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Sedimentary environments after Kuroko deposits around 13 Ma: mineralogical and geochemical studies on pyrite framboids

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In the Hokuroku district of Akita Prefecture, Kuroko deposits were formed at ~13 Ma by submarine hydrothermal activities. Previous study (e.g., Komuro et al., 2004) suggested that, during the formation of Kuroko deposits bottom of an ocean water become anoxic locally. When an ocean becomes anoxic, it may further become euxinic by either hydrothermal or microbial activities. Extents of anoxic or euxinic ocean and their duration have been poorly understood during and after the formation of Kuroko deposits. In this study, geological, geochemical, and mineralogical investigations, including the size measurements of pyrite framboids, were carried out on mudstones in the Hokuroku district. Size distribution of pyrite framboids in sedimentary rocks has been used as indicators for distinguishing oxic and euxinic ocean water (Wilkin et al., 1996). Sulfur isotope ratios of pyrite in the rocks were also analyzed to evaluate activities of sulfate reducers.

Mudstones, named M3, M2b, M2a and M1 were collected from outcrops in the Hokuroku district. The size and chemical compositions of pyrite framboids in the samples were examined by standard petrographic microscopy, SEM, and EPMA. Contents of organic carbon and pyrite sulfur of the samples were determined by an elemental analyzer (EA). The sulfur isotope compositions of the samples were determined by EA-IRMS.

Detailed size analyses of the pyrite framboids showed that mean sizes of pyrite framboids in the lower M2b mudstones (~5.2 micro meters) were smaller than those of the upper M2b, M2a and M1 mudstones (~6.3 micro meters). This trend indicates that the lower M2b mudstones were deposited under euxinic conditions, and that the upper M2b, M2a and M1 mudstones were deposited under oxic conditions. Therefore, the bottom oceans were euxinic soon after the Kuroko formation, and the euxinic water overlaid the entire Hokuroku basin. Here we propose that such euxinic conditions prevent the oxidation of Kuroko deposits and contributed to their preservation. Then the bottom oceans became oxic a few million years after the Kuroko formation. The sulfur isotope compositions of pyrites in the mudstones deposited in euxinic environments range from -50 to -30 per mil, which indicates that redox sulfur cycling were driven by sulfate-reducing and sulfur-oxidizing bacteria at the redox boundary in a water column. Interestingly, there is no signs of hydrothermal sulfur in pyrites in the lower M2b, suggesting the euxinic condition was generated by microbial activities. The results of sulfur isotope analyses suggest that microbial activities were involved in the change of oceanic environments to euxinic, even near submarine hydrothermal activities. On the other hand, the sulfur isotope compositions of pyrites in the M2a and M1 mudstones range from -30 to -15 per mil, which suggests that only sulfate reducing bacteria were active in the sediments a few million years after the Kuroko formation.

References

Komuro K., Kubota H., Sato T., Kajiwara Y. and Tanimura S. (2004) Trace fossils and sulfur isotopes in mudstones around the Kuroko deposits in Hokuroku basin, northeast Japan: an attempt to delineate the depositional environment. *Resource Geology*, 54, 4, 425-436

Wilkin R. T., Barnes H. L. and Brantley S. L. (1996) The size distribution of framboidal pyrite in modern sediments: An indicator of redox conditions. *Geochimica et Cosmochimica Acta*, 60, 20, 3897-3912

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