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Formation of ordered dolomite in anaerobic photosynthetic biofilms

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ABSTRACT

Dolomite enabled the preservation of fine microbial textures in some Archean and Proterozoic marine microbialites, but has rarely done so during the Phanerozoic. Here, we report precipitation of dolomite in anoxygenic photosynthetic biofilms grown under chemical conditions relevant for Archean seawater. Ordered dolomite nucleates primarily on the surfaces of photosynthetic cells when manganese(II) is present, and nanocrystals of disordered dolomite form on exopolymeric substances in microbial cultures grown either in the dark or without manganese. Dolomite nucleation and maturation on different surfaces in photosynthetically active cultures amended with 0.1–1 mM manganese(II) enables the preservation of biofilm textures at scales larger than individual microbial cells. This provides a new model for the preservation of microbial textures by dolomite before the oxygenation of the oceanic photic zone.

INTRODUCTION

Microbes, exopolymeric substances (EPS), and organic surfaces can mediate the nucleation of protodolomite in some shallow hypersaline and supratidal evaporation-prone environments (Shinn et al., 1965; Sánchez-Roman et al., 2008; Bontognali et al., 2010) and deep organic-rich sediments colonized by methanogenic Archaea and sulfate reducing bacteria (Kenward et al., 2009; Krause et al., 2012). High-Mg phases that form in this manner typically do not preserve the primary textures of photosynthetic microbial mats or fine ooid laminae (Spadafora et al., 2009; Bontognali et al., 2010). Thus, these models do not adequately account for the origin of dolomite with a high content of manganese or iron, which preserved fine microbial textures in some Archean and Proterozoic microbialites (e.g., Veizer et al., 1990; Wright and Tucker, 1990; Wright, 2000; Fig. DR1 in the GSA Data Repository[1]).

Here, we use experiments to investigate the preservation potential of benthic photosynthetic communities under chemical conditions relevant for carbonate-depositing marine environments during the Archean and the Proterozoic Eons. Benthic communities before the rise of atmospheric oxygen are thought to have relied on sulfide, Fe(II), Mn(II), or hydrogen as electron donors, and the oceans contained ~0.1 mM of iron and manganese (Beukes, 1987; Anbar and Holland, 1992), although more recent estimates suggest lower iron concentrations in the deep ocean (Eroglu et al., 2018). This motivates our use of microbial communities driven by sulfide-based photosynthesis in solutions that are in equilibrium with a high pCO_2. The culture medium contained <0.9 µM sulfate, 8 µM Fe(II), and <4 nM O_2 (Pajusalu et al., 2018), was amended by 0.05 mM H_2S and 0.1–1 mM $MnCl_2$, and was in equilibrium with an atmosphere of 80% N_2 and 15% CO_2 at pH 7. We describe the mineral composition, nucleation, and maturation as a function of the medium composition, microbial activity, and types of microbial surfaces. The detection of ordered dolomite as the primary precipitate in our cultures inspires a new model for the formation of early, fabric-retentive high-Mg carbonate phases in manganese-rich sediments.

METHODS

Samples of sediments were retrieved from Fayetteville Green Lake (FGL), New York (United States), by a metallic gravity scoop, and photosynthetic biofilms were enriched from these samples. All batch enrichment cultures were grown anaerobically in a minimal photosynthetic medium for 2 weeks (see the Data Repository). 50 µM sulfide reduced the medium and was also the main electron donor for photosynthesis. The composition of microbial communities in enrichment cultures was analyzed by high-throughput Illumina sequencing. The biofilms did not contain abundant sulfate-reducing bacteria. All photosynthesizing cultures, dark culture controls, and sterile controls (without microbes) were incubated for 2 weeks or longer. The medium was supersaturated with respect to the precipitation of both calcite ($SI_{Calcite} = 0.85$) and dolomite ($SI_{dolomite} = 2.42$) (see the Data Repository), but sterile controls did not contain precipitates. Precipitates from all microbial cultures were characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) (see the Data Repository). Each experiment was performed at least three times.

RESULTS

The green sulfur bacterium *Chlorobium limicola* was the most abundant microbe and the only photosynthetic organism in the red-brown biofilms. Various anaerobic non-photosynthetic bacteria such as *Geobacter* sp. and *Acholeplasma* sp. were also present (our unpublished data). *Chlorobium* sp. that was incubated in the presence of light was photosynthetically active, and ~0.5–1-mm-thick biofilms grew in 2 weeks. The pH in the active cultures increased from 7.24 to 7.33 (0.6%) and the alkalinity decreased from 3958.3 mg/L to 3858.5 mg/L (2%) (see the Data Repository).

[1]GSA Data Repository item 2019187, materials and methods for media and enrichment protocol, X-ray diffraction, scanning electron microscopy, transmission electron microscopy, and saturation indices; and Figures DR1–DR6 and Table DR1, is available online at http://www.geosociety.org/datarepository/2019/, or on request from editing@geosociety.org.

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Sterile controls did not contain any detectable precipitates after 2 weeks, but an ordered dolomite phase was abundant in photosynthetic cultures amended with $MnCl_2$ (Fig. 1; Fig. DR2 and Table DR1 in the Data Repository). This mineral was identified by the $2\Theta^\circ = 30.9$ peak corresponding to the basal reflections of (104) crystal plane, the presence of superstructure reflections (hkl), and the match with the dolomite standard (Fig. DR2). The 101 ordering reflection was not visible, but 015, 113, and 021 ordering reflections were present (Reeder, 1983; Gregg et al., 2015) (Figs. DR2, DR3A, and DR3B). Dolomite in these cultures encrusted the surfaces of cells (Fig. 1; Figs. DR4A–DR4C) and nucleated on EPS (Fig. DR5). Calcium carbonate and elemental sulfur, which is the expected product of sulfide-based photosynthesis by Chlorobi (green sulfur bacteria), were the main precipitates in photosynthetic cultures that were not amended with $MnCl_2$ (Fig. DR2; Table DR1). Only small amounts (per ~10 mg of the analyzed biofilm) of disordered dolomite formed in the dark cultures amended with $MnCl_2$ or in photosynthesizing cultures that were not amended with $MnCl_2$ (Figs. DR1, DR4D, and DR4E; Table DR1). These minerals nucleated on EPS, and did not encrust cell surfaces (Figs. DR6 and DR7). Dark cultures without Mn(II) did not contain any detectable minerals (Fig. DR8). Thus, anaerobic photosynthetic biofilms promoted the precipitation of ordered dolomite only in the presence of light and Mn(II).

Dolomite in photosynthesizing, Mn-amended cultures nucleated after 1 week as an amorphous Ca-Mg carbonate phase with <5 nm domains (Figs. 1A–1D). This phase nucleated on the surfaces of cells and contained manganese (Fig. 1B). After an additional week, the amorphous nuclei matured into <5 nm, rounded nanocrystals in polycrystalline aggregates. The more mature nanocrystals had a uniform lattice fringe and interplanar spacing of 2.19Å corresponding to (11–3) crystal plane of dolomite (Figs. 1E–1H). Both the amorphous phase and the more mature nanocrystals were detected primarily on the surfaces of *Chlorobium* sp. cells, recognized by both spinae (Figs. 1A and 1E), and chlorosomes, i.e., complexes of photosynthetic antennae (Figs. DR4A–DR4C). Some dolomite grains <200 nm in diameter were also present on the fibrous EPS (Fig. DR5). Cell surfaces in photosynthesizing cultures that were incubated without Mn(II) were not encrusted by any minerals (Figs. DR4D and DR4E), but <200-nm-wide dolomite grains in these cultures nucleated on EPS and matured into 1 µm aggregates (Fig. DR6). Calcite nucleated on EPS in dark cultures (Fig. DR7).

To further characterize the organic surfaces and microbial textures in anoxygenic photosynthetic biofilms, we imaged horizontal cryo–thin sections of a 400-µm-thick biofilm by scanning electron microscopy / energy dispersive X-ray spectroscopy (SEM/EDS) (Fig. 2; Figs. DR9 and DR10). The crystal sizes and the extent of mineral coverage depended both on the type and the depth (age) of organic surfaces. At 25 µm below the surface of the biofilm (Fig. 2A), dense aggregates of cells contained >2-µm-wide aggregates of dolomite crystals. These crystals nucleated on cell surfaces, did not replicate the shapes of individual cells, and were distributed sporadically across the horizontal surface (Fig. 2B). Globular dolomite 5 to 10 µm wide covered cell-rich zones more extensively deeper in the biofilm (Figs. 2E and 2F) and in older biofilms (Figs. DR9 and DR10). Spatially discontinuous minerals <1 µm were directly associated with fibrous exopolymeric substances 50 µm below the surface of the 2-week-old biofilm (Figs. 2C and 2D). Thus, differences in the shape and size of dolomite crystals reflected the relative densities of cells and EPS. SEM imaging of 2-month-old biofilms confirmed the persistence of these trends over time (Figs. DR9 and DR10), and the dolomitizing biofilms did not exhibit evidence of extensive degradation or mineral dissolution. Rather, small minerals that nucleated on EPS matured into ~2-µm-wide grains.

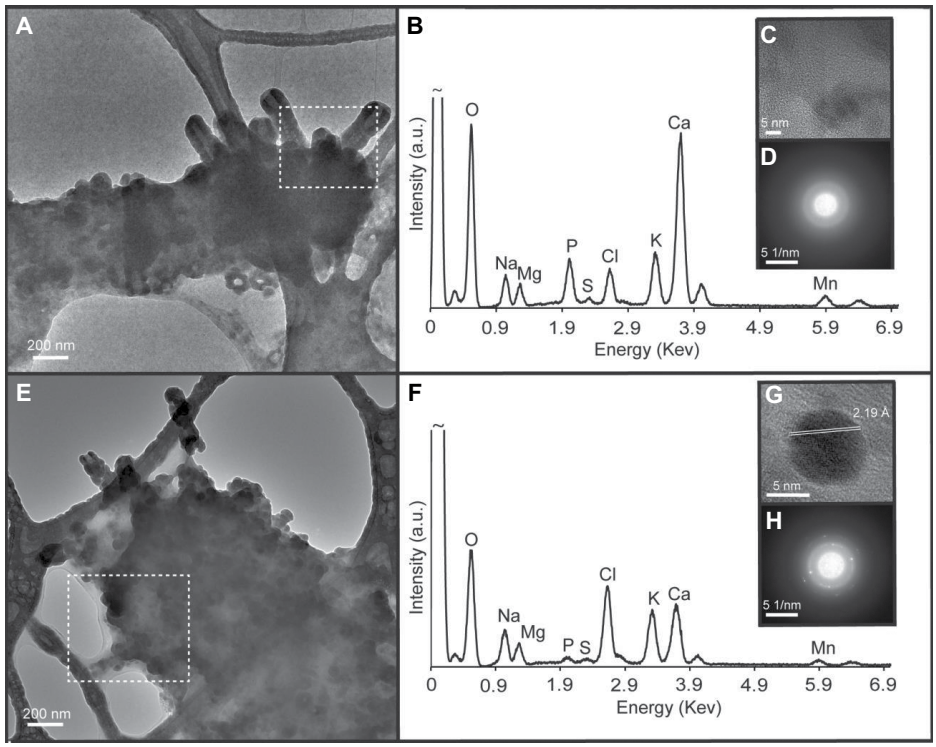

Figure 1. Transmission electron micrographs (TEMs) of cells incubated in the light with 1 mM Mn(II) for 2 weeks. Darker areas in A and E are covered by minerals; long protuberances are *Chlorobium* sp. spinae. A: TEM at 200 kV of a *Chlorobium limicola* cell. Dotted rectangles mark the areas analyzed by energy dispersive X-ray spectroscopy (EDS), high-resolution TEM (HRTEM), and selected area X-ray diffraction (SAED). B: EDS spectrum of the area shown in A. C: HRTEM shows only an amorphous phase. D: Diffraction pattern of the same amorphous phase. E: TEM at 200 kV of a cell with spinae. Dotted rectangle marks the area analyzed by EDS HRTEM and SAED. F: EDS spectrum of the area shown in E. G: HRTEM shows the lattice fringe of dolomite nanocrystals at the cell surface. H: Diffraction pattern corresponds to dolomite with (104) superstructure diffraction.

DISCUSSION

Active anoxygenic photosynthetic microbes, exopolymeric substances, and dissolved manganese stimulate the nucleation and early maturation of ordered dolomite. This process occurs in a well-buffered bulk medium and does not depend on large, metabolically induced changes in pH and alkalinity (Bosak and Newman, 2003), but requires the surfaces of photosynthetically active *Chlorobium* cells, as well as EPS (Fig. 1; Figs. DR5–DR7). Our observations are consistent with a report of dolomite in the zones of some modern microbialites where manganese oxyhydroxides are brought in close contact with intermediate and reduced-sulfur species (Petrash et al., 2016). The potential of different sulfur-cycling or oxygen-producing photosynthetic microbes to mediate the formation of dolomite and other high-Mg carbonate phases remains an open question.

Previous studies proposed roles for organic compounds in the desolvation of Mg^{2+}-water complexes on the growing surfaces of carbonate crystals to form dolomite (Roberts et al., 2013; Zhang et al., 2015). This process, mediated by EPS, carboxylic groups, or dead cells under aerobic or anaerobic conditions,

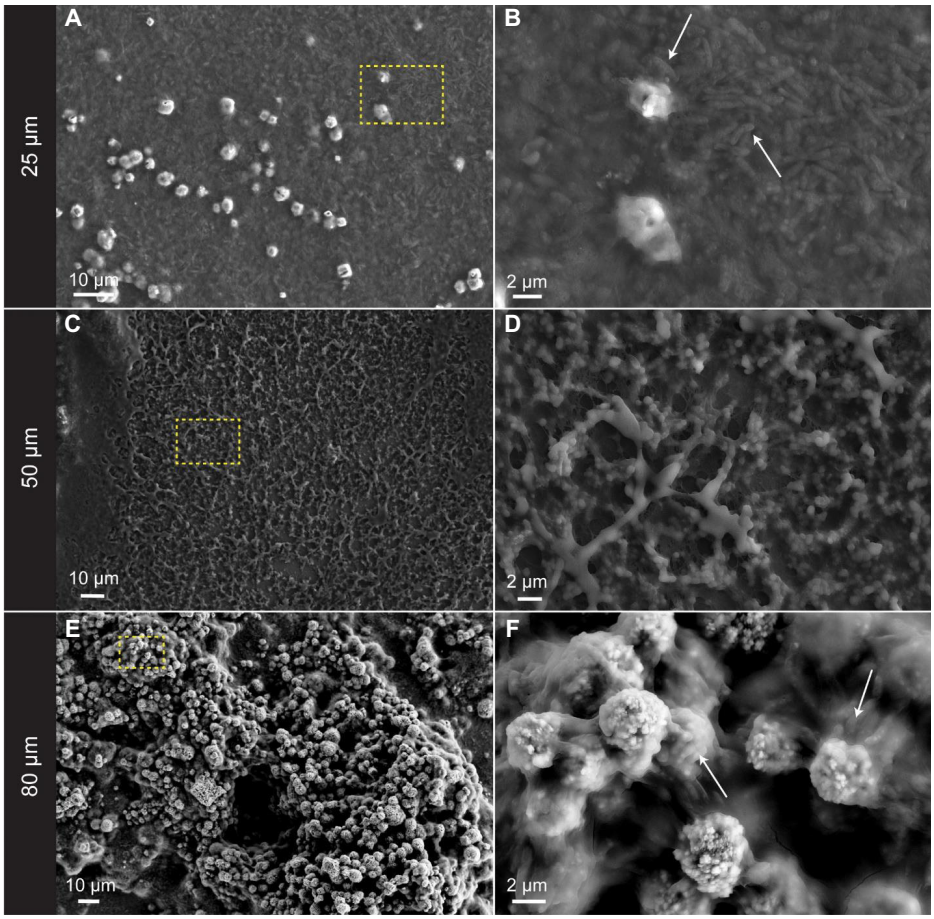

Figure 2. Cryo–scanning electron microscopy of horizontal sections through a 2-week-old biofilm. A: Cell-rich area 25 µm below the surface. Bright granules are dolomite. Dashed rectangle shows the area magnified in B. B: White arrows point to bacterial cells; the two bright globules are dolomite. C: Porous exopolymeric substances (EPS) 50 µm below the surface. Dashed rectangle outlines the area magnified in D. D: EPS network with sporadically distributed brighter areas that contain minerals. E: Cell-rich area 80 µm below the surface. The area contains numerous dolomite grains. Dashed rectangle outlines the area magnified in F. F: White arrows point to bacterial cells; the very bright round aggregates are dolomite crystals.

likely accounts for the nucleation of poorly crystalline, less-ordered, high-Mg calcite and protodolomite (Roberts et al., 2013; Bontognali et al., 2014). In contrast to many of these studies, we observe ordered dolomite. Given that the intensities of the 015 and 110 ordering reflections were not equal, the mineral formed under our experimental conditions was not perfectly ordered (Gregg et al., 2015). This can be attributed primarily to the incorporation of Mn(II) into the dolomite crystal structure. This process should cause the disappearance of the 101 ordering reflection and a shift toward larger interatomic spacings.

The mechanism by which manganese helps nucleate dolomite in systems where the concentration of magnesium exceeds that of calcium is currently not known. Previous studies showed that Mn(II) inhibits the formation of synthetic dolomite at high temperatures (Lumsden et al., 1989). However, the addition of 0.1–1 mM Mn(II) to our culture media markedly increased both the abundance and the ordering of dolomite in photosynthetic biofilms (Figs. 1B and 1F; Fig. DR2). This is consistent with the previously noted requirement for Mg(II) in the formation of high-Mn dolomite-type mineral phases in inorganic ternary systems of $CaCO_3$-$MnCO_3$-$MgCO_3$ carbonates (Mucci, 2004). The phases formed in these inorganic experiments did not contain more than 10% Mg (Mucci, 1988), but our observations suggest that the formation of authigenic high-Mg carbonate phases in Mn-rich anoxic, microbially colonized, marine sediments is also possible.

Microbial textures preserved by microcrystalline dolomite or high-Mg calcite record information about microbial processes and interactions with sediments at the sediment-water interface and/or during early burial. Micrometer-size dolomite grains that form in anoxygenic photosynthetic biofilms, the expected products of their maturation/diagenesis, and the reduction of sediment porosity due to the presence of microbial mats may account for the exceptional preservation of textures in some Archean and Proterozoic Mn- or Fe-rich dolomitic microbialites and grains. In all these instances, the fabric-retentive, Mn- or Fe-rich dolomite that contains organic inclusions is interpreted as a product of early diagenesis of a high-Mg precursor under anaerobic conditions (Wright and Tucker, 1990; Simonson and Jarvis, 1993; Wright, 2000). If high-Mg phases are already abundant at the sediment-water interface, different compositions of Ca and Mg isotopes can be expected (Blättler et al., 2015; Higgins et al., 2018). We hypothesize that fabric-retentive early dolomite that nucleates in benthic communities will appear sediment-buffered (*sensu* Higgins et al., 2018), perhaps due to the sealing properties of mineral-rich microbial mats. These predictions can be tested by studies of fabric-retentive dolomites.

Our new model for microbial dolomite formation, and the reports of well-preserved textures of Archean dolomitic microbialites, inspire the following hypothesis: the distribution of texture-preserving dolomite in time and space may reflect the changing abundances of anoxygenic or oxygenic phototrophs and concentrations of reduced ions in the pore fluids due to the progressive oxygenation of the marine realm. For example, the abundant limestone in the shallower stromatolitic and oolitic strata in the Neoarchean Ghaap Group (Campbellrand-Malmani carbonate platform, South Africa) is consistent with the inferred redoxcline on the shelf of the Campbellrand-Malmani platform based on iron minerals and isotopes (Eroglu et al., 2018). By the same token, the fine dolomitic laminae from the older, Mesoarchean microbialites (Fig. 1; Bosak et al., 2013; Siahi et al., 2016) may record active anoxygenic photosynthesis in those benthic environments. These hypotheses can be explored by comparing the preservation potential of different microbial communities under a range of redox and other chemical conditions, the composition of minerals in these communities, and the associated calcium and magnesium isotope signatures.

CONCLUSION

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REFERENCES CITED

Anbar, A.D., and Holland, H.D., 1992, The photochemistry of manganese and the origin of banded iron formations: Geochimica et Cosmochimica Acta, v. 56, p. 2595–2603, https://doi.org/10.1016/0016-7037(92)90346-K.

Beukes, N.J., 1987, Facies relations, depositional environments and diagenesis in a major early Proterozoic stromatolitic carbonate platform to basinal sequence, Campbellrand Subgroup, Transvaal Supergroup, Southern Africa: Sedimentary Geology, v. 54, p. 1–46, https://doi.org/10.1016/0037-0738(87)90002-9.

Blättler, C.L., Miller, N.R., and Higgins, J.A., 2015, Mg and Ca isotope signatures of authigenic dolomite in siliceous deep-sea sediments: Earth and Planetary Science Letters, v. 419, p. 32–42, https://doi.org/10.1016/j.epsl.2015.03.006.

Bontognali, T.R.R., McKenzie, J.A., Warthmann, R.J., and Vasconcelos, C., 2014, Microbially influenced formation of Mg-calcite and Ca-dolomite in the presence of exopolymeric substances produced by sulphate-reducing bacteria: Terra Nova, v. 26, p. 72–77, https://doi.org/10.1111/ter.12072.

Bontognali, T.R.R., Vasconcelos, C., Warthmann, R.J., Bernasconi, S.M., Dupraz, C., and McKenzie, J.A., 2010, Dolomite formation within microbial mats in the coastal sabkha of Abu Dhabi (United Arab Emirates): Sedimentology, v. 57, p. 824–844, https://doi.org/10.1111/j.1365-3091.2009.01121.x.

Bosak, T., Knoll, A.H., and Petroff, A.P., 2013, The meaning of stromatolites: Annual Review of Earth and Planetary Sciences, v. 41, p. 21–44, https://doi.org/10.1146/annurev-earth-042711-105327.

Bosak, T., and Newman, D.K., 2003, Microbial nucleation of calcium carbonate in the Precambrian: Geology, v. 31, p. 577–580, https://doi.org/10.1130/0091-7613(2003)031<0577:MNOCCI>2.0.CO;2.

Eroglu, S., Schoenberg, R., Pascarelli, S., Beukes, N.J., and Swanner, E.D., 2018, Open ocean vs. continentally derived iron cycles along the Neoarchean Campbellrand-Malmani Carbonate platform, South Africa: American Journal of Science, v. 318, p. 367–408, https://doi.org/10.2475/04.2018.01.

Gregg, J.M., Bish, D.L., Kaczmarek, S.E., and Machel, H.G., 2015, Mineralogy, nucleation and growth of dolomite in the laboratory and sedimentary environment: a review: Sedimentology, v. 62, p. 1749–1769, https://doi.org/10.1111/sed.12202.

Higgins, J., Blättler, C., Lundstrom, E., Santiago-Ramos, D., Akhtar, A., Ahm, A.C., Bialik, O., Holmden, C., Bradbury, H., and Murray, S., 2018, Mineralogy, early marine diagenesis, and the chemistry of shallow-water carbonate sediments: Geochimica et Cosmochimica Acta, v. 220, p. 512–534, https://doi.org/10.1016/j.gca.2017.09.046.

Kenward, P.A., Goldstein, R.H., Gonzalez, L.A., and Roberts, J.A., 2009, Precipitation of low-temperature dolomite from an anaerobic microbial consortium: The role of methanogenic Archaea: Geobiology, v. 7, p. 556–565, https://doi.org/10.1111/j.1472-4669.2009.00210.x.

Krause, S., Liebetrau, V., Gorb, S., Sánchez-Roman, M., and McKenzie, J.A., 2012, Microbial nucleation of Mg-rich dolomite in exopolymeric substances under anoxic modern seawater salinity: New insight into an old enigma: Geology, v. 40, p. 587–590, https://doi.org/10.1130/G32923.1.

Lumsden, D.N., Shipe, L.G., and Lloyd, R.V., 1989, Mineralogy and Mn geochemistry of laboratory-synthesized dolomite: Geochimica et Cosmochimica Acta, v. 53, p. 2325–2329, https://doi.org/10.1016/0016-7037(89)90354-2.

Mucci, A., 1988, Manganese uptake during calcite precipitation from seawater: Conditions leading to the formation of a pseudokutnahorite: Geochimica et Cosmochimica Acta, v. 52, p. 1859–1868, https://doi.org/10.1016/0016-7037(88)90009-9.

Mucci, A., 2004, The behavior of mixed Ca-Mn carbonates in water and seawater: Controls of manganese concentrations in marine porewaters: Aquatic Geochemistry, v. 10, p. 139–169, https://doi.org/10.1023/B:AQUA.0000038958.56221.b4.

Pajusalu, M., Borlina, C.S., Seager, S., Ono, S., and Bosak, T., 2018, Open-source sensor for measuring oxygen partial pressures below 100 microbars: PLoS One, v. 13, p. e0206678, https://doi.org/10.1371/journal.pone.0206678.

Petrash, D.A., Lalonde, S.V., González-Arismendi, G., Gordon, R.A., Méndez, J.A., Gingras, M.K., and Konhauser, K.O., 2016, Can Mn-S redox cycling drive sedimentary dolomite formation? A hypothesis: Chemical Geology, v. 404, p. 27–40, https://doi.org/10.1016/j.chemgeo.2015.03.017.

Reeder, R.J., 1983, Crystal chemistry of the rhombohedral carbonates: Reviews in Mineralogy and Geochemistry, v. 11, p. 1–47.

Roberts, J.A., Kenward, P.A., Fowle, D.A., Goldstein, R.H., Gonzalez, L.A., and Moore, D.S., 2013, Surface chemistry allows for abiotic precipitation of dolomite at low temperature: Proceedings of the National Academy of Sciences of the United States of America, v. 110, p. 14540–14545, https://doi.org/10.1073/pnas.1305403110.

Sánchez-Roman, M., Vasconcelos, C., Zenobi, R., and Rivadeneyra, M.A., 2008, Aerobic microbial dolomite at the nanometer scale: Implications for the geologic record: Geology, v. 36, p. 879–882, https://doi.org/10.1130/G25013A.1.

Shinn, E. A., Ginsburg, R. N., and Lloyd, R. M., 1965, Recent supratidal dolomite from Andros Island Bahamas, *in* Pray, L.C., and Murray, R.C., eds., Dolomitization and Limestone Diagenesis, A Symposium: Society of Economic Paleontologists and Mineralogists Special Publications, v. 73, p. 112–123.

Siahi, M., Hofmann, A., Hegner, E., and Master, S., 2016, Sedimentology and facies analysis of Mesoarchaean stromatolitic carbonate rocks of the Pongola Supergroup, South Africa: Precambrian Research, v. 278, p. 244–264, https://doi.org/10.1016/j.precamres.2016.03.004.

Simonson, B.M., and Jarvis, D.G., 1993, Microfabrics of oolites and pisolites in the early Precambrian Carawine Dolomite of Western Australia, *in* Rezak, R., and Lavoie, D., eds., Carbonate Microfabrics: Heidelberg, Springer-Verlag, p. 227–237, https://doi.org/10.1007/978-1-4684-9421-1_17.

Spadafora, A., Perri, E., McKenzie, J.A., and Vasconcelos, C., 2009, Microbial biomineralization processes forming modern Ca:Mg carbonate stromatolites: Sedimentology, v. 57, p. 27–40, https://doi.org/10.1111/j.1365-3091.2009.01083.x.

Veizer, J., Clayton, R.N., Hinton, R.W., Brunn, V.V., Mason, T.R., Buck, S.G., and Hoefs, J., 1990, Geochemistry of Precambrian carbonates: 3-shelf seas and non-marine environments of the Archean: Geochimica et Cosmochimica Acta, v. 54, p. 2717–2729, https://doi.org/10.1016/0016-7037(90)90007-8.

Wright, D.T., 2000, Benthic microbial communities and dolomite formation in marine and lacustrine environments—A new dolomite model, *in* Glenn, C.R., et al., eds., Marine Authigenesis: From Global to Microbial: Society for Sedimentary Geology Special Publications, v. 66, p. 7–20, https://doi.org/10.2110/pec.00.66.0007.

Wright, V.P., and Tucker, M.E., 1990, Carbonate Sedimentology: London, Blackwell Scientific Publications, 482 p.

Zhang, F., Xu, H., Shelobolina, E.S., Konishi, H., Converse, B., Shen, Z., and Roden, E.E., 2015, The catalytic effect of bound extracellular polymeric substances excreted by anaerobic microorganisms on Ca-Mg carbonate precipitation: Implications for the dolomite problem: The American Mineralogist, v. 100, p. 483–494, https://doi.org/10.2138/am-2015-4999.

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