

## **Examining Fe-cycling in microbial mats as a lithification mechanism and possible stromatolite biosignature**

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The biogenicity of stromatolites is a hotly debated subject. Stromatolites are abundant in Archean/Proterozoic successions, however they reached a form diversity and abundance peak ~1.0 billion years ago, declined through the Neoproterozoic, and became comparatively rare throughout the remaining 600 million years of Earth history. The mechanisms behind stromatolite formation, and this abundance pattern, remain unsolved. For example, the evolution of widespread burrowing/grazing metazoans that might disrupt microbial mats occurs too late to explain stromatolite decline. Additionally, the two most common microbial metabolisms attributed to stromatolite formation/lithification, oxygenic photosynthesis and sulfate reduction, are ubiquitous today, yet modern stromatolites are comparatively rare. Here, we investigate a possible role for iron oxidation/reduction in microbial mat lithification and suggest that changes in dissolved marine iron concentration through time may link to the decline in stromatolite abundance well before the evolution of animals.

Before widespread marine oxygenation, the oxygen produced locally by cyanobacteria during sunlight hours could induce iron oxide precipitation in microbial mats (a process that we have observed in modern hot spring mats). At night, when the mat would be anoxic, iron-reducing bacteria could exploit the iron oxides to respire, releasing iron into pore waters. During microbial iron reduction, the boost of alkalinity can shift the local geochemical environment in favor of calcium carbonate precipitation (more than any other common metabolism, ~10-fold alkalinity increase vs. sulfate reduction). We have investigated this hypothesis in several ways. Iron isotope/genomic data from siliceous stromatolites in Obsidian Pool Prime Hot Spring (Yellowstone National Park) are consistent with the Fe-redox cycling within the laminations. In addition, we note that the decline of stromatolites tracks the loss of ferruginous oceans as indicated by Mo and Cr proxies preserved in the rock record. Finally, micro-elemental and mineralogical examination of some ancient stromatolites demonstrates enrichment of iron in light vs. dark laminae consistent with the predicted iron cycling. These results lead us to suggest that the distribution of iron within ancient stromatolite laminae may be useful as a biosignature.