Sulfur cycles around ca. 15 Ma Kuroko deposits and new perspective for causative factors of mass-independent fractionation of sulfur

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Mass-independent fractionations of sulfur isotopes (MIF-S) are recorded in sulfides and sulfates in Archean sedimentary rocks. Such MIF-S are considered proxies of anoxic environments of the early Earth. On the other hand, it has been known that abiotic interaction of organic matter with sulfur species could cause MIF-S. There exists a minor sediment-hosted Kuroko in the Hokuroku district in Japan. A significant interaction of organic matter with hydrothermal fluids is expected in those sediment-hosted Kuroko, potentially recording MIF-S. Therefore, sediment-hosted Kuroko were examined geologically and mineralogically and analyses of ^{32}S, ^{33}S, and ^{34}S were performed in the present study.
Shinsawa and Kowarizawa Kuroko were formed on the top and in mudstones. Concentrations of organic carbon ranged from 0.1 to 0.2 wt% in all mudstones. Those mudstones contain abundant framboidal pyrites. $\delta^{34}S$ values of framboidal pyrite-bearing mudstone ranged from -42 to +4‰. That indicates the significant bacterial sulfate reduction (BSR) in mudstone independently from ore-forming processes. Geochemical characteristics of mudstone change from ore-forming sites to distal zones at Shinsawa and Kowarizawa. The S content of the distal mudstones ranged from 0 to 0.6 wt%, but those of Kuroko-hosted mudstones ranged from 0.9 to 35.6 wt% at Shinsawa and Kowarizawa. Concentrations of Ba changed from 0 wt% (distal zone) to 1.3 to 20 wt% (ore-forming site) at Shinsawa and Kowarizawa.
Shinsawa and Kowarizawa ores contain abundant barite. $\delta^{34}S$ values of sulfates ranged from +20 to +25 ‰. Such ^{34}S-enriched values indicate the sulfate reduction in mudstone (i.e., in closed system) followed by Rayleigh isotope fractionation. Such shallow sulfate reduction is not common and only possible by thermochemical sulfate reduction using sedimentary organic matter. $\delta^{34}S$ values of sulfides in those deposits were from 0 to +6.0 ‰.
The $\Delta^{33}S$ values of sulfates and sulfides showed MIF-S signatures, ranging from -1.5 to +1.5 ‰. This is the first report of MIF-S signatures found in Kuroko deposits. The TSR by interaction of hot hydrothermal fluids with sedimentary organic matter was most likely responsible for MIF-S in the examined samples. Carbon cycles are, in general, not linked to formation of Kuroko and other VMSs. On the other hand, it is found that small or immature Kuroko has a signature of interaction with organic matter followed by precipitation of sulfate and sulfide with MIF-S. This further indicates the importance of C-S coupled cycles at venting sites at the initial stage of VMS growth.

