

Redox-record from sulfur-selenium isotope decoupling at the sulfide scale

S. KÖNIG^{1,*}, B. EICKMANN¹, T. ZACK², A. YIERPAN¹, H. TAUBALD¹, R. SCHOENBERG¹

¹Isotope Geochemistry, Department of Geosciences, University of Tübingen, Germany (*correspondence: stephan.koenig@uni-tuebingen.de)

²Department of Earth Sciences, University of Gothenburg, Sweden

A combination and eventual cross-calibration of established and novel geochemical proxies may lead to more refined constraints on terrestrial redox variations crucial for the emergence and evolution of life on Earth. Within this scope we present the first combined high-precision S-Se isotope analyses applicable to single sulfide minerals for studying Earth's redox evolution at the mineral and microscale. We focus in a case study on a hydrothermal pyrite from the mesozoic Cameros Basin, Spain, for which age, growth conditions and geological context are well constrained [1]. Previously detected S isotope variations among pyrites from the basin are attributed to mixing of H₂S-bearing fluids from two sources that were subject to different magnitudes of abiotic redox variations, respectively [1]. Moreover, microscale systematics indicates one single pyrite specimen alone is representative regarding the redox record of all pyrite formations of the basin [1; 2]. Selenium isotopes obtained via double spike MC-ICP-MS [3; 4] with a precision of 0.09 ‰ (2SD) reveal a range of $\delta^{82/76}\text{Se}_{\text{NIST3149}}$ from -4.48 to -0.39 ‰ in separated and individually analyzed splits of the same pyrite crystal. S isotopes of these samples, analyzed by gas-IRMS with an accuracy of 0.3 ‰ (2SD), reveal $\delta^{34}\text{S}$ values from -7.1 to -4.4 ‰. Together with additional LA-ICP-MS data, these signatures are shown to be unrelated to sorption or incorporation during hydrothermal pyrite formation but indeed mirror the S-Se isotope signatures of the sources that contributed these elements. Moreover, our data reveal S-Se isotope decoupling that results in near-complementary trends: Variable S isotope values within the analyzed pyrite coincide with rather constant Se isotope values and vice versa. Our observations are in agreement with a larger range in redox potential of several redox species of Se relative to S and, within the context of Navajun pyrite genesis [1], allow more robust constraints on the range of redox variations in the source. Hence combined S-Se isotopes of pyrite may be a new powerful proxy to constrain the range of redox variations throughout Earth's history beyond the bulk rock scale.

[1] Alonso-Azcárate, J. et al. (1999). *J. Metam. Geol.* **17**, 339-348. [2] Alonso-Azcárate, J. et al. (2001). *Chem. Geol.* **174**, 389-402. [3] Kurzawa, T. et al. (2017) *Chem. Geol.* **466**, 219-228. [4] Yierpan et al. (2018) *G-cubed* **19**, 516-533