

Redox processes and metal sources recorded by Se and S 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 the potential input of magmatic fluids. Advances in analytical techniques allow the 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 (König et al. 2019; Rosca et al. 2022).

We sampled different zones of black smoker chimneys from the Nifonea vent field (New Hebrides Arc, W Pacific) 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 attached to a ThermoFisher Scientific® *NeptuneXT*TM MC-ICP-MS at the IACT, Granada. Fractions of the same powders were also analyzed for S isotopes and the resulting data was combined with in-situ trace element data of genetically related sulfides.

The $\delta^{82/76}\text{Se}$ values (relative to NIST-3149) of chimney sulfides range from -3.7 ‰ to 0.6 ‰ \pm 0.2 ‰ (2SD) (Fig. 1), in accordance with previously reported values of seafloor hydrothermal sulfides (Rouxel et al. 2004). The $\delta^{34}\text{S}$ values (relative to VCDT) range between 2.1 ‰ and 4.0 ‰ reflecting typical mixing of H_2S derived from the host rocks and from thermochemical seawater sulfate reduction lacking any evidence for magmatic fluid input. The highest $\delta^{82/76}\text{Se}$ values occur in chalcopyrite that precipitated from high temperature fluids (370 °C) and overlap with $\delta^{82/76}\text{Se}$ values of fresh basaltic glass from the surrounding Nifonea caldera (Fig. 1). This suggests that metals were leached from the host rocks and that no significant isotope fractionation occurred during high temperature precipitation of chalcopyrite.

Decreasing Se/Tl and Co/Tl ratios of pyrite from the inner to the outer chimney wall record a temperature decrease. A coupled decrease of $\delta^{82/76}\text{Se}$ and $\delta^{34}\text{S}$ values towards the outer and low temperature zones (Fig. 1) can be related to local temperature-dependent isotope fractionation during redox reactions induced by mixing of the hydrothermal fluid with seawater. 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.

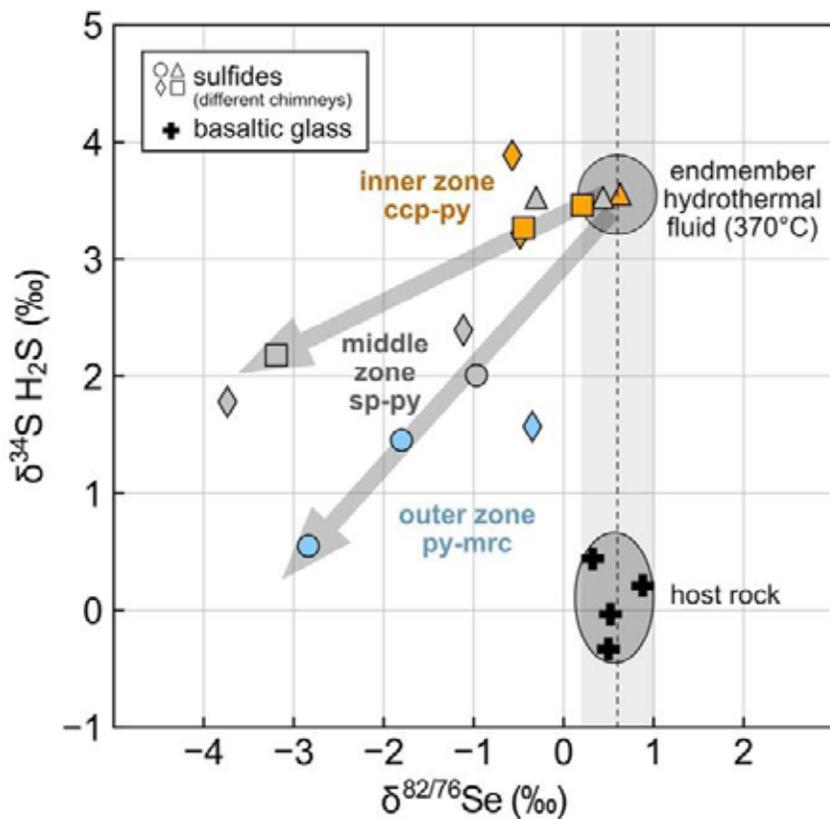


Figure 1. $\delta^{82/76}\text{Se}$ (relative to NIST-3149) versus $\delta^{34}\text{S}$ (relative to VCTD) values of black smoker sulfides and volcanic glass from Nifonea. The colors indicate whether the sulfide powder was derived from the inner, middle, or outer chimney zone. The symbols mark different vent sites. The $\delta^{34}\text{S}$ values of H_2S were calculated from the $\delta^{34}\text{S}$ value of the sulfide powder using the equilibrium isotopic fractionation factors by Ohmoto & Rye (1979) for the dominant sulfide phase at estimated fluid temperatures of 370°C (inner zone), 270 °C (middle zone), and 200 °C (outer zone). ccp = chalcopyrite, py = pyrite, sp = sphalerite, mrc = marcasite.

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