Redox processes and metal sources recorded by Se isotopes of black smoker sulfides and host rocks

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Black smoker chimneys are products of submarine hydrothermal venting and have a complex internal zoning that is the result of mineral precipitation and maturation at evolving fluid conditions. The composition of the hydrothermal sulfides is thereby controlled by the fluid composition (e.g., temperature, pH, salinity), processes like fluid boiling, and potential input from magmatic fluids. Advances in analytical techniques allow quantitative analysis of stable isotope ratios of heavy elements, such as Se, which can provide new insights into the cycling of chalcophile elements in magmatic-hydrothermal systems [1, 2].

We sampled different zones of black smoker chimneys from the Nifonea vent field from the inner chalcopyrite lining towards the outer rim. Homogeneous sulfide powders were analyzed for high-precision Se isotopes using a double spike and hydride generation sample introduction system with a ThermoFisher Scientific[®] *NeptuneXT*TM MC-ICP-MS at the IACT, Granada. The same powders were analyzed for S isotopes and the isotope data was combined with in-situ trace element analysis of genetically related sulfides.

The $\delta^{82/76}$ Se values (relative to NIST-3149) of chimney sulfides range from -3.7% to $0.6\% \pm 0.2\%$ (2SD), in accordance with previous analysis of seafloor hydrothermal sulfides [3]. The highest $\delta^{82/76}$ Se values occur in chalcopyrite that precipitated from high temperature fluids (370°C) and overlap with $\delta^{82/76}$ Se values of fresh basaltic glass from the surrounding Nifonea caldera. This suggests that metals were leached from the host rocks and that no significant isotope fractionation occurred during high temperature precipitation of chalcopyrite. Decreasing $\delta^{82/76}$ Se values towards the outer and low temperature zones of the black smoker chimney can be related to redox changes during mixing of the hydrothermal fluid with seawater, in accordance with trace element variations in pyrite. Understanding Se isotope fractionation during hydrothermal sulfide precipitation is crucial to subsequently identify the metal sources and the effect of fractionation processes in the upflow zone of submarine hydrothermal systems using Se isotopes.

[1] Yierpan et al. (2018) Geochemistry, Geophysics, Geosystems 19, 516–533.

[2] König et al. (2019) *Geochimica et Cosmochimica Acta* 244, 24–39.

[3] Rouxel et al. (2004) *Geochimica et Cosmochimica Acta* 68 (10), 2295–2311.