Microbial precipitation of dolomite in methanogenic groundwater

Jennifer A. Roberts Department of Geology, University of Kansas, Lawrence, Kansas 66045, USA
Philip C. Bennett Department of Geological Sciences, University of Texas at Austin, Texas 78712, USA
Luis A. González
G.L. Macpherson Department of Geology, University of Kansas, Lawrence, Kansas 66045, USA
Kitty L. Milliken Department of Geological Sciences, University of Texas at Austin, Texas 78712, USA

ABSTRACT

We report low-temperature microbial precipitation of dolomite in dilute natural waters from both field and laboratory experiments. In a freshwater aquifer, microorganisms colonize basalt and nucleate nonstoichiometric dolomite on cell walls. In the laboratory, ordered dolomite formed at near-equilibrium conditions from groundwater with molar Mg:Ca ratios of <1; dolomite was absent in sterile experiments. Geochemical and microbiological data suggest that methanogens are the dominant metabolic guild in this system and are integral to dolomite precipitation. We hypothesize that the attached microbial consortium reacts with the basalt surface, releasing Mg and Ca into solution, which drives dolomite precipitation via nucleation on the cell wall. These findings provide insight into the long-standing dolomite problem and suggest a fundamental role for microbial processes in the formation of dolomite across a wide range of environmental conditions.

Keywords: dolomite, biomineralization, methanogenesis, basalt weathering.

INTRODUCTION

Low-temperature laboratory nucleation and precipitation of dolomite constitutes one of the most taxing and trying exercises in geochemical research (Land, 1985, 1998; McKenzie, 1991). Ubiquitous in the rock record, yet rarely found forming today, dolomite defies the notion that the present is the key to the past. The thermodynamics of dolomite solubility in water are difficult to characterize because of dolomite's slow rate of dissolution, its incongruent dissolution behavior, and the absence of laboratory data on dolomite precipitation. While there is no simple abiotic recipe for dolomite precipitation, recent discussions suggest that microbes are paramount to overcoming kinetic barriers to low-temperature precipitation (Burns et al., 2000).

Controversy over the origin of ancient massive dolomites is partly fueled by the inference that dolomite forms in a variety of environments, including meteoric, hypersaline, schizohaline, marine, reflux, subsurface brines, and hydrothermal (Hardie, 1987). Few reports of laboratory dolomite precipitation at low temperature exist (Vasconcelos et al., 1995; Warthmann et al., 2000), and debate on specific geochemical and microbial controls continues.

Present-day low-temperature dolomite formation is most abundant in restricted-marine or hypersaline coastal environments, where fluids are greatly supersaturated with dolomite [$SI = \log(IAP/K_{sp}) > 2$, where SI is saturation index, IAP is the ion activity product, and K_{sp} is the equilibrium constant] and molar Mg:Ca ratios are $\gg$1 (e.g., Wright, 1999; Vasconcelos and McKenzie, 1997; Carballo et al., 1987). Freshwater dolomite is present in the rock record, although few modern locales exist. Capo et al. (2000) reported pedogenic dolomite associated with young basaltic soils on the island of Hawaii, where the alteration of ferromagnesian minerals by infiltrating water supplied the Mg for precipitation of well-ordered dolomite.

Modern dolomite precipitation is often associated with dissimilatory sulfate-reducing bacteria (DSRB) that remove sulfate, produce alkalinity, and presumably drive dolomite formation (e.g., Wright, 1999; Vasconcelos and McKenzie, 1997). The $\delta^{13}C$ signatures in ancient dolomites indicate that high rates of carbon oxidation and methanogenic conditions also favor dolomite formation (e.g., Mozely and Burns, 1993). This finding supports the growing realization that near-surface, low-temperature dolomite forms in association with microorganisms in a wide range of redox environments.

Microbial biomineralization is common in a variety of environments in which microbes precipitate sulfides, phosphates, oxyhydroxides, clays, and carbonates (Ehrlich, 2000). In some cases microbial metabolism drives precipitation by changing bulk water chemistry (e.g., Ferris et al., 1994), but microorganisms can also precipitate minerals by concentrating metals and nucleating crystals on their cell walls and associated exopolysaccharides (Schultze-Lam et al., 1996; van Lith et al., 2003).

We report here on freshwater precipitation of dolomite influenced directly by microbes observed in field studies and controlled laboratory experiments. Geochemical and microscopy data indicate that dolomite forms on microbial cell walls under highly reducing conditions. Unlike other modern examples of low-temperature dolomite formation (e.g., Whipkey et al., 2002), precipitation occurs from dilute solutions that are near equilibrium with dolomite and have relatively low Mg:Ca ratios (<1).

FIELD MICROBIAL DOLOMITE PRECIPITATION

A field experiment was conducted in a petroleum-contaminated aquifer near Bemidji, Minnesota, a U.S. Geological Survey Toxic Substances Hydrology Program site. There, groundwater is anaerobic, and changes in groundwater chemistry in the contaminated zone suggest accelerated dissolution of silicates (Bennett et al., 2001). Based on 20 years of geochemical data, the most reducing waters are near equilibrium or slightly supersaturated with dolomite, although dolomite precipitation has not been documented previously. Dissimilatory iron-reducing bacteria (DIRB) are the dominant metabolic guild within the contaminated zone coexisting with methanogens, which are found in narrow and spatially distinct zones (Bekins et al., 1999). Calcite precipitation has been reported in the methanogenic zone (Bennett et al., 2001), and ferroan calcite has been proposed as a sink for Fe^{2+} (Tucillo et al., 1999). Groundwater in the study zone is anaerobic, with a pH of 6.74, 3.4 m*M* dissolved organic carbon (DOC), 0.66 m*M* Fe^{2+}, 0.74 m*M* CH_4, and 1.2 m*M* Si. The water also contains 4.58 m*M* Ca^{2+}, 1.35 m*M* Mg^{2+}, 12.4 m*M* HCO_3^-, and <0.01 m*M* Al, K, Na, SO_4, NO_3, and PO_4 (each).

Microbial mineralization associated with basalt weathering was characterized using in situ microcosms (Hiebert and Bennett, 1992; Rogers et al., 1998). A sample of Columbia River Basalt was used as a growth substratum and source of mineral nutrients, Ca, and Mg for all experiments. An abbreviated whole-rock chemistry of this specimen (Bennett et al., 2001) includes 51.0% SiO_2, 13.7% Al_2O_3, 14.1% Fe_2O_3, 8.9% CaO, and 4.5% MgO, with a total P concentration of ~3000 ppm that occurs as chlorapatite. Sterile basalt fragments (1–5 mm) in sterile polyethylene flow-through microcosms were suspended in boreholes (7 m below land surface in well 9017)

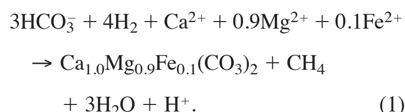
© 2004 Geological Society of America. For permission to copy, contact Copyright Permissions, GSA, or editing@geosociety.org.

and recovered anaerobically after three months. Samples were fixed in the field for microbial characterization by fluorescence in situ hybridization (FISH) using Bacteria probe Eub338 and Archaea probe Arch915 (Amann et al., 1990), counterstained with 4′,6-diamindino-2-phenylindole (DAPI); the samples were imaged using a scanning-laser confocal microscope. Additional samples were preserved for conventional and environmental scanning electron microscopy (SEM and ESEM) and secondary-mineral identification. For ESEM, samples were stored anaerobically in native groundwater and imaged without fixation within 24 h of retrieval on a Peltier stage at 5.0 °C and 6 torr H_2O_{vap}. For SEM, the samples were fixed in the field by using a chemical critical-point drying method (Vandevivere and Bevaye, 1993). Secondary mineral precipitates were identified using X-ray powder diffraction (XRD).

Microbes colonizing the basalt surface after three months of exposure to groundwater are typically ~1 μm rods found in irregular groups around areas of etching on the basalt (Bennett et al., 2001). Angular, deformed rhombohedra are observed on the surfaces of some of the colonizing cells (Fig. 1A), suggesting a mineral precipitate rather than a bacteriophage (size variation also precludes possibility of a phage), budding features, or amorphous organic material. Some cells are almost completely covered with crystals, whereas nearby cells with slightly different morphologies are barren of crystals (Fig. 1A). XRD analysis of the in situ microcosm material shows a peak at a *d* spacing of 2.90 Å, not found on the reference material, corresponding to ferroan dolomite. This peak disappears after treatment with dilute hydrochloric acid. Mg-rich calcite and Ca-rich dolomite are also present. Although the exact composition of the precipitating phase is not known, crystals with this characteristic *d* spacing precipitating from a solution near dolomite saturation suggest that the precipitate is a calcium-rich, disordered, ferroan dolomite. ESEM and XRD were used to identify a divalent-cation–substituted smectite on the reacted surface not present on the starting basalt. This clay was not associated with microbial cell walls, but precipitated on the basalt surface.

FISH analysis showed that the attached cells are ~60% Archaea and ~40% Bacteria (Fig. 1B), probably a consortium of methanogens and fermenters. The absence of SO_4^{2-} in the groundwater (<10 μ*M*) and the low DSRB cell counts in situ (Bekins et al., 1999) eliminate the possibility of vegetative DSRB.

As the colonized basalt weathers to clay, it releases Ca, Mg, and Fe into a neutral pH groundwater that is near equilibrium with calcite and dolomite and has a high concentration of Fe^{2+} and dissolved CH_4. Basalt dissolves only near attached cells (Fig. 1A), and previous studies have shown that colonizing microorganisms destroy the silicate to access apatite inclusions in this P-limited (<0.01 m*M* PO_4) groundwater (Rogers et al., 1998). At the surface of the dissolving basalt, we hypothesize that methanogens locally initiate precipitation of ferroan dolomite by consuming CO_2 in an environment of released Ca, Mg, and Fe, driving the system even further toward carbonate supersaturation, e.g.,



$$3HCO_3^- + 4H_2 + Ca^{2+} + 0.9Mg^{2+} + 0.1Fe^{2+} \rightarrow Ca_{1.0}Mg_{0.9}Fe_{0.1}(CO_3)_2 + CH_4 + 3H_2O + H^+. \quad (1)$$

Observations from these field experiments suggest that extreme supersaturation and high Mg:Ca ratios are not necessary for dolomite precipitation, but rather that microbial cell walls nucleate dolomite in freshwater very near dolomite equilibrium. Controlled laboratory experiments were designed to both test this hypothesis and to further constrain the geochemical and microbiological conditions necessary for dolomite precipitation.

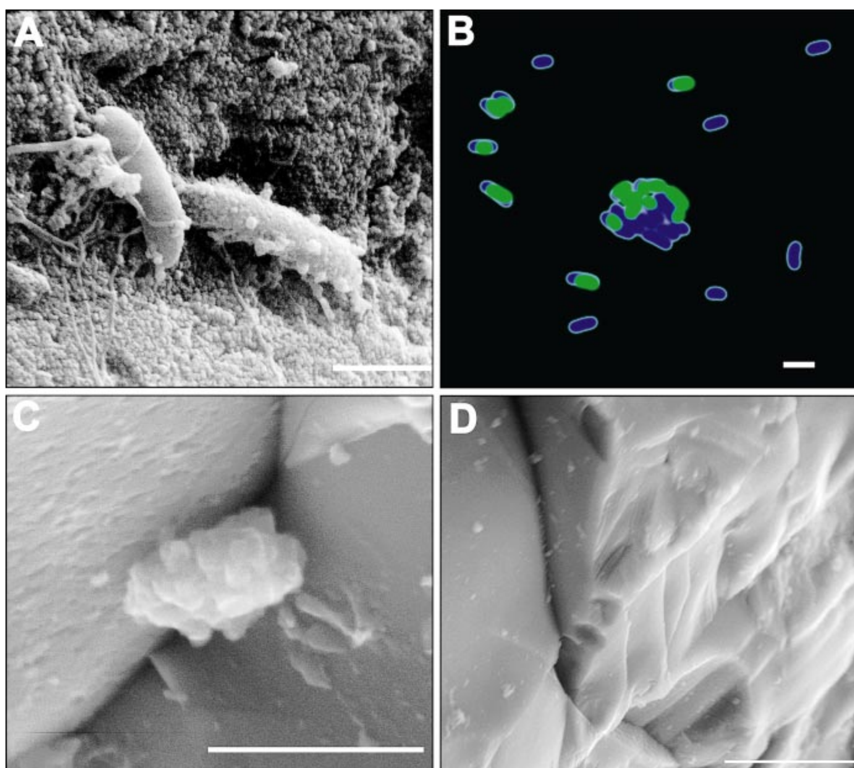


Figure 1. A: Scanning electron microscope (SEM) photomicrograph of rod-shaped cells on basalt surface with precipitation of ferroan dolomite on cell surfaces after three months in anaerobic groundwater. Scale bar is 0.5 μm. Differences in crystal encrustation may be due to cell residence time on mineral surface or may reflect differences in metabolic activity. B: Scanning-laser confocal microscope image of cells on basalt surface. Scale bar is 1 μm. Green cells were probed with Arch915 tagged with fluoroscein (identifies Archaea). 4′,6-diamindino-2-phenylindole (DAPI) stains all cells blue. On this sample, Archaea make up ~60% of cells on surface. C: Environmental (E)SEM photomicrograph of rod-shaped cell on basalt surface from laboratory experiment. Note surface-precipitating crystals. Scale bar is 2 μm. D: ESEM photomicrograph of basalt surface from laboratory sterile control. No cells are present, nor is there evidence of secondary-mineral precipitation. Scale bar is 20 μm.

LABORATORY SYNTHESIS OF DOLOMITE BY MICROORGANISMS

Laboratory microcosms were constructed from sterile glass bottles filled with 5 g of dry sterilized basalt (0.5–1 mm size fraction) and 40 mL of Bemidji anaerobic groundwater. Groundwater and native microbes were collected from zones dominated by DIRB and methanogens (Table 1), respectively, to investigate the role of these microorganisms in dolomite precipitation. Native microbial populations were extracted from cores of aquifer sediment by using a nonionic surfactant. Cells were concentrated with centrifugation, rinsed with formation water, and inoculated to a final concentration of 10^7 cells mL^{-1}. The only

TABLE 1. GEOCHEMISTRY OF GROUNDWATER AND SELECT MICROCOSMS

	IR-GW	IR-2	IR-3	IR-7S	M-GW	M-8	M-16	M-17S
pH	6.73	6.97	6.99	7.1	6.87	7.05	7.03	7.21
CH_4	1.20	0.129	0.121	0.001	1.20	0.072	0.076	0.001
DOC	3.50	9.81	11.84	1.83	2.10	4.13	5.98	1.58
HCO_3	8.39	7.60	7.78	4.82	10.7	6.60	7.35	5.61
Ca	3.60	1.90	1.93	1.28	3.71	1.88	1.84	1.46
Mg	1.28	1.34	1.36	1.29	1.34	1.30	1.31	1.21
Fe	0.388	0.166	0.186	<0.001	0.75	0.163	0.143	<0.001
Si	0.86	1.16	1.21	1.14	0.47	1.30	1.15	0.95
SI-calcite	−0.23	0.02	0.02	−0.17	0.11	−0.05	0.02	0.00
SI-dolomite	−0.94	0.02	−0.02	−0.21	−0.30	−0.16	0.01	−0.01
Mg:Ca	0.40	0.71	0.70	1.01	0.43	0.69	0.71	0.83

Note: Concentrations are in m*M*; Na, K, Cl are <0.3 m*M*; NO_3 and SO_4 are <0.01 m*M*. Solubility constants for calcite and dolomite were $10^{-8.4}$ and $10^{-17.1}$, respectively; Mg:Ca molar ratio at equilibrium with both calcite and dolomite is ~0.6 (Stumm and Morgan, 1996). IR is iron-reducing, and S is a sterile control. Numbers designate laboratory experiments. M is methanogenic, GW designates the groundwaters used to prepare microcosms. DOC is dissolved organic C; SI is saturation index.

source of phosphate was the apatite inclusions in the basalt, and a few microliters of petroleum were added as a source of carbon. Sterile controls were made with identical materials but autoclaved for 20 min at 120 °C. The microcosms were assembled and stored in an anaerobic chamber and incubated in darkness at 25 °C for 8 months.

Several factors were considered in the microcosm design. The study aquifer has detrital calcite and dolomite dispersed in the sediment, a high pCO_2, and primarily DIRB, fermenters, and methanogens. To mimic these aquifer conditions, 1 cm^3 pieces of dolomite and calcite (Wards Scientific) were enclosed in dialysis tubing (regenerated cellulose) and suspended in the assembled bottles. This technique allowed slow reaction over the duration of the experiment so that pH, Ca, and Mg concentrations were buffered, as they are in the aquifer. The dialysis tubing prevented direct microbial interaction with the carbonate mineral surfaces as well as contamination of the microcosm with small particles of these minerals.

After reaction the laboratory microcosm solutions were sampled anaerobically and analyzed for anions, cations, DOC, and alkalinity. CO_2 and CH_4 were measured in the headspace. Basalt, dolomite, and calcite chips were analyzed with SEM and ESEM as described in the previous section. Secondary-mineral precipitates were identified with XRD. The $\delta^{13}C$ and $\delta^{18}O$ values of the carbonate fraction were measured on the precipitated carbonate mixture as well as the dolomite fraction after treatment with a 1% acetic acid solution, and are reported relative to Vienna Peedee belemnite (VPDB).

ESEM analysis indicates that crystals, similar to those that formed in field experiments (Fig. 1C), apparently nucleated on cells colonizing the basalt surfaces. The observed crystals are aligned on the cell, possibly because of oriented nucleation by the cell wall. Carbonate mineral crystals (0.02 to ~5 μm) are also observed on the basalt surface where they are embedded in a slime layer, apparently part of a biofilm. SEM–energy-dispersive spectrometer (EDS) analysis produced peaks corresponding to both calcium carbonate and calcium and magnesium carbonate for larger crystals; only spectra without Si were attributed to carbonates because of background emission from the basalt groundmass. XRD analysis identified carbonate peaks with *d* spacings of 3.03 Å and 2.89 Å, corresponding to calcite and dolomite, respectively (Fig. 2). Dolomite ordering is indicated by the presence of superstructure reflections (Fig. 2). No evidence of other secondary carbonate minerals (e.g., siderite) was found by using XRD and SEM. In sterile controls only calcite precipitated, and the sterile basalt surfaces were barren of cells or visible precipitate (Fig. 1D). Cells were absent from the calcite and dolomite crystals within the dialysis tubing, and there was no evidence of dissolution or precipitation (e.g., etch pits or surface imperfections).

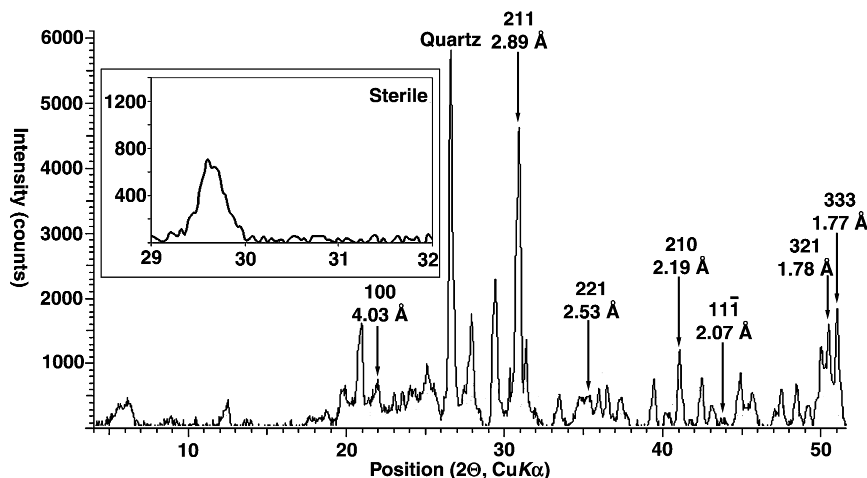


Figure 2. Dolomite peaks and superstructure reflections are noted with arrows and labeled by *hkl* indices and *d* spacings. Superstructure reflections are indicated by odd-numbered *l*. Ordered dolomite (*d* spacing = 2.89 Å) is detected in live laboratory experiments, as is calcite (29.48 2Θ). Shoulder peak on dolomite may correspond to ferroan dolomite phase, although siderite (32.08 2Θ) is absent. Ordered and disordered dolomite peaks are absent from sterile control, but peak at 29.68 2Θ may be calcite.

The starting solution chemistry in the microcosms was derived from the collected groundwater, though modified slightly by gas exchange and iron oxide precipitation during microcosm construction. Initially the solutions reacted abiotically with the basalt, calcite, and dolomite, illustrated by the small changes observed in dissolved CH_4 and Fe^{2+} in the sterile control samples (Table 1). In the live experiments, microorganisms consumed hydrocarbon and produced CO_2 while dissolving basalt near attached cells, releasing Ca, Mg, and Si (compared to the sterile controls; Table 1). The significantly higher dissolved silica in the live experiments compared to sterile controls supports a microbial role in basalt weathering. Evidence of basalt alteration with negligible dissolution of the dolomite and calcite in the dialysis tubing suggests that Mg and Ca are derived from the basalt rather than from carbonate phases.

The mixture of precipitated calcite and dolomite has $\delta^{13}C = -0.59‰ \pm 0.28‰$ and $\delta^{18}O = -5.75‰ \pm 0.63‰$. Dolomite separates (calcite removed by acetic acid leaching) have $\delta^{13}C = -0.03‰ \pm 0.49‰$ and $\delta^{18}O = -3.93‰ \pm 0.90‰$. Under the assumption that the mixtures had 30% dolomite (a conservative estimate based on SEM-EDS), the composition of calcite would be $\delta^{13}C = -0.83‰ \pm 0.27‰$ and $\delta^{18}O = -6.53‰ \pm 0.58‰$. The calcite in the dialysis tubing has $\delta^{13}C = +2.83‰$ and $\delta^{18}O = -5.31‰$, whereas for the dolomite, $\delta^{13}C = -1.15‰$ and $\delta^{18}O = -16.61‰$. The isotopic composition of precipitated dolomite and that estimated for cal-

cite are distinct from the minerals in the dialysis tubing, and no possible combination of contamination from those by themselves or with either calcite or dolomite precipitates can produce the isotopic composition of the precipitates.

Little reducible hydrous ferric oxyhydroxides were available for the DIRB population, and only small increases in Fe^{2+} were documented in laboratory experiments, so these bacteria are probably not the dominant metabolic guild. CH_4 concentration, however, increased significantly in all live microcosms (compared to sterile controls), suggesting that methanogenesis was the principal metabolic pathway (Table 1). The $\delta^{13}C$ values of the secondary precipitate, coupled with the large amount of CO_2 (derived from oxidation of the petroleum with $\delta^{13}C < -25‰$) and CH_4 produced, require that most of the carbonate precipitated only after significant CH_4 production (through CO_2 reduction) had taken place to buffer the $\delta^{13}C$ of DIC (dissolved inorganic carbon) to $\sim -2.0‰$. The most positive $\delta^{18}O$ value of inorganic calcite that could precipitate from groundwaters at the study site ($\delta^{18}O < -11‰$ relative to standard mean ocean water) is $-12‰$ (VPDB), implying major kinetic or biogenic effects on the secondary carbonate composition or major ^{18}O (and ^{2}H) enrichment of fluid through reduction of CO_2.

The release of Ca and Mg from basalt and the microbial consumption of CO_2 resulted in the precipitation of carbonate minerals. The calculated saturation indices from the microcosm solutions (Table 1) suggest that the waters, with Mg:Ca ratios of ~0.7, remained near equilibrium with dolomite (log SI = 0 ± 0.2). The evidence from XRD and SEM-EDS suggests that ordered dolomite and not ferroan dolomite precipitated in the laboratory microcosms, probably because of the much lower Fe^{2+} activity.

IMPLICATIONS

This study demonstrates that dolomite precipitates in dilute solutions due to the metabolic activity of native microbial communities. We observe dolomite formation as part of a two-step process in which microorganisms first weather basalt and incidentally release Mg, Ca, and Fe. Dolomite precipitation is then initiated by methanogenic metabolic activity and crystal nucleation on the cell wall. The rapid weathering of basalt and formation of dolomite was identified in both field and laboratory settings at low temperature, with measurable mineral precipitate forming after only a few months.

Clearly, the origin of extensive dolomite cannot be resolved by applying a narrow range of chemical conditions or a single abiotic kinetic model for dolomite nucleation and precipitation. Our observation of microbially mediated dolomite precipitation in a dilute, low-temperature environment is a significant departure from previous attempts to form dolomite in the laboratory and expands our understanding of the geochemical and microbiological constraints on this notorious mineral. Our findings demonstrate that in some microbially active systems, neither extremely Mg-rich fluids nor highly supersaturated conditions are required for the nucleation and precipitation of dolomite. Microorganisms, either by their metabolic processes or owing to the nature of their outer cell membranes, directly influence the rate-controlling step in dolomite precipitation. In this study, methanogens and not sulfate reducers were found to be the principal organisms in dolomite nucleation and precipitation. This discovery adds to our knowledge of dolomite precipitation at low temperature and opens up the possibility of new models for the origin and diagenetic history of ancient dolomites.

ACKNOWLEDGMENTS

We acknowledge gratefully the assistance of R. Goldstein, D. Eberl, R. Mathis, and B. Hughes. We thank D. Budd, R. Arvidson, J. McKenzie, and an anonymous reviewer for helpful comments. This research was funded the Geology Associates of the University of Kansas Geology Department (grant to Roberts) and the National Science Foundation (grant EAR-9903267 to Bennett).

REFERENCES CITED

Amann, R.I., Krumholz, L.R., and Stahl, D.A., 1990, Fluorescent-oligonucleotide probing of whole cells for determinative, phylogenetic, and environmental studies in microbiology: Journal of Bacteriology, v. 172, p. 762–770.

Bekins, B.A., Godsy, E.M., and Warren, E., 1999, Distribution of microbial physiologic types in an aquifer contaminated by crude oil: Microbial Ecology, v. 37, p. 263–275.

Bennett, P.C., Rogers, J.R., Hiebert, F.K., and Choi, W.J., 2001, Silicates, silicate weathering, and microbial ecology: Geomicrobiology Journal, v. 18, p. 3–19.

Burns, S.J., McKenzie, J.A., and Vasconelos, C., 2000, Dolomite formation and biogeochemical cycles in the Phanerozoic: Sedimentology, v. 47, p. 49–61.

Capo, R.C., Whipkey, C.E., Blachere, J.R., and Chadwick, O.A., 2000, Pedogenic origin of dolomite in a basaltic weathering profile, Kohala peninsula, Hawaii: Geology, v. 28, p. 271–274.

Carballo, J.D., Land, L.S., and Miser, D.E., 1987, Dolomitization of supratidal sediments by active tidal pumping, Sugarloaf Key, Florida: Journal of Sedimentary Petrology, v. 57, p. 153–165.

Ehrlich, H.L., 2000, Geomicrobiology: New York, Marcel Dekker, 719 p.

Ferris, F.G., Wiese, R.G., and Fyfe, W.S., 1994, Precipitation of carbonate minerals by microorganisms: Implications for silicate weathering and the global carbon dioxide budget: Geomicrobiology Journal, v. 12, p. 1–13.

Hardie, L.A., 1987, Dolomitization: A critical view of some current views: Journal of Sedimentary Research, v. 57, p. 166–183.

Hiebert, F.K., and Bennett, P.C., 1992, Microbial control of silicate weathering in organic-rich ground water: Science, v. 258, p. 278–281.

Land, L.S., 1985, The origin of massive dolomite: Journal of Geological Education, v. 33, p. 112–125.

Land, L.S., 1998, Failure to precipitate dolomite at 25 °C from dilute solution despite 1000-fold oversaturation after 32 yr: Aquatic Geochemistry, v. 4, p. 361–368.

McKenzie, J.A., 1991, The dolomite problem: An outstanding controversy, *in* Muller, D.W., et al., eds., Controversies in modern geology: New York, Academic Press, 490 p.

Mozely, P.S., and Burns, S.J., 1993, Oxygen and carbon isotopic composition of marine carbonate concretions: An overview: Journal of Sedimentary Petrology, v. 63, p. 73–83.

Rogers, J.R., Bennett, P.C., and Choi, W.J., 1998, Feldspars as a source of nutrients for microorganisms: American Mineralogist, v. 83, p. 1532–1540.

Schultze-Lam, S., Fortin, D., Davis, B.S., and Beveridge, T.J., 1996, Mineralization of bacterial surfaces: Chemical Geology, v. 132, p. 171–181.

Stumm, W., and Morgan, J.J., 1996, Aquatic chemistry: New York, John Wiley and Sons, 1022 p.

Tucillo, M.E., Cozzarelli, I.M., and Herman, J.S., 1999, Iron reduction in the sediments of a hydrocarbon-contaminated aquifer: Applied Geochemistry, v. 14, p. 655–667.

Vandevivere, P., and Bevaye, P., 1993, Improved preservation of bacterial exopolymers for scanning electron microscopy: Journal of Microscopy, v. 167, p. 323–330.

van Lith, Y., Warthmann, R., Vasconcelos, C., and McKenzie, J.A., 2003, Microbial fossilization in carbonate sediments: A result of the bacterial surface involvement in dolomite precipitation: Sedimentology, v. 50, p. 237–245.

Vasconcelos, C., and McKenzie, J.A., 1997, Microbial mediation of modern dolomite precipitation and diagenesis under anoxic conditions, Lagoa Vermelha, Rio de Janeiro, Brazil: Journal of Sedimentary Research, v. 67, p. 378–390.

Vasconcelos, C., McKenzie, J.A., Bernasconi, S., Grujic, D., and Tien, A.J., 1995, Microbial mediation as a possible mechanism for natural dolomite formation at low temperatures: Nature, v. 377, p. 220–222.

Warthmann, R., van Lith, Y., Vasconcelos, C., McKenzie, J.A., and Karpoff, A.M., 2000, Bacterially induced dolomite precipitation in anoxic culture experiments: Geology, v. 28, p. 1091–1094.

Whipkey, C.E., Capo, R.C., Hsieh, J.C.C., and Chadwick, O.A., 2002, Development of magnesian carbonates in Quaternary soils on the Island of Hawaii: Journal of Sedimentary Research, v. 72, p. 158–165.

Wright, D., 1999, The role of sulfate-reducing bacteria and cyanobacteria in dolomite formation in distal ephemeral lakes of the Coorong region, South Australia: Sedimentary Geology, v. 126, p. 147–157.

Manuscript received 30 September 2003
Revised manuscript received 11 December 2003
Manuscript accepted 12 December 2003

Printed in USA