

Fe isotope fractionations relating to the ore formation processes in volcanogenic massive sulfide deposits

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The Hokuroku district in Northeast Japan hosts many large volcanogenic massive sulfide (VMS) deposits called Kuroko deposits, which were formed around 15 Ma by ancient submarine hydrothermal activity. Because they are composed of sulfide minerals that are stable in a reducing environment, redox environment on the seafloor during the formation of Kuroko deposit may play an important role in the preservation of the sulfide ores. Furthermore, factors controlling the size and grade for VMS deposits have not been well understood. Previous studies have shown that Fe isotope ratios as well as Rare Earth Element (REE) patterns of ferruginous cherts that associated with Kuroko deposits may reflect the depositional environments. However, sulfides containing in the sedimentary rocks may affect the bulk Fe isotope ratio. Therefore, the objective of this study is to understand formation processes of a large and high-grade VMS deposit based on Fe isotope variations in the sulfide ores and ferruginous cherts with considering the effect of Fe mineralogy to the bulk Fe isotope ratios.

Studies samples were obtained from several VMS deposits from the Hokuroku district as well as Palmer deposit in Alaska, USA. Microscopic observations of the polished sections and the major element contents obtained by X-ray Florescence (XRF) analysis demonstrated that the samples are typical black ores, containing sphalerite and galena, yellow ores, containing chalcopyrite and pyrite, and ferruginous cherts, containing quartz and minute grains of hematite. Some ferruginous cherts also contains iron sulfide (e.g., pyrite, pyrrhotite) as it was concerned. Most ferruginous chert samples also show a distinct positive Eu anomaly in their REE patterns, suggesting that they are affected by high temperature hydrothermal fluids. Fe isotope ratios of sulfide minerals physically separated from ferruginous chert samples were not significantly different from those of the bulk samples, indicating that the presence of iron sulfides in the ferruginous cherts does not affect the bulk Fe isotope ratio. The bulk Fe isotope analysis of ferruginous chert samples from all the studied deposits using multi-collector inductively coupled plasma-mass spectrometry (MC-ICP-MS) shows large variations in the $\delta^{56}\text{Fe}$ values (-1.55–+2.04‰). The variations in Fe isotope ratios suggest 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 likely anoxic during the formation of Kuroko deposits. Furthermore, while samples from some deposits (e.g., Matsumine, Kosaka) tend to show more negative $\delta^{56}\text{Fe}$ values, those from other deposits (e.g., Fukazawa, Palmer) tends to show more positive $\delta^{56}\text{Fe}$ values. The difference may be stemmed from their formation processes. Near equilibrium conditions between hydrothermal fluids and sulfides in the ore bodies by a long-term circulation may have lead to a steady $\delta^{56}\text{Fe}$ value (e.g., -0.5‰) of dissolved iron in the hydrothermal fluids and negative values of ferruginous chert by a Raleigh-type fractionation. On the other hand, rapid precipitation of sulfides ore body under dynamic conditions may have caused a kinetic isotope fractionation, leading to shift $\delta^{56}\text{Fe}$ value of both hydrothermal fluids and ferruginous cherts to more positive values.

Keywords: Fe isotope, VMS deposit, Chemical Sedimentary rock, Seafloor hydrothermal activity