Microbially catalyzed cementation of modern gypsum-dominated microbialites

D.A. Petrash*, S.V. Lalonde, E. Pecoits, M. Gingras and K.O. Konhauser

Department of Earth and Atmospheric Sciences. University of Alberta. Edmonton T6G 2E3, Alberta, Canada (*email: petrash@ualberta.ca)

Introduction

Microbial mats are widely distributed in modern marine hypersaline environments. In these environments, their adsorptive properties and metabolic activities drive mineral dissolution and precipitation reactions, exerting strong control over the lithification process and influencing the morphology of the resulting microbialites (Chafetz and Buczynski 1992, Duprazhttp://www.sciencedirect.com/science?_ob=ArticleURL&_udi=B6TD0-4GTW8PD-1&_user=1067472&_rdoc=1&_fmt=&_orig=search&_sort=d&_docanchor=&view=c&_searchStrId=1132303458&_rerunOrigin=google&_acct=C000051251&_version=1&_urlVersion=0&_userid=1067472&md5=5aa4c75f8d33de8a9d112c3c8bc5b2be - aff1 and Visscher 2005). Gypsum is a typical evaporative mineral phase in hypersaline environments, however the occurrence of modern gypsum-dominated microbialites is unusual, and most modern subaqueous marine microbialites are calcareous. Even though gypsum is rarely found forming domal stromatolitic structures today, it likely played an important role in the stromatolite rock record, including Precambrian stromatolites (Schopf 1983, and references therein) and in more modern examples such as the Neogene evaporitic sequence of the Mediterranean Basin (Rouchy and Monty 2000). A more complete understanding of the mechanisms by which subaqueous gypsum-dominated microbialites form today is critical understanding the significance of these features in the rock record, and may provide important revisions to modern evaporitic facies models. The bacterial role in gypsum precipitation in modern microbial mats, nonetheless, has yet to be fully explored.

Only a few concrete examples of modern subaqueous gypsum-dominated microbialites have been reported (*e.g.* Kobluk and Crowford 1990) to date. In this study, we report the formation of subaqueous gypsum-rich domal microbialites from a restricted hypersaline lagoon located at the Archipelago Los Roques, a rimmed shelf located in southern Caribbean Sea, Venezuela. This contribution specifically evaluates the formation of carbonate cements in these microbialites in an effort to define how microbes influence the lithification process. While carbonate formation in these domal microbialites appears to proceed via the intragranular replacement of gypsum and as the result of second generation porosity infilling of Mg-rich cement, the role of microbes in these processes is poorly understood. Here we employ standard and fine scale petrography, stable carbon and oxygen isotopic analysis, and inductively coupled plasma mass spectrometry (ICP-MS) to better understand the role that microbes have on their own lithification in gypsum-dominated evaporitic systems.

Major geochemical features of Laguna Pirata

The study area, the restricted lagoon Laguna Pirata, is located 160 km west of Bonaire island. Kobluk and Crowford (1990) first reported the occurrence of subaqueous gypsum-dominated microbialites at this location. Laguna Pirata is a seepage lagoon which has maximum and average depths of 1.6 and 0.45 m, respectively, and is characterized by hypersaline (90 ‰) and naturally alkaline (pH 9.1) waters with temperatures in excess of 30ºC. In this organic mud- and gypsum-dominated lagoon, bacterial activity is high, and shallow areas are dominated by a biogeochemically-stratified biofilm up to 2 cm thick (Fig.1). This bacterial mat is associated to the growth of the microbialites from shallow waters to a depth of >1 m. The microbial mat In

Laguna Pirata consist of several photosynthetic layers intermixed with zones dominated by heterotrophic bacteria. Information regarding the vertical zonation of this complex microbial mat is provided through physiochemical profiles obtained using glass microelectrodes (Fig.1A). Owing to diurnal variations in light, photosynthetic O_2 production varies dramatically, with chemical microgradients in the photic layers undergoing extreme variations between anoxia and sulfide accumulation at night, and oxygen supersaturation during the day. The bottom of the mat, inferred to be dominated by sulfate reducing bacteria, is attached to the uppermost surface of the lithified microbialites, which possess a thrombolitic fabric (clotted internal to crudely laminated). The lagoon is high in dissolved organic matter, and in its deepest areas sunlight penetration does not sustain the prolific cyanobacterial activity observed in the margins; in these deeper locations sediment consists on gypsum nodules 'floating' in a non-cohesive purple organic matrix. These nodular gypsum crystals can grow up to 1 cm diameter.
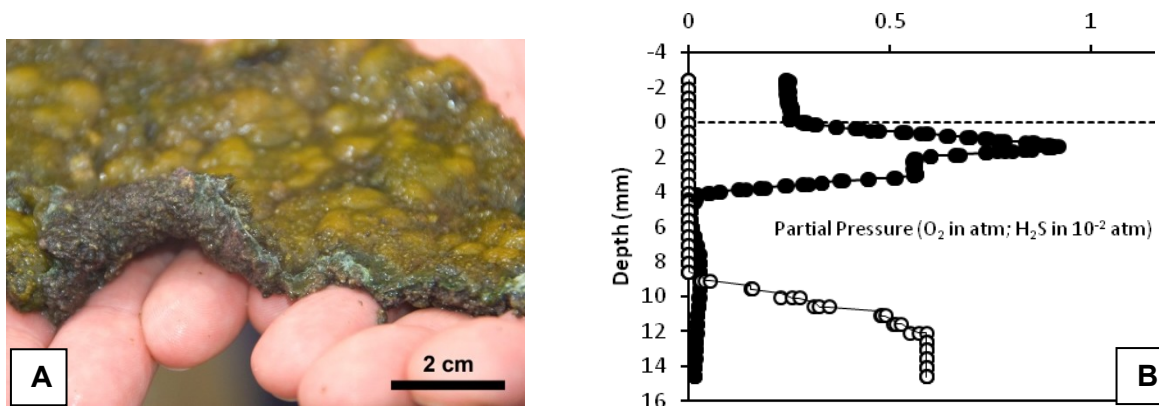

Figure 1. (A) Bacterial mat associated with accreting thrombolitic structures in Laguna Pirata. The upper layer is dominated by cyanobacteria, with algae and diatoms also present; underneath the upper layer, between 4 and 10 mm depth, a purple to green layer can be distinguished. The metabolism of anoxygenic photosynthetic bacteria use sulfide as electron acceptor, producing elemental sulfur as *a* by product, a process visually evident by the presence of a thin white layer of elemental sulfur within the green zone of the mat. (B) Daylight microelectrode profile of the bacterial mat shown in (A). The partial pressure of oxygen in the mat/water interface rises dramatically near the surface, from 0.25 to 0.95 atm. From 4 to 10 mm there is a zone of steep opposing gradients of oxygen (from above) and sulfide produced by sulfate reducing bacteria (from below). The balance between the penetration of O_2 and the penetration of light into the sulfide-rich zone creates favourable conditions for sulfide-oxidation, and correspondingly this zone is dominated by purple and green sulfur bacteria.

Theory and Methods

Owing to its polyanionic properties, biofilms are thought to decrease diffusion rates of certain dissolved ions, resulting in microenvironments that are significantly different from corresponding surface waters. In order to evaluate plausible down-depth isotopic and major elemental shifts that would result from microbially mediated dissolution-precipitation processes, four subsamples from different calcified crusts were taken from the specimen shown in Fig 2A. In addition, 12 mg of authigenic carbonate grains were carefully picked from the biofilm material coating the lithified structure. The authigenic nature of these grains is indicated by their distinctive morphological and optical features under reflected light and epifluorescence microscopy. Selected samples were analyzed for C and O isotopic composition according to procedures described in McCrea (1950), and Mg profiles with depth were generated using laser ablation ICP-MS.
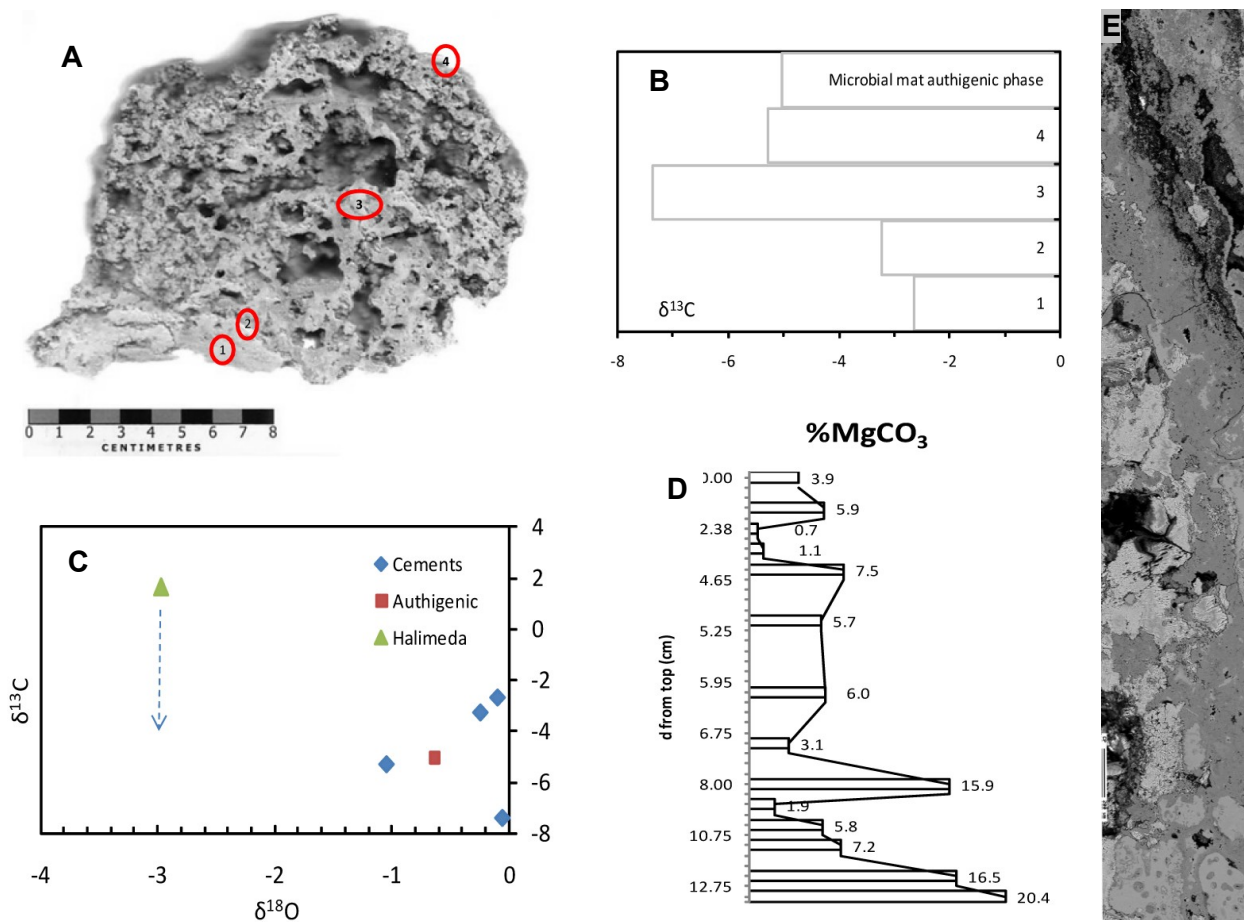
Figure 2. (A) Mesostructural features of the thrombolites from Laguna Pirata and location of the samples for isotopic/ geochemical analysis. Note the porosity, which can reach up to 45%. (B) Down-depth variation of ^{13}C. (C) The carbon and oxygen isotopic composition of the carbonate phases within the thrombolitic fabric reflect the timing of precipitation and the interplay of organic and inorganic carbon reservoirs incorporated into dissolution-enhanced early-diagenetic cements, which are relatively enriched in both Mg^{2+} and ^{13}C ($\delta^{13}C \approx$ -2 ‰) as compared to authigenic and gypsum replacing carbonates ($\delta^{13}C \approx$ -5‰). The oxygen isotopic composition ($\delta^{18}O_{PDB} \approx$ -0.6 to -0.1 ‰) results from equilibrium mineral precipitation from seawater evaporating in equilibrium with the atmosphere (δ_{SMOW}= +2.0 to +4.0 ‰); the uniformity of the $\delta^{18}O$ values, as compared with allochemical grains in the basin (aeolian transported *Halimeda* flakes, $\delta^{18}O_{PDB}$ = -3.0‰) suggests that precipitation exceeds trapping and neomorphism within the microbial mat. (D) Down-depth variation of $MgCO_3$. (E) Fine-scale features of the base of the specimen in A, darker zones are Mg enriched. Scale bar 200 µm.

Discussion

Thompson and Ferris (1990) experimentally demonstrated that bacterial alkalinization and the resultant oversaturation with respect to calcite can be linked with a simultaneous drop in the saturation state of gypsum. Dissolution of gypsum and precipitation of carbonates may result from bacterial sulfate reduction (BSR), which, through a direct reductive attack on the sulphate moiety, releases Ca^{2+} and induces calcite precipitation (Wright 1999). Microbial degradation of organic matter catalyzes this early diagenetic reaction, where the source of reducing power is the degradation of the exopolymeric substances (EPS) copiously produced by photoautotrophs in the top layer of the biofilm.

As revealed by petrographic analysis (Fig 2E), Mg-calcite can occur as a dissolution enhanced cement (micrite/ microspar), infilling intergranular spaces to form zones which exhibit fine micrometre-scale lamination, largely defined by the relative abundance of magnesium. The calcification mechanism is thought to proceed as follows. First, extra-cellular polysaccharides

(EPS) concentrate Ca ions by adsorption from the hypersaline waters into the mat. Second, carbonate phases nucleated within the EPS may partially dissolve, due to SOB activity; the remaining stable fraction may later serves as nuclei for the precipitation of microcrystalline cements, a process that occurs on available nucleation sites of the more refractory organic matrix. Third, calcium ions from bacterially-induced dissolution of gypsum precipitate immediately under alkaline conditions as a replacement phase of the precursor gypsum, and exhibit both a lighter carbon isotopic signal and relatively low Mg content. Fourth, the remaining marine-derived carbonate species, because of high alkalinity, are shifted toward CO_3^{2-} equilibrium thus growing second generation cements that may potentially incorporate Mg^{+2} together with the excess Ca^{+2}.

The microbial induced cementation at the bottom may be rich in Mg^{+2} because, in contrast to Ca^{2+}, it does not form as tight a coordination environment within the polysaccharidic network of the mat organic matrix (Davies et al. 2003). Mg enrichment of cements is an early digenetic feature initiated within the mats and is probably enhanced by the EPS matrix providing reducing power for microbial biomineralization down-depth. The diffusion of Mg-rich waters from the mat/thrombolite interface to more active precipitation zones at depth is likely responsible for the formation of the most Mg-rich carbonates at the bottom of the thrombolites. The interplay of organic and inorganic carbon reservoirs incorporated into dissolution-enhanced early-diagenetic cements are responsible for variations in ^{13}C values.

Conclusions

In Laguna Pirata the production of EPS by photoautotrops and its degradation by chemolithotrophic communities promote the partial dissolution of gypsum; microbially-generated alkaline conditions together with the metabolic activity of sulfate-reducing bacteria favour replacement and cementation of gypsum by carbonates. The interactions among the metabolic activities of several different groups of microorganisms comprising the microbial mats create chemical gradients that influence diffusive transport within the porous structure. Preferential binding of Ca by EPS may contribute to the development of a Mg-enriched microenvironment, with diffusive transport to depth in the porous structure, producing Mg-rich carbonate cements that are isotopically heavier due to decreased heterotrophic activity and increased incorporation of inorganic carbon. Where carbonate replaces gypsum, isotopically lighter carbon isotopic compositions are observed, most likely related to increased incorporation of organic carbon derived from the heterotrophic activities of sulfate-reducing bacteria.

References

Chafetz HS and Buczynski C., 1992, Bacterially induced lithification of microbial mats, PALAIOS 7: 277-293.
Davis T.A, Volesky B., and Mucci A., 2003, A review of biochemistry of heavy metal biosorption by brown algae: Water Research, 37, 4311–4330.
Dupraz http://www.sciencedirect.com/science?_ob=ArticleURL&_udi=B6TD0-4GTW8PD-1&_user=1067472&_rdoc=1&_fmt=&_orig=search&_sort=d&_docanchor=&view=c&_searchStrId=1132303458&_rerunOrigin=google&_acct=C000051251&_version=1&_urlVersion=0&_userid=1067472&md5=5aa4c75f8d33de8a9d112c3c8bc5b2be - aff1 C. and. Visscher P.T., 2005, Microbial lithification in marine stromatolites and hypersaline mats:Trends in Microbiology, 13, 429-438.
Kobluk D. and Crowford D.R., 1990, A Modern Hypersaline Organic Mud- and Gypsum-Dominated Basin and Associated Microbialites: PALAIOS, 5, 134-148.
Rouchy J.M and Monty C., 2000, in R. Riding & S.M. Awramik (Eds.): Microbial Sediments, Springer ,Berlin, pp. 209-216.
Schopf J.W., 1983, Earth's Earliest Biosphere. Its Origin And Evolution. Princeton University Pressm Princeton, 543 pp.

Thompson, J.B. and Ferris, F.G., 1990, Cyanobacterial precipitation of gypsum, calcite, and magnesite from natural alkaline lake water: Geology, 18, 995-998.

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