Unknown mass-independent fractionation of sulfur isotope in middle Miocene Kuroko deposits in the Hokuroku district, Akita, Japan.

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Mass-independent fractionations (MIFs) of sulfur isotopes are recorded in Archean sulfides and sulfates. Such MIFs are considered as tracers of UV radiation on sulfur species in Archean anoxic environments. On the other hand, it has been unclear if significant MIFs can be caused other than UV radiation. Here we analyzed ^{32}S, ^{33}S and ^{34}S compositions of sulfides and sulfates from ca. 15 Ma Kuroko deposits in the Hokuroku district in Japan, with geological and mineralogical examinations. In particular, we focus on carbonaceous-sediment-hosted Kuroko deposits (Shinsawa and Kowarizawa deposits), which may have recorded thermochemical sulfate reduction.

Sulfate minerals commonly occur at the Shinsawa and Kowarizawa deposits with massive sulfides and in carbonaceous sediments. Sulfur isotopic compositions of sulfates range from +20‰ to +24‰, and +21‰ to +25‰, respectively at Shinsawa and Kowarizawa deposits. In particular, ^{34}S-enriched values (i.e., +24 and +25 ‰) in sulfate indicate thermochemical sulfate reduction in sediments. It is found that $\Delta^{33}S$ (V-CDT) values of sulfide and sulfate minerals at both deposits show MIF signatures. For example, $\delta^{33}S$ (V-CDT) values of sulfides at Kowarizawa deposit show -0.9‰.

The MIFs of sulfur isotope compositions in both deposits were most likely caused by thermochemical sulfate reduction by the interaction between organic matter and sulfate-bearing hydrothermal fluids (c.f., Watanabe et al., 2009). This further implies the UV radiation is not the single causative factor of MIFs and many Phanerozoic geological samples, especially organic-rich samples, may have recorded MIFs of sulfur isotopes.

