

**STROMATOLITES, THROMBOLITES AND OTHER MICROBIALITES IN MODERN ENVIRONMENTS: EMERGING PATTERNS OF METABOLIC PRODUCTS AND PRECIPITATION?** P.T. Visscher<sup>1,2</sup>, C. Dupraz<sup>1,2</sup>, K.L. Gallagher<sup>2</sup>, K.L. Myshrall<sup>1</sup>, A.J. Fowler<sup>1</sup>, N.J. Stork<sup>1</sup>, O. Braissant<sup>1,3</sup>, C. Glunk<sup>4</sup>, B. Burns<sup>5</sup>, C. Vasconcelos<sup>6</sup>, J.A. McKenzie<sup>6</sup>, <sup>1</sup>Center for Integrative Geosciences, Univ Connecticut, U-2045, Storrs, CT 06269, USA, pieter.visscher@uconn.edu, <sup>2</sup>Dept. Marine Sciences, Univ Connecticut, Grorton, CT 06355, USA, <sup>3</sup>Pharma Center, Univ Basel, Basel, Switzerland, <sup>4</sup>Geology & Paleontology Institute, Univ Lausanne, Lausanne, Switzerland, <sup>5</sup>Australian Centre for Astrobiology, Univ New South Wales, Sydney, Australia, <sup>6</sup>Geology Institute, ETHZ, Zurich, Switzerland.

Microbial mats are organosedimentary biofilm communities that greatly impacted the geochemical and physicochemical conditions of Earth's lithosphere and atmosphere through geological time. These laminated ecosystems, which date back possibly as much as > three billion years [1], are characterized by extremely high metabolic rates. Coupled to this, rapid cycling of major elements occurs, perhaps most prominently that of carbon, on scales that span micrometers to millimeters. On a microscopic scale, the biological activity of mat communities has changed the geochemical conditions through the formation of resilient biofilms that stabilize sediments through binding and trapping [2] and *in situ* precipitation [3]. On the macroscale of Earth as a planet, this microbial activity (particularly that associated with mats) is believed to have led to a major shift in redox conditions, which allowed for the evolution of an oxygen-containing atmosphere and complex reduction-oxidation reactions that support a plethora of microbial life.

The interpretation of fossil microbial mats in the rock record and, consecutively, assessment of their potential role in the alteration of Earth's geochemical environment through time is hampered by the poor preservation of these organic-rich sediment systems [1]. This preservation potential, however, can be enhanced through microbially-mediated lithification [3,4]: Carbonate precipitation resulting from microbial metabolisms is perhaps the most important and best-studied mechanisms that increase the conservation potential of mats. The two key components of the microbially-mediated mineralization process are the "alkalinity" engine (i.e., microbial metabolism and environmental conditions impacting the calcium (or magnesium) carbonate saturation index) and the complex organic matrix comprised of exopolymeric substances (EPS) [3].

While the various types of microbial metabolism and their effect on the alkalinity of their immediate environment have been well-documented [5,6,7], the role of EPS is less clear. The extracellular matrix contains both high and low-molecular weight components, the latter resulting from incomplete oxidation of or-

ganic substrates [8]. Both components play an important role in carbonate precipitation by providing  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  as well as a nucleation template for mineral growth. Furthermore, both components, but predominantly the high molecular weight fraction (the polymer backbone) contains several negatively charged functional groups, which, depending on the pH, can be deprotonated (each group has unique pK value(s)) and, thus, bind cations [9] at different a pH). This binding capacity can deplete the surrounding environment of cations (e.g.,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) and, thus, may inhibit carbonate precipitation [3]. Therefore, organomineralization (i.e., carbonate precipitation on the organic EPS matrix [4]) is only possible if the inhibition potential is reduced through oversaturation of the EPS binding capacity or alternatively EPS degradation.

The EPS properties change with changes in microbial community composition and also with depth due to microbial and chemical alteration of these complex polymers [8,9]. We will present a model of EPS-Ca interactions, microbial alteration and successive carbonate precipitation that are based on field and laboratory observations. Clearly, changes in EPS composition with depth have a potentially profound impact on the mineral composition: in two geographically-separated microbialite systems, we observed changes of the Ca:Mg ratio in carbonate minerals in different lithified depth horizons [10,11].

While mineral shape and composition may be a function of the EPS properties [12] and therefore has the potential to reflect a specific signature of the microbial community [4], it is unresolved how, for example, a continuous lamina forms. The cyanobacterial community, situated near the surface according to the ambient light conditions, provides the organic carbon for heterotrophs. All these respiring organisms (including "strict" anaerobes, such as sulfate-reducing bacteria and methanogens; [13,14]) display their maximum metabolic activity along a surface horizon that may lithify [15]. Some ideas emerge how chemical communication may play a role in this, and how microbial signaling compounds may be used to detect specific environmental conditions (e.g., pH, sulfide,

oxygen) and may allow synchronizing of intra- and interspecies metabolic activities [16,17]. These recent observations and ideas are, however, merely a first step in the understanding of microbialite formation, and their potential to weather the diagenetic processes so that some of the biological signatures are preserved.

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