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## THE BIOGEOCHEMISTRY OF MICROBIAL MATS, STROMATOLITES AND THE ANCIENT BIOSPHERE

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Stromatolites offer an unparalleled geologic record of early life, because they constitute the oldest (3.5 Ga) and most abundant recognizable remains of microbial ecosystems. Microbial mats are living homologs of stromatolites, thus we can study the physiology of the microbiota as well as the processes which create those features of mats (e.g., "biomarker" organic compounds, elemental and stable isotopic compositions) which are preserved in the ancient record.

Our observations of the carbon isotopic composition ( $\delta^{13}\text{C}$ ) of stromatolites and microbial mats are consistent with the hypothesis that atmospheric  $\text{CO}_2$  concentrations have declined by at least one to two orders of magnitude during the past 2.5 Ga. Whereas  $\delta^{13}\text{C}$  values of carbonate carbon average about 0 permil during both the early and mid-Proterozoic, the  $\delta^{13}\text{C}$  values of stromatolitic organic matter increase from an average of -35 between 2.0 and 2.6 Ga ago to an average of about -28 about 1.0 Ga ago. Modern microbial mats in hypersaline environments have  $\delta^{13}\text{C}$  values typically in the range of -5 to -9, relative to an inorganic bicarbonate source at 0 permil. Both microbial mats and pure cultures of cyanobacteria grown in waters in near-equilibrium with current atmospheric  $\text{CO}_2$  levels exhibit minimal discrimination against  $^{13}\text{C}$ . In contrast, hot spring cyanobacterial mats or cyanobacterial cultures grown under higher  $\text{CO}_2$  levels exhibit substantially greater discrimination. If care is taken to compare modern mats with stromatolites from comparable environments, it might be possible to estimate ancient levels of atmospheric  $\text{CO}_2$ .

In modern microbial mats a tight coupling exists between photosynthetic organic carbon production and subsequent carbon oxidation, mostly by sulfate reduction. The rate of one process fuels a high rate of the other, with much of the sulfate reduction occurring within the same depth interval as oxygenic photosynthesis. That sulfate reduction activity occurs within a well-oxygenated environment questions the conventional view that this is an obligately anaerobic process. Also contrary to conventional thought, appreciable isotopic discrimination is observed even at the highest rates of sulfate reduction (>12 millimolar per day). The sulfide has an isotopic composition ( $\delta^{34}\text{S}$ ) about 45% lighter than that of the sulfate from which it is produced. This large isotopic discrimination might allow us to search for the evolution of sulfate reduction as a carbon mineralization process in stromatolites. This process was indeed an important addition to the cycling of carbon on the early earth.