

Large Fe isotope fractionations in ferruginous sedimentary rocks above Kuroko deposits in the Hokuroku district

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The Hokuroku district in Akita Prefecture, Japan, hosts many large volcanogenic massive sulfide (VMS) deposits called Kuroko deposits formed around 15.3 million years ago by ancient submarine hydrothermal activity. VMS deposits were formed by the precipitation of metals from hydrothermal fluids and could have contacted with seawater in geological timescales. Because they are composed of sulfide minerals that are stable in a reducing environment, such as pyrite and chalcopyrite, an anoxic environment in the Hokuroku basin may play an important role in the preservation of the sulfide ores containing valuable metals in Kuroko deposits. However, geochemical evidence of such an environment occurring in Hokuroku district is currently lacking. Therefore, objective of this study is to investigate the distribution of REEs and the variation of Fe isotope compositions in the Fe-Mn-rich sedimentary rocks associated with VMS deposits in the Hokuroku district to understand the depositional environments and ancient sea-floor hydrothermal systems in the Hokuroku basin. Sedimentary rock samples obtained from both outcrops and mines in the Hokuroku district include ferruginous cherts occurring directly on or above a Kuroko deposit, manganese-rich siliceous mudstone, and amber in mudstone or tuff. Samples were analyzed by XRD, petrography, and SEM-EDS for mineralogy, by XRF and LA-ICPMS for chemical composition and MC-ICPMS for iron isotope composition ($\delta^{56}\text{Fe}$ (‰) = $1000 * [(^{56}\text{Fe}/^{54}\text{Fe})_{\text{sample}} / (^{56}\text{Fe}/^{54}\text{Fe})_{\text{IRMM-14}} - 1]$).

The results of these analyses show the $\delta^{56}\text{Fe}$ values of mine samples occurring directly on and above Kuroko deposits were -1.5 to 0.5 ‰. These values are largely fractionated from $\delta^{56}\text{Fe}$ value that is similar with igneous rock's $\delta^{56}\text{Fe}$. Iron isotopic fractionation occurs when ferrioxide precipitate part of the bivalent iron present in the reservoir. These values are largely fractionated from the $\delta^{56}\text{Fe}$ value of the standard (i.e., 0 ‰), which is a similar to that of igneous rocks. The samples that have a large negative value also bears negative Ce anomaly. These signatures indicate that partial oxidation of dissolved ferrous iron occurred by mixing ferrous iron-bearing anoxic water with oxygen-bearing seawater, and therefore that the sea-floor of the Hokuroku Basin was anoxic. On the other hand, $\delta^{56}\text{Fe}$ values of chemical sedimentary rocks formed during 2 -3 Ma after Kuroko deposits formed ranges from -0.8 to -0.3 ‰. These values are similar to that of dissolved ferrous ion in a modern sea-floor hydrothermal fluid. Therefore, the $\delta^{56}\text{Fe}$ values of the samples indicate near complete oxidation of dissolved ferrous iron in an oxic environment. Therefore, the results of this Fe isotope study suggest that the depositional environment in the Hokuroku basin shifted from anoxic to oxic after the formation of Kuroko deposit.

Keywords: iron isotope, rare earth pattern, anoxic environment, Volcanogenic massive sulfide, hydrothermal system