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

April 2014
Mt. Holyoke College, South Hadley, MA

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ISSN# 1528-7491

The Consortium Colleges  The National Science Foundation  ExxonMobil Corporation
KECK GEOLOGY CONSORTIUM
PROCEEDINGS OF THE TWENTY-SEVENTH ANNUAL KECK RESEARCH SYMPOSIUM IN GEOLOGY
ISSN# 1528-7491
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Funding Provided by:
Keck Geology Consortium Member Institutions
The National Science Foundation Grant NSF-REU 1062720
ExxonMobil Corporation
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

INTRODUCTION

Dolomite (CaMg(CO$_3$)$_2$) is a prevalent carbonate mineral throughout Earth history, forming large (~10$^8$ m$^3$) units in formations across geologic time (Warren, 2000). However, experimental (Land, 1998) and field (Warren, 2000) studies have struggled to understand dolomite formation in terms of modern laboratory or field contexts. Previous workers at Deep Springs Lake in eastern California, an ephemeral lake at the southern end of Deep Springs Valley, have examined a wide variety of geological and geochemical aspects of the dry lake, and have repeatedly documented (Jones, 1965; Peterson, et al, 1963; Peterson, et al, 1966; Meister et al, 2011) the presence of authigenic dolomite within the lake sediments, as fine-grained oozes composed of 20 nm to 20 μm euhedral rhombs of dolomite. Examination of the aqueous and isotope geochemistry and mineralogy has lead workers to conclude that the dolomite is precipitating directly from the hyperalkaline brine of Deep Springs Lake, a process potentially mediated by microbes living in the sediment (Meister et al, 2011).

This study characterizes the cementation and lithification of dolomite-bearing sediments in Deep Springs Lake (DSL) in an attempt to understand how lithification and cementation interact geochemically with dolomite formation. To accomplish this aim, this project synthesizes x-ray diffractometry, isotope geochemistry, scanning electron microscopy, and geochemical modeling to understand the role of thenardite (NaSO$_4$) and nahcolite (NaHCO$_3$) responding to the geochemical environment in which ongoing dolomite formation is occurring.

METHODS

In the summer of 2013, a team funded by the Keck Geology Consortium extracted a broad range of materials, including pore waters, emitted and dissolved gases, and several <1 m long gravity cores of sediment to further examine the geobiological aspects of dolomite formation in Deep Springs Lake. The water level of the lake during the field season was below the sediment surface, revealing a few small (~0.2 m diameter), shallow springs containing water. Proximal to these springs, instruments (‘peepers’) were placed to measure ion concentrations of pore waters. Unidentified biogenic material was collected from the springs for subsequent analysis with microbiological and molecular techniques. Additionally, ~1 m long gravity cores were used to collect sediment columns near to the springs, as well as one core (“FO”) taken near the center of the lake. These cores were subdivided into 2 cm sections to enable subsequent analysis of chemical and mineralogical changes with depth.

Upon return to Amherst College, samples were washed with deionized water and dried at ~50˚C. Powders for X-ray diffractometry were prepared and analyzed using a Scintag, Inc. X-Ray Diffractometer at Smith College, Northhamton, MA which scanned at a rate of 2˚ per minute from 5˚ to 70˚ in 0.02˚ increments. These data were subsequently analyzed by members of the team using “RockJock,” an Excel program for the quantitative estimation of mineralogy by weight percent for XRD spectra (Eberl, 2003). Pore water samples retrieved from ‘peepers’ were analyzed for ion concentration by ICP-OES and IC at Amherst College. These data were used in the geochemical
modeling application React of the Geochemists’ Workbench software suite to establish stable mineral phases given ion concentrations and compare these to observed mineralizations previously established via XRD. These models simulated evaporation of 1 kg of brines of variable composition and the resulting mineral species precipitated during evaporation, and also accounted for increased \( pCO_2 \) in deeper sediments resulting from methanogenic disproportionation of organic carbon. Scanning electron microscopy was used to investigate the textural properties of sediment cores and was coupled with EDS to investigate spatial distribution of mineral species.

RESULTS

Sediment cores are composed of a variety of authigenic mineral precipitates, some previously documented (see Jones, 1965). Previously observed authigenic minerals in the sediments include thenardite \((Na_2SO_4)\), halite \((NaCl)\), dolomite, and a range of authigenic clay minerals (Fig. 1). Most cores were primarily composed of clays and unlithified dolomite ooze, the latter discovered in previous work (see Meister et al, 2011). The core taken at the deepest accessible location, core FO, of the lake featured large (up to 3 cm) crystalline masses, primarily composed of thenardite crystals and nahcolite concretions. Thenardite crystals contained dark clay inclusions. Nahcolite concretions, which grew in a variety of shapes contained minor thenardite intergrowths throughout the fine-grained nahcolite matrix and displayed well-developed cleavage (Figs. 2, 3). SEM imagery revealed localized regions of thenardite crystals of similar size (~100 μm). SEM-EDS documented localization of similar mineral species occurring in deeper sediments of the core FO, in which Cl-, Mg-, Ca-, and S-bearing species are grouped into ~100 μm areas forming incipient halite, dolomite, and thenardite authigenic mineral precipitates, respectively (Fig. 4).

Evaporation modeling of brines with compositions measured ICP-OES replicate previously-documented mineral assemblages at Deep Springs Lake. A simulation of evaporation of pore water and spring brines produce assemblages which include nahcolite, halite, thenardite, gaylussite, dolomite, and burkeite. Brine compositions derived from pore waters of cores, peepers, and spring waters display a range of authigenic mineral assemblages which predict the order of precipitation (Fig. 5). Simulated methanogenic disproportionation of organic carbon into \( CO_2 \), thus elevating \( pCO_2 \) in sediments, results in the replacement of several mineral species (e.g. trona) with nahcolite, and reduces the amount of dolomite precipitation.

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**Figure 1.** Representative X-ray diffraction spectra of core FO, including a) thenardite cements, b) nahcolite concretions with minor thenardite, and c) unlithified lake sediment, displaying authigenic dolomite, nahcolite, and clay species.
Figure 2. SEM imagery depicting authigenic mineral precipitates identified through EDS of a) thenardite cements with late halite precipitation on thenardite surface, b) nahcolite concretion with clay + dolomite + nahcolite aggregate adhered to surface c) nahcolite concretion with thenardite intergrowths d) nahcolite concretion with adhered clay + dolomite + nahcolite aggregate, and e), f) nahcolite concretion with thenardite intergrowths.
Figure 3. SEM-EDS spectra of representative mineral species in lake sediments, including a) halite, b) thenardite, c) nahcolite, and d) a dolomite, nahcolite and clay aggregate appearing in Fig. 2b and 2d, displaying minimal dolomite component.

Figure 4. SEM-EDS elemental mapping displaying Cl, Mg, Ca, and S domains in un lithified sediment from core FO, representing halite, dolomite, and thenardite authigenic mineral precipitates.

DISCUSSION

Nahcolite rarely forms as concretions as have been found here, with only a handful of documented nahcolite concretions from organic-rich lacustrine sediments (Ertl, 1947; Reitsema, 1980) and sediments of a crater lake in Sudan (Mees, et al., 1998). Given the high solubility of sodium bicarbonate under the pH range of most natural fluids, the preservation potential for such concretions is low, but when found in modern sediments can still present important information about the geochemistry of the system. Typically, workers have interpreted nahcolite concretions as representative of high pCO$_2$ in host sediments, as it is clear that the formation of nahcolite requires an excess of CO$_2$ to avoid the preferential precipitation of trona (Na$_3$(CO$_3$)(HCO$_3$) • 2H$_2$O), regardless of salinity (Ertl, 1947; Bradley and Eugster, 1969; Reitsema, 1980). This concentration of CO$_2$ has been suggested to arise from a variety of mechanisms, both biotic (such as the oxidation of organic matter) and abiotic (from evaporation-driven salinity changes; see Mees, 1998).
Meister et al. (2011) concluded that dolomite oozes were precipitating directly from solution through a cation-limited concentration of an extremely alkaline brine through progressive evaporation, a conclusion supported by the likely mechanism for nahcolite concretion formation: excess pCO$_2$ generated through changes in salinity. A lack of textural observations suggesting significant growth of dolomite within deeper sediments (such as those at FO) supports this interpretation of dolomite formation.

Modeling results support interpretations of textural observations. Evaporation models for almost all brines from DSL predict a small amount of dolomite precipitated first from the drying brine, decreasing only slightly through the drying process. These modeled brines, in the case of most pore water brines, have previously undergone evaporation, and therefore these models represent further evaporation. Although the small amount of dolomite precipitation predicted in these models is far below that observed in from semi-quantitative XRD (~0.1 g dolomite per 1 kg brine vs. ~50% by weight), this discrepancy clearly results from the cation-limited nature of dolomite precipitation, as well as the previously-noted fact that modeled brines have likely already lost significant Ca and Mg to precipitation of dolomite in surface lake brines as documented earlier by Meister et al. (2011).

Reflecting the saturation indices calculated previously by Meister et al. (2011) and in this volume, dolomite is precipitated almost instantly from simulated brines under evaporation, and is entirely dependent on initial Ca$^{2+}$ and Mg$^{2+}$ concentrations. This model is based upon thermodynamic calculations, and therefore kinetic factors limiting the precipitation of dolomite, which are deeply significant to understandings of dolomite formation across the rock record, are not accounted for. However, Meister et al. (2011) documented euhedral dolomite rhombs ~2 nm across indicative of only minor kinetic inhibition, suggesting that cation limitation, as documented in modeling results of this study, is of primary importance in understanding dolomite formation in Deep Springs Lake. Interestingly, aragonite precipitation, which is clearly documented in XRD analysis of sediments, is not predicted through these evaporative models, suggesting changes in lake chemistry through time.
likely resulting from changes in Mg concentrations, which are understood to control calcite vs. aragonite precipitation from seawater over geologic timescales.

Introducing heightened $pCO_2$ in the models to account for methanogenic disproportionation of organic matter to $CO_2$ permits the precipitation of nahcolite while eliminating some mineral species observed in sediments via XRD, suggesting a localization of $CO_2$ enabling nahcolite precipitation while simultaneously permitting trona and burkeite precipitation. Also, the nahcolite-thenardite concretions documented in core FO can be further examined in the context of modeling results, which predict the order of precipitation of the two mineral phases. Models predicting nahcolite precipitation for brines of core FO predict the formation of thenardite before nahcolite.

This relative sequence further supports a localized, pervasive cementation of the nahcolite concretions, as they contain thenardite mineralizations which could not have grown after their nahcolite host due to the termination of thenardite precipitation coincident with nahcolite precipitation (Fig. 5). Cores from methane-producing springs (such as core MS) may seem to contradict the assertion that nahcolite concretions are methanogenically mediated, as these do not contain nahcolite concretions but are also located proximal to disproportionating, methanogenic microbial communities in the sediment. However, the saturation of these sediments due to their proximity to springs, relative to the drier sediments of core FO, suggest that these sediments have not undergone sufficient desiccation to allow for nahcolite precipitation (Fig. 5).

Figure 5. Modeled evaporation of lake brines using React of Geochemist’s Workbench predicting order of mineral precipitation for various brines: a) spring water of “9” spring, which displayed significant methane release, b) pore water of core taken in vicinity of “9” spring with elevated $pCO_2$ conditions from methanogenesis, c) pore water of core FO without elevated $pCO_2$, d) with elevated $pCO_2$, e) pore water of core “MS,” where isotope geochemical data precludes ongoing methanogenesis. XRD-derived mineral weight percentages from after Plon (2014) are listed.
CONCLUSIONS

Textural observations of nahcolite-thenardite concretions and dolomite-bearing sediment, geochemical modeling of lake brines, and isotope geochemistry all suggest cation-limited precipitation of dolomite primarily in surface brines. Deeper lake sediments, while lacking evidence of dolomite crystal growth through further precipitation, indicate the role of localized, heightened $pCO_2$ in sediments to produce nahcolite concretions proximal to trona and gaylussite deposits, potentially resulting from methanogenic disproportionation of organic carbon which is documented in cores through heavy $\delta^{13}C$ values for DIC and in methane-producing springs on the lake surface. These concretions grew pervasively in the sediment after the termination of thenardite precipitation, suggested by the order of crystallization dictated by modeling of lake brines.

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