATHRUST EARTHQUAKES: A FIELD INVESTIGATION OF CONVERGENT MARGIN MORPHOTECTONICS, NICOYA PENINSULA, COSTA RICA**

Faculty: *JEFF MARSHALL*, Cal Poly Pomona, *TOM GARDNER*, Trinity University, *MARINO PROTTI*, *OVSICORI-UNA*, *SHAWN MORRISH*, Cal Poly Pomona

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**HOLOCENE AND MODERN CLIMATE CHANGE IN THE HIGH ARCTIC, SVALBARD NORWAY**

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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**

Faculty: DAVID S. JONES, Amherst College  
JASON M. TOR, Hampshire College

**MICROBIAL COMMUNITY ANALYSIS OF DEEP SPRINGS LAKE, CA: EXPLORING THE ROLE OF AEROBIC BIOFILMS IN BIOGENIC DOLOMITE PRECIPITATION**

KYRA BRISSON, Hampshire College  
Research Advisor: Jason M. Tor

**GEOCHEMICAL EVOLUTION OF BRINES CONSTRAINED BY NAHCOLITE CONCRETIONS OF DEEP SPRINGS LAKE, CA**

K.S. METCALFE, Pomona College  
Research Advisors: David Jones and Robert Gaines

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

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

**MAGNESIUM ISOTOPE RECORDS ASSOCIATED WITH DOLOMITE FORMATION IN A MODERN LAKE**

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

**GEOCHEMISTRY OF PORE WATERS, SPRINGS, AND SEDIMENTS AT DEEP SPRINGS LAKE, CA: IMPLICATIONS FOR DOLOMITE FORMATION**

HANNAH PLON, Wesleyan University  
Research Advisor: Timothy Ku

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

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# GEOCHEMISTRY OF PORE WATERS, SPRINGS, AND SEDIMENTS AT DEEP SPRINGS LAKE, CA: IMPLICATIONS FOR DOLOMITE FORMATION

**HANNAH PLON**, Wesleyan University

**Research Advisor:** Timothy Ku

## INTRODUCTION

Dolomite is a carbonate mineral,  $\text{CaMg}(\text{CO}_3)_2$ , that is common in the geologic record, but is rarely found in Holocene sediments. Dolomite does not readily precipitate in the laboratory at Earth surface temperatures and pressures without the addition of microbes (Warren, 2000). Today, dolomite is formed in a small number of Earth surface environments such as Deep Springs Lake, CA, which contain hypersaline, alkaline waters and sulfate-reducing bacteria (Warren, 2000). Recent studies of this hypersaline playa lake have hypothesized models for the local process of dolomite formation (Meister et al., 2011). However, questions still remain regarding the mechanism of dolomite formation, the specific roles of bacterial communities, and how modern lacustrine dolomite formation is related to marine-influenced dolomite units in the geologic record (Warren, 2000). This study presents spring water and pore waters chemistries and sediment mineral analyses to better understand how and why dolomite is forming at Deep Springs Lake.

Deep Springs Lake is in the southeast corner of Deep Springs Valley, covering 13 km<sup>2</sup> (Jones, 1965). Many ephemeral streams drain to the alluvial fans surrounding the valley, but rarely reach the lake. Rather, surface water that flows into Deep Springs Lake is mostly from the neighboring springs (Jones, 1965). Inflow water to the playa comes from the Bog-mound Springs to the North, Corral Springs to the East, and Buckhorn Springs to the Southeast. These springs are recharged by Wyman-Crooked Creek and Birch Creek-Antelope Creek (Eugster and Hardie, 1978). During sample collection for this study, (June

17-21, 2013) there was no standing water in Deep Springs Lake and water was only found at spring locations in playa and lakebed surface.

## PREVIOUS WORK

Jones (1965) studied the geology and hydrology of Deep Springs Lake, including geochemistry of the lake inputs (bog springs, streams) and lake waters and created a map of the mineralogy of evaporative crusts on the lakebed. The mineralogical zones are imperfect concentric circles; from the center to the margins the surface mineralogy is characterized by burkeite, thenardite, gaylussite, dolomite, then aragonite/calcite (Jones, 1965). Meister et al., (2011) examined the processes of modern dolomite precipitation at Deep Springs Lake by sampling lake waters, pore waters, and sediments. This study concluded that authigenic fine-grained dolomite is precipitating in the water column and not in the subsurface. This is because the evaporite crust limits the downward flux of  $\text{Mg}^{+2}$  and  $\text{Ca}^{+2}$  concentrations, and the textural properties of the dolomite show perfect euhedral growth and no cementation. Carbon and oxygen isotope data and leaching experiments supported this conclusion. This dolomite formation process was hypothesized to be similar to the type-A formation of dolomite described from the Coorong Lagoon area in Australia (Rosen et al., 1989).

## METHODS

Water and sediment samples were collected from five spring sites (9S, CS, ES, PS, SS) and two non-spring sites (MS and FO) on the lake bed. Site MS

was within 20m from spring 9S, while FO was much farther out in the lake away from the springs. For spring waters, pH, temperature, and salinity were analyzed in the field. Spring waters were filtered through 0.2 micron Sterivex filters and preserved in 50 mL centrifuge tubes for later analyses. To estimate pore water chemistry at sites 9S and MS, peepers were installed in situ. Two peepers, each extending to a depth of 50 cm, were prepared by filling the wells with deionized water and covering the wells with dialysis paper prior to insertion into the sediment. The peepers were retrieved after four days and pore waters were filtered through 0.45  $\mu\text{m}$  filters and preserved for subsequent analyses. Samples for  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\delta^{13}\text{C}_{\text{CH}_4}$  analysis were collected and preserved from the pore and spring waters in pre-vacuumed Exetainers. Sediment cores were collected in two-inch diameter polycarbonate tubes at MS, FO, and 9S (right next to the 9S spring). Cores at sites MS and FO were extruded after collection and sediments were sampled every 2 cm. At the FO site, centrifuge tubes were filled completely during the extrusion and then centrifuged at Amherst College to extract pore water.

In the lab at Amherst College, alkalinity was determined by Gran titration using the online Alkalinity Calculator provided by the USGS and Oregon Water Science Center. Cation ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{+2}$ ,  $\text{Ca}^{+2}$ ) and anion ( $\text{Cl}^-$ ,  $\text{SO}_4^{-2}$ ) concentrations were determined on diluted samples at Amherst College using a Leeman Labs ICP-OES and a Dionix ion chromatograph. The UC-Davis Stable Isotope Laboratory determined DIC concentrations and measurements of  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\delta^{13}\text{C}_{\text{CH}_4}$ . Mineral saturation states were calculated from water chemistries in Geochemist Workbench 6.0 software using alkalinity and field temperatures. If calcium or magnesium concentrations were below the calibration range, a maximum concentration of 0.02 ppm was assumed. Evaporation paths were calculated using Geochemist Workbench 6.0.

Epoxy impregnated polished thin sections were made at Amherst College and examined by polarized light microscopy and by SEM (JOEL JSM-6390LV) using TEAM-EDAX software for elemental and phase composition mapping. Mineral concentrations were determined on bulk sediments using XRD patterns and

RockJock version 11 software (Eberl, 2003). Samples were run from 5° to 65° (2 $\theta$ ) and mineral peaks were quantified by comparison with an internal corundum standard at a 1: 0.25 (sample/corundum) weight ratio.

## RESULTS

In the 9S and MS sediment cores, dolomite is the most prevalent mineral, averaging 20% and 18%, respectively, with no clear depth trend (Fig. 1ab). In the FO core, dolomite comprises between 8% and 14% of the sediment and is lower in concentration compared to smectite clay minerals and thenardite (Fig. 1c). Sediments at site 9S consist of 27% carbonates (dolomite, aragonite, and calcite), 7% evaporites (halite, thenardite), 19% detrital silicates (feldspars and quartz), 24% smectite and chlorite clay minerals, and 24% other minerals (mainly other clays, amphibole, and nahcolite). Sediments at site MS have similar values, consisting of 31% carbonates, 8% evaporites, 20% detrital silicates, 24% smectite and chlorite clay minerals, and 16% other minerals. At the FO site, carbonates are not the dominant mineral group. Sediments at site FO consist of 15% carbonates, 23.9% evaporites, 17% detrital silicates, 21% smectite and chlorite clay minerals, and 23% other minerals. In the 9S, MS, and FO cores, on average dolomite makes up 80%, 90%, and 60% of the carbonate minerals, respectively. FO is the only core with significant amounts of thenardite with three of the five depth intervals containing between 16 and 36%. Thenardite concentrations are less than 5% in the 9S and MS cores. Aragonite is only found at depths more than 20cm in the 9S and MS cores.

Polarized light microscopy and SEM-EDS analyses reveal dolomite to be fine-grained and a common matrix component, usually mixed with Mg-rich clays and other minerals. Under plane light the dolomite is clear and colorless and difficult to differentiate from other matrix minerals (Fig. 2a). Similarly the high birefringence of dolomite is difficult to identify under cross-polars due to the small crystal size (Fig. 2b). The SEM backscatter, elemental, and phase maps illustrate that dolomite (Ca, Mg, O) or other Ca-Mg carbonates are interspersed with aluminosilicate phases and cannot be easily identified except when present as detrital grains, pieces eroded off of nearby mountains and transported to the lake (Fig.



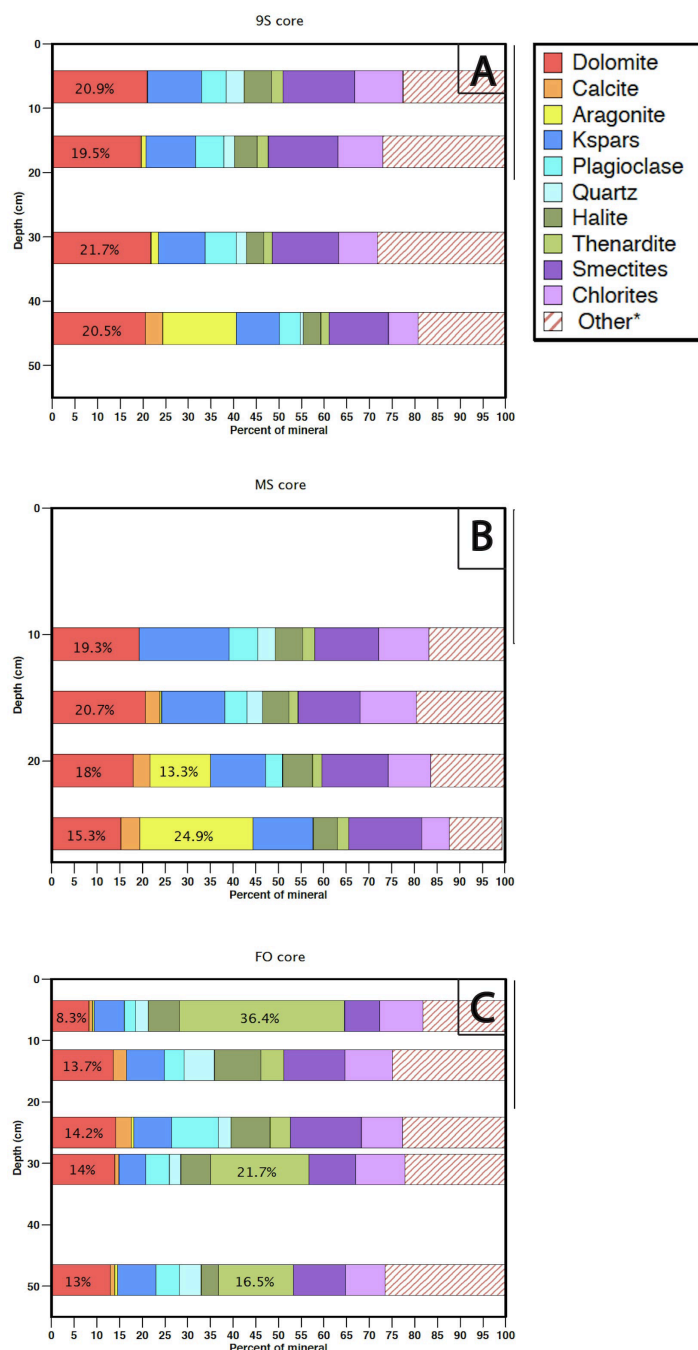


Figure 1. Normalized mineral weight percentages per core depth from sites 9S (A), MS, (B), and FO (C). "Other" includes magnesite, gypsum, sylvite, celestine, amphibole, chabazite, nahcolite, anglesite and clays that are not chlorites or smectites. Data collected using RockJock.

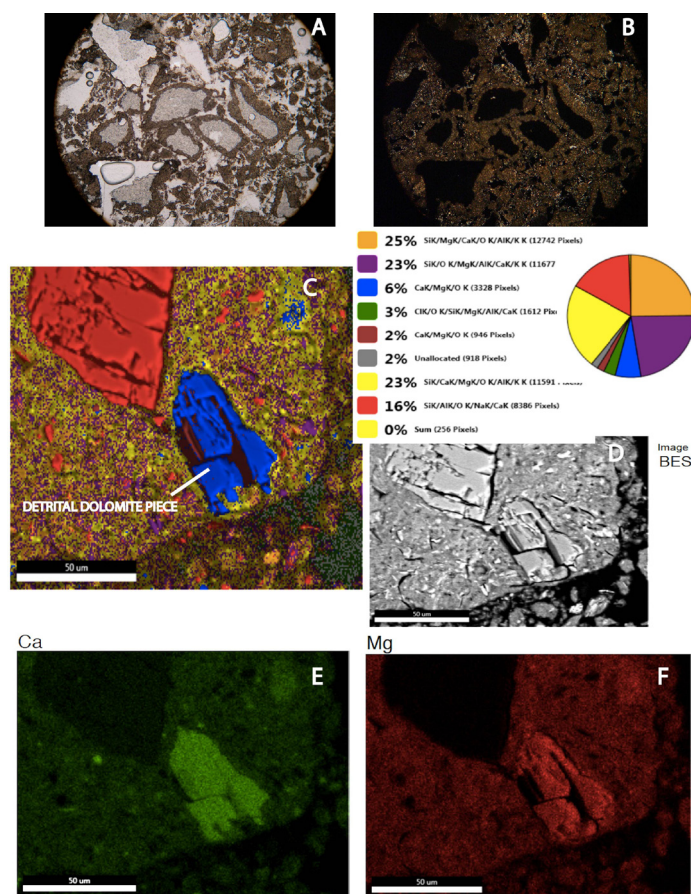


Figure 2. PPL (A) and XPL (B) images at 10x magnification, from 9S core. SEM phase map with pie chart of phase concentrations (C), image (D) and elemental maps for Ca (E) and Mg (F) from 9S core showing a piece of detrital dolomite in blue. The colors on the elemental maps (E and F) do not correspond to the phase map colors.

2c-f). A common feature is amorphous silica phases surrounded by a dolomite-clay matrix. In some cases, the inside silica phase appears highly weathered or is completely missing (Fig. 2a).

The 9S peeper had very little water in the top two intervals even though they were submerged in the sediment. The top 3 cm of the MS peeper were sticking out above the sediment and so no water was collected. The pH values of the pore waters range from 8.0 to 9.8 with the lowest in 9S and the highest in FO (Fig. 3a). For the springs, the pH values range between 8.0 to 8.2. The average alkalinity of the 9S, MS, and FO pore waters is 36 meq/kg, 393 meq/kg, and 893 meq/kg, respectively (Fig. 3b). The alkalinities of the springs range from 47 meq/kg in 9S to 504 meq/kg in CS.

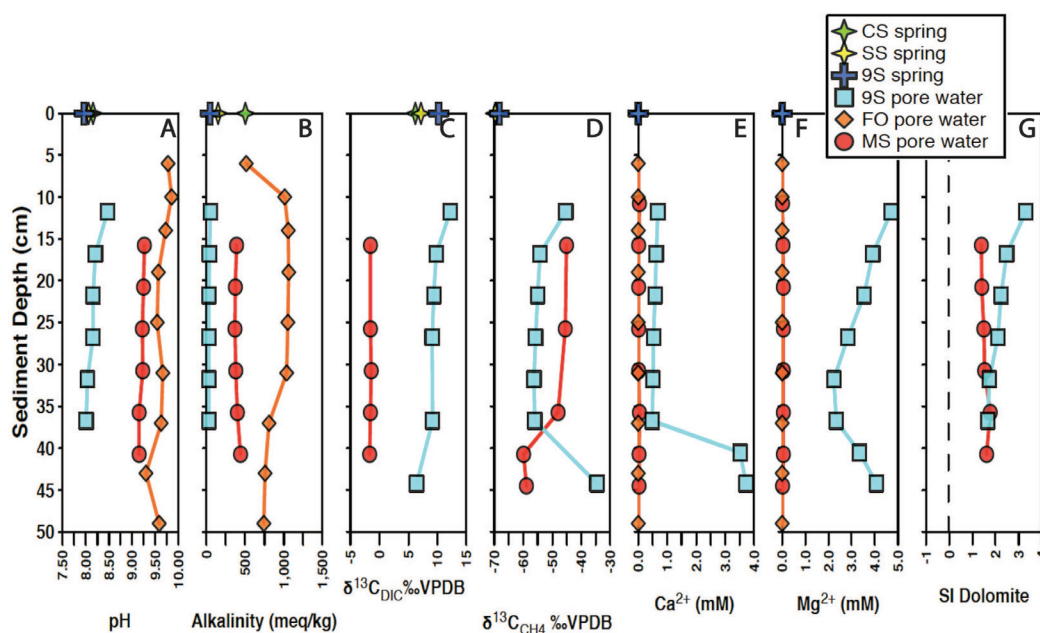


Figure 3. Pore water depth profiles from sites 9S, MS, and FO of pH (A), alkalinity (meq/kg) (B),  $\delta^{13}\text{C}_{\text{DIC}}$  (C),  $\delta^{13}\text{C}_{\text{CH}_4}$  (D),  $\text{Ca}^{2+}$  (E) and  $\text{Mg}^{2+}$  concentrations (mM) (F), and SI dolomite (G). Dashed line on G indicates line of saturation, at 0.

$\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations were below calibration range for the FO pore waters as well as all of the spring waters (Fig. 3ef). In the 9S pore water,  $\text{Ca}^{2+}$  concentrations decrease with sediment depth from 0.7 mM to 0.5 mM at 36.75 cm then increase to 3.7 mM at 44.25 cm. The  $\text{Mg}^{2+}$  concentrations gradually increase then decrease with depth in the 9S pore water, starting at 4.7 mM, coming down to 2.2 mM at a depth of 31.75 cm, then rising gradually to 4.1 mM at a 44.25 cm depth. In the MS pore water,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations are both 0.05 mM or less. Saturation Indices ( $\text{SI} = \log \text{IAP/K}$ ) for all depths of the 9S and MS peepers are supersaturated for dolomite (Fig. 3g). Because of low  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations in the FO pore waters, saturation indexes were not calculated.

Carbon isotope compositions of DIC and methane were measured for the 9S and MS pore waters and springs (Fig. 3cd). In 9S,  $\delta^{13}\text{C}_{\text{DIC}}$  decreases with depth from +12.2‰ to +6.4‰. In MS pore waters,  $\delta^{13}\text{C}_{\text{DIC}}$  is invariant with depth, averaging -1.5‰. In 9S,  $\delta^{13}\text{C}_{\text{CH}_4}$  decreases gradually starting at -45.4‰ at a depth of 11.75 cm and reaches -56‰ at 36.75 cm before increasing to -34.6‰ at 44.25 cm. In MS,  $\delta^{13}\text{C}_{\text{CH}_4}$  decreases fairly gradually from -45.5‰ at 26.75 cm down to -59.9‰ at a depth of 40.75 cm. In the springs,  $\delta^{13}\text{C}_{\text{DIC}}$  ranges from +0.1 to +10‰ while the  $\delta^{13}\text{C}_{\text{CH}_4}$  values are all between -68 and -70‰. The  $\delta^{13}\text{C}$  of the bulk carbonate is typically +3 to +4‰ in

the 9S, MS, and FO cores, and the  $\delta^{13}\text{C}$  of the organic matter averages -22 to -23‰ for the three cores (Streiff, 2014).

## DISCUSSION

The bulk XRD data demonstrate that dolomite is the most abundant mineral phase at the 9S and MS sites and a significant percent at the FO site (Fig. 1). The 9S and MS sites were in the thenardite mineral zone of Jones (1965) though little thenardite is detected throughout the core. The FO site lies in the thenardite zone of Jones (1965) and the XRD analyses finds high concentrations of thenardite at this site. In general, the mineralogy results agree with prior studies showing that dolomite is usually significant, aragonite appears at depth when it is present, and the rest of the sediment is composed of mostly quartz, feldspars, and clays. Meister et al (2011) described the dolomite as fine-grained un lithified ooze. The SEM-EDS analyses could not separate dolomite from the clay minerals, except when present as detrital grains, so the dolomite must exist as a fine-grain matrix usually mixed with Mg-rich aluminosilicate clays.

Meister et al. (2011) argued that dolomite is precipitating directly from the Deep Springs Lake water column based on the very low  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations. Pore water at sites MS and FO has negligible  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  and high alkalinity



concentrations, similar to the chemistries of Meister's pore waters. However, there are much higher concentrations of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  at the 9S site, which also contains water supersaturated with respect to dolomite (Fig. 3). Meister argued for water column dolomite precipitation in Deep Springs Lake, in part, because low pore water  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations precluded dolomite precipitation in the sediment. Meister suggested that the evaporite crusts of thenardite act as an impermeable boundary between the lake water and the sediment, prohibiting these ions from diffusing downwards into the pore water. At site 9S and other sites in close proximity to springs that discharge directly into the lake, perhaps the downward diffusion of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  is not limited as Meister suggests because spring water continuously spills out over the bank and keeps the surrounding surfaces wet. The pore waters are also likely influenced by upward moving spring water and horizontal transport of ions to and from the spring system.

The spring waters have chemistries unlike previously documented spring waters from outside the lake and are distinct from the Deep Springs lake brines (Fig. 4a). The inflow waters from the three sets of springs outside the lake have comparatively low  $\text{Cl}$ , and evaporation modeling of these inflow waters shows they do not eventually become water with chemistries matching those of the lakebed spring waters or the 9S pore water chemistries (Fig. 4b). The spring waters likely gained solutes by traveling through deeper rock units.

Microbial methanogenesis is clearly identified in the 9S spring and pore waters by the high  $\delta^{13}\text{C}_{\text{DIC}}$  around +10‰ and the low  $\delta^{13}\text{C}_{\text{CH}_4}$  values around -60‰ (Fig. 5). These isotopic compositions would be produced by methanogenesis,  $2\text{CH}_2\text{O} \rightarrow \text{CO}_2 + \text{CH}_4$ , assuming an organic matter  $\delta^{13}\text{C}$  value of about -23‰ and dissolution of  $\text{CO}_2$  into the water (Clark and Fritz, 1997; Streiff, 2014). The relatively lower  $\text{SO}_4^{2-}$  concentrations at 9S compared to the other sites agree with methanogenesis occurring, since sulfate must have been significantly reduced first. The MS  $\delta^{13}\text{C}_{\text{DIC}}$  values are similar to previously determined values (~-2‰) and can be explained by evaporation, exchange with the atmospheric  $\text{CO}_2$ , and carbonate mineral precipitation. The spring waters span the range in

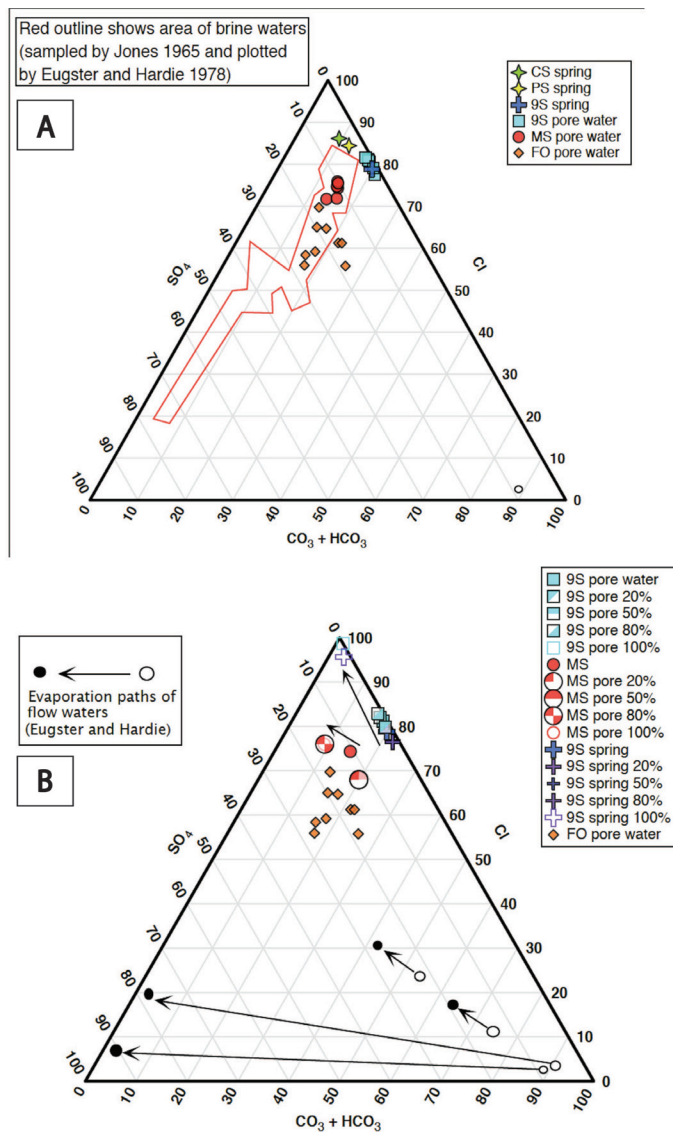


Figure 4. (A) Ternary plot of anions from this study, with range from brine samples for comparison (analyzed by Jones 1965, plotted by Eugster and Hardie 1978). The plot normalizes ion concentrations to the sum of the inorganic carbon ( $\text{HCO}_3^- + \text{CO}_3^{2-}$ ),  $\text{Cl}$ , and  $\text{SO}_4^{2-}$  concentrations. (B) Ternary plot of evaporation paths of inflow spring waters for comparison (analyzed by Jones 1965, plotted by Eugster and Hardie 1978). Percentages given in legend denote percent that has been evaporated at that point. The plot normalizes ion concentrations to the sum of the inorganic carbon ( $\text{HCO}_3^- + \text{CO}_3^{2-}$ ),  $\text{Cl}$ , and  $\text{SO}_4^{2-}$  concentrations.

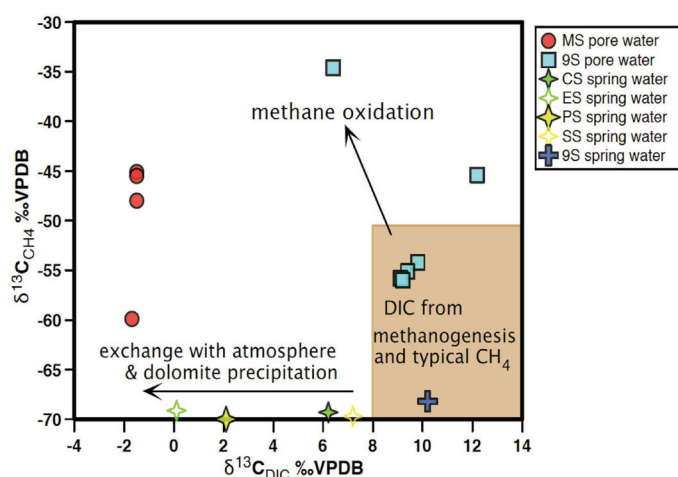


Figure 5.  $\delta^{13}\text{C}_{\text{DIC}}$  plotted against  $\delta^{13}\text{C}_{\text{CH}_4}$  for 9S, MS, and spring waters. Arrows show direction of processes.

between the 9S and MS  $\delta^{13}\text{C}_{\text{DIC}}$  values, suggesting these processes take place somewhere along this pathway (Fig. 5).

Importantly, all of the carbonate minerals in Deep Springs Lake have  $\delta^{13}\text{C}$  values near +3‰, which is in the range of the predicted values if the dolomite precipitated in equilibrium from a  $\delta^{13}\text{C}_{\text{DIC}}$  of -1 or -2‰ (Streiff, 2014). If dolomite precipitated in equilibrium from the 9S spring or porewaters, the dolomite would have  $\delta^{13}\text{C}$  values of +14-15‰. Since such high  $\delta^{13}\text{C}$  values are not observed in the sediments, it is unlikely that dolomite is presently forming in the 9S spring system. It appears that dolomite is formed after subsequent evaporation in the lake basin. As the spring and lake water exchanges carbon with the atmosphere, the water's  $\delta^{13}\text{C}_{\text{DIC}}$  values should move towards 0‰. Progressive methane oxidation would also increase the  $\delta^{13}\text{C}_{\text{CH}_4}$  and decrease the  $\delta^{13}\text{C}_{\text{DIC}}$  values (Fig. 5).

## CONCLUSIONS

This study examined previously undocumented pore water and spring water chemistries at Deep Springs Lake. The spring waters sampled have different chemistries from one another, as well as from the main inflow waters to the lake, and pore waters by the 9S spring indicate methanogenesis has occurred somewhere along the spring pathway.

Further research to understand the processes taking place at Deep Springs Lake should explore the roles of authigenic clays and microbial mediation. The thorough mixing of the dolomite and clay could be caused by similar sedimentation rates and/or authigenic precipitation of the two phases. Additionally, the overall influence of microbial methanogenesis and methane oxidation should be evaluated in greater detail.

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