

Multiple sulfur isotope composition analysis in sphalerite by SIMS : importance of instrumental mass fractionation effects

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Sulfur isotope composition is an established proxy for tracing the origin of fluid associated with sulfide mineralization in ore deposits, for understanding the redox state of the early Earth's atmosphere, and for tracking microbial activities in various environments and within the geological record. Most of our current understanding on sulfur biogeochemical cycle is based on bulk chemistry of sulfide minerals and in situ measurements in pyrite. So far, other sulfide minerals like sphalerite (ZnS) have been rarely studied by secondary ion mass spectroscopy (SIMS) with the exception of the pioneer study of [1]. This study has highlighted the difficulty to get accurate sulfur isotopes measurements by SIMS in sphalerite, probably associated to crystal orientation effect. Here we investigated five different sphalerite populations covering a wide range of chemical compositions with Fe(wt%) 0.01-7.70. The SIMS measurement settings were tuned to resolve all interferences with the neighbouring peaks, such as sulfhydryl and doubly charged zinc isotopic species. Results show no compositional matrix effect affecting the IMF and no clear orientation effect. Within a potential standard, grain population can be highly heterogeneous in ³³S and ³⁴S signatures (based on 7-8 grains) with standard deviation >1 ‰ (2σ), whereas the external error of measurements (³³S and ³⁴S) performed on a single grain is homogeneous, i.e. <0.3 ‰ (2σ). The origin of this isotopic spread was investigated: (1) The precision of the measurements is not improved with different SIMS transmission setups; (2) The use of a projected beam improves the precision of the measurements, which creates a flatter and shallower pit compared to typically used gaussian beam (e.g. [1]), but might not be better than 0.6-1.5‰ (2sd); (3) The effect of sample rotation is minor; (4) Inversed pole figures obtained by EBSD measurements coupled with ^{XX}S_{Raw} data does not reveal obvious crystal orientation effect. Further tests on new potential reference material will be

conducted to better constrain the IMF and improve the analytical precision.

REFERENCES

[1] Kozdon, R., Kita, N. T., Huberty, J. M., Fournelle, J. H., Johnson, C. A., John W. Valley, J. V. (2010), Chemical Geology 275, 243-253.