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秋田県北鹿地域に産する泥岩 (15-10 Ma) の急激な堆積環境変動：黄鉄鉱含有泥岩の鉱物学的地球化学的研究
Rapid change of sedimentary environments in ca. 13Ma at Hokuroku area: mineralogical and geochemical studies on pyrite

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Previous study suggested that the bottom water locally become anoxic after the formation of Kuroko deposits in the Hokuroku district, Akita in Japan (Komuro et al., 2004). However, the temporal and spatial distribution of anoxic water during 15 to 10 Ma are still poorly understood. Anoxic bottom water may be a critical factor in the initial preservation of volcanogenic massive sulfide deposit (VMS) (Eastoe and Gustin, 1996). Therefore, the importance exists as to if the Kuroko deposits were also preserved in anoxic conditions or not.

Size distribution of pyrite framboids in carbonaceous sedimentary rocks is one indicator to identify the presence of anoxic ocean water. Carbonaceous sedimentary rocks, which age range from 15 to 10 Ma, are availabe in the Hokuroku district. In addition to age distribution, the same-aged carbonaceous sedimentary rocks are largely extended. Therefore, those carbonaceous sedimentary rocks have potential to examine temporal and spatial distribution of anoxic water in the past Hokuroku district.

In this study, geological, geochemical, and mineralogical investigations were carried out on mudstones in the Hokuroku district. In particular, the size distributions of pyrite framboids were analyzed using SEM. The mudstones from M3, M2 Ma and M1 were collected from outcrops in the large area of the Hokuroku district. The M3 mudstone, which age is most likely between 15 to 14 Ma, was deposited before the formation of Kuroko deposits. M2 mudstone was deposited soon after Kuroko hydrothermal activity (ca.14 to 13 Ma). Ma and M1 mudstones, which ages are ranging from 13 to 10 Ma were deposited with no relation to Kuroko hydrothermal activity.

Detailed size analyses showed that mean sizes of pyrite framboids in the M2 mudstones (5.0 to 5.2 micro meters) were smaller than those of M3, Ma and M1 mudstones (5.0 to 9.7 micro meters). The standard deviation of pyrite framboids in the M2 (2.0), were also smaller than those of others (2.4 to 4.2). These results above indicate that M2 mudstones were deposited under euxinic conditions, and M3, Ma and M1 mudstones were deposited under oxic conditions. The examined M2 mudstones were collected both near and far from the ore bodies and all show the same size distribution of framboidal pyrite. This suggests that anoxic water were rather widespread at the bottom of the Hokuroku ocean between 14 to 13 Ma. On the other hand, anoxia of bottom ocean water only restricted during sedimentation of M2 mudstones. The total range of sulfur isotopic compositions of pyrites were range from -44 to -15 per mil. In particular, the sulfur isotope compositions of pyrites in M2 were range from -37 to -34 per mil. Such light values indicate microbial sulfur cycling by sulfate-reducing, sulfur-oxidizing and/or sulfur-disproportionating bacteria in the anoxic water column. On the other hand, S(pyrite)/C(organics) in M2 mudstone is not high compared to Black Sea sediments, which deposited in euxinic conditions and redox boundary reached to photic zone. Those facts indicate that euxinic bottom water at the pale-Hokuroku ocean were created by microbial activities, not submarine hydrothermal activities. The anoxic water at this age was limited at the bottom of deep ocean and did not reached to photic zone, so that the magnitude of microbial productivities (and pyrite precipitation) at redox boundary were limited.

On the other hand, the sulfur isotope compositions of pyrites in the upper part of Ma and M1 range from -30 to -15 per mil. M1 mudstones contain the secondary pyrite (e.g., pyrite overgrowth on primary framboidal pyrite). Such secondary pyrite often contain unusual amounts of Mn. Texture and chemistry of secondary pyrite suggest that those were formed during late diagenetic stage by dissolving and reprecipitating primary framboidal pyrite. Such diagenetic process, accompanied with change of clastic sediments and sedimentation rates, may affected on sulfur isotope compositions of M1 and Ma.

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