Multiple sulfur isotope constraints on microbial processes in Archaean seafloor environments

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Significant mass-dependent sulfur isotope fractionation accompanies microbial utilization of sulfur, particularly sulfate reduction that is the most important process for mineralization of organic matter in modern marine sediments. Proterozoic and Phanerozoic sedimentary sulfides exhibit a wide range of δ^{34} S values that have been interpreted to reflect the fractionation accompanying microbial sulfate reduction [1]. Microbial disproportionation of sulfur compounds is another process implicated in the global sulfur cycle since the Mesoproterozoic [2]. In contrast, most Archaean and early Proterozoic sedimentary sulfides exhibit a narrow range of δ^{34} S values of 0 ± 10 per mil, which may result from microbial sulfate reduction under sulfate-limiting conditions [3]. It has been argued, moreover, that higher fractionations between pyrite and barite in the 3.5 Ga Dresser Formation of the Pilbara, Western Australia provide evidence for early microbial sulfate reduction [4]. This interpretation is contradicted by the $\delta^{34}S-\Delta^{33}S$ systematics of Dresser Formation samples and the oxygen isotope compositions of black cherts interbedded with the barites, which indicate the sulfates precipitated from hydrothermal fluids in a white smoker seafloor environment. The barites and associated sulfides exhibit negative Δ^{33} S that we attribute to an ultimate seawater sulfate source. On the other hand, the majority of sedimentary sulfides older than 2.8 Ga including pyrites in the Dresser Formation black cherts have positive Δ^{33} S, which implicates an elemental sulfur source of atmospheric origin [5]. These multiple sulfur isotope data are consistent with but do not unambiguously indicate an early origin for sulfur reducers as the isotopic fractionation associated with microbial reduction of elemental sulfur is poorly contrained. In contrast, Archaean sedimentary sulfides younger than 2.8 Ga record both positive and negative Δ^{33} S; the latter samples have ³⁴S-depleted δ^{34} S values providing good evidence for microbial sulfate reduction.

References

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