Copper Isotope Systematics of Chalcopyrites in Ancient and Modern Seafloor Hydrothermal Deposits, Measured by a Femtosecond LA-MC-ICP-MS

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Copper isotope geochemistry has seen an increased interest as a potential tool for discerning copper sources and geochemical processes for dissolution, transport, and precipitation of copper in ore-forming environment. We measured copper isotope ratios of chalcopyrites from Besshi-type (Besshi Ikadatsu and Mio mines) and Kuroko-type (Hanaoka and Kosaka mines) ancient volcanogenic massive sulfide deposits, Japan and modern sea-floor hydrothermal mineralization (Southern Mariana Trough) by using a femtosecond-pulsed laser ablation multiple collector inductively coupled plasma mass spectrometry (fs-LA-MC-ICPMS).

The $\delta^{65}Cu$ (where $\delta^{65}Cu = [(^{65}Cu/^{63}Cu)_{sample}/ (^{65}Cu/^{63}Cu)_{NIST\text{-}SRM976}\text{-}1] \times 1000$) variations of chalcopyrites in Besshi-type ($\delta^{65}Cu$ = -0.3 to 0.3‰; Ikehata et al., 2011) and Kuroko-type (Kuroko, black ore part: $\delta^{65}Cu$ = -0.2 to -0.1‰; Oko, yellow ore part: $\delta^{65}Cu$ = 0.1 to 0.4‰) sulfide deposits are significantly small compared to those of chalcopyrites in chimney samples from the active sea-floor hydrothermal site ($\delta^{65}Cu$ = -0.7 to 4.0‰. Temperature-dependent isotope fractionation during ore formation may be important to explain the isotope characteristics of the chalcopyrites in the Kuroko ore part and Oko ore part. The large range of copper isotope compositions of the chimney samples are probably due to redox-dependent isotope fractionation during alteration and weathering processes of primary hydrothermal copper sulfides by seawater and hydrothermal fluids, involving the preferential incorporation of heavy copper isotope in secondary Cu(II) solutions. Our results also indicate that, though sub-seafloor recrystallization, diagenesis, and metamorphic reequilibration may have reduced the original copper isotope variations in the ore minerals, their original copper isotope signatures are generally preserved.