Micro-elemental Analysis of Stromatolites Reveal Fe as Potential Biosignature and Remnant of a Lithification Mechanism

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Stromatolites—lithified, laminated organosedimentary structures typically built by microbes—are found in geological settings spanning at least the last 3.5 billion years, and act as the major record of life for 7/8ths of Earth’s history, yet the details of their formation and lithification remain poorly understood. Additionally, the history of stromatolite abundance and diversity remains difficult to explain, with stromatolites increasing in abundance toward their peak in the Mesoproterozoic followed by dramatic decline after 1 Ga into the Phanerozoic, after which they remain rare. The leading hypothesis explaining stromatolite decline implicated burrowing/grazing metazoans in microbial mat destruction; however, metazoans arose after stromatolite decline began. Here, we hypothesize that dissimilatory iron reduction—a metabolism not previously recognized as important in stromatolites—may have a central role in microbial mat lithification and throughout the Precambrian. Within stromatolite laminae, iron oxides may form in the presence of oxygen produced via cyanobacterial photosynthesis during daylight hours. During local anoxia at night, iron reducing bacteria may use iron oxides as electron acceptors producing Fe\(^{2+}\). This metabolic process increases local alkalinity more than other common metabolisms and favors CaCO\(_3\) precipitation. Since Fe\(^{2+}\) can substitute for Ca\(^{2+}\) in the CaCO\(_3\) crystal lattice, evidence of iron reduction may be preserved within stromatolite laminae. To test this, we examined the distribution of Fe, Ca, Mg, S, Si, Al, Ti, and Sr in several stromatolites with ages spanning their historic rise, peak, and decline using micro X-ray Fluorescence Spectrometry and Raman Spectroscopy. We find that stromatolites with presumed biogenic origin show a heterogeneous distribution of iron inextricably linked to stromatolite laminae and the presence of Ca and not S, indicating that the iron is located within CaCO\(_3\) and not pyrite. Additionally, background levels of detrital input gleaned from Si, Al, Ti, and Sr are insufficient to explain cyclic increases in iron corresponding to laminations. An abiogenic stromatolite sample displayed a homogenous iron distribution and no association with laminae. This indicates that iron association with laminae in biogenic stromatolites may be a genuine biosignature of microbial iron reduction and Fe-cycling and suggest the presence of a critical stromatolite lithification mechanism.