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Instrumental mass fractionation correction of SIMS sulfur isotope measurement in synthetic/non-stoichiometric iron sulfides

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Sulfur isotopic ratios in terrestrial materials provide information about the volatile recycling and redox evolution in the silicate Earth. Secondary ionization mass spectrometry (SIMS) is an in situ analytical method of S isotopes advantageous to small sulfide grain measurements. SIMS analysis requires reference materials to calibrate instrumental mass fractionation (IMF), and stoichiometric natural sulfides are commonly used for this. However, even Fe-S pyrrhotite can be diverse in its composition and crystallographic structure depending on their formation conditions. For example, magmatic quenched pyrrhotites are typically non-stoichiometric and hexagonal, unlike stoichiometric and monoclinic pyrrhotites commonly observed in highly crystalline sulfide deposits. Can one pyrrhotite standard be used as a calibration for all Fe-S sulfides? Here, we report the variation of IMF among synthesized non-stoichiometric sulfides, which were fully characterized for their crystallographic structure, major composition, and bulk sulfur isotopic ratios. Nine pyrrhotitic iron sulfides (monoclinic or hexagonal, Fe/S ranging from 0.82 to 0.95) were synthesized at three temperatures, 125, 950, and 1210 °C, with the sealed silica tube method. The isotopic ratios were determined in two ways, by the fluorination method at IPGP, Paris providing the "true" bulk values and by SIMS analysis at CRPG, Nancy for microsanalysis. The reproducibility of SIMS measurements was ±0.15 ‰ (2 s.e.). The IMF of the synthetic sulfides varied within 2 ‰, and negatively correlated to Fe/S. The decreasing Fe/S of sulfide from unity leads to the increasing involvement of Fe^{3+}–S bond in the sulfide due to the charge compensation. Because the bonding of this pair is stronger than that of Fe^{2+}–S, we interpret that the IMF is a function of the average bond energy in the sulfides. Our results suggest that the compositional mismatch of sulfide can possibly lead to a bias of approximately 1 ‰. It should be noted that, given the variation of many reported S isotope ratios exceed this 1 ‰ bias, our results do not challenge the validity of previous SIMS studies. Rather, we stress that it is critical to account for the compositional diversity of sulfide in achieving sub-‰ level precision, for example in calibrating isotopic fractionation factors.