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Iron isotope fractionation in sulfides: constraints on mechanisms of sulfide formations in hydrothermal and magmatic systems.

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Data on non-traditional stable isotope fractionations (e.g., Fe, Cu) provide further insight into mechanisms of sulfide mineralization. Correct interpretation of these data is impossible without knowledge on equilibrium isotopic fractionation factors of sulfides. We present data on iron isotope fractionation factors (β-factors) of chalcopyrite ($CuFeS_2$) and mackinawite (FeS). Iron β-factors for chalcopyrite were derived from synchrotron experimental data on inelastic nuclear resonant x-ray scattering (INRXS) [1] using the method described elsewhere [2,3]. The β-factors for mackinawite were found from the Moessbauer second-order Doppler shift data [4] by the method presented in [5]. The temperature dependence of the iron β-factors are fitted by following third-order polynomials:

$$10^3 \ln\beta_{cpy} = 0.82560x - 0.01298x^2 + 0.0005246x^3$$

$$10^3 \ln\beta_{mcw} = 0.2542x - 0.0001847x^2 + 2.072\cdot 10^3 x^3$$

where $x=10^6/T^2$

Using these data along with β-factors for pyrite and troilite [3,6], we compared iron isotope fractionation between pyrite and chalcopyrite in hydrothermal and magmatic conditions. Rouxel et al. [7] studied iron isotope of seafloor of hydrothermal vents in detail. They found that pyrite is enriched in light iron isotope relative to chalcopyrite in the case of black smoker Bio 9. This result evidences absence of iron isotope equilibrium between pyrite and chalcopyrite, because in equilibrium pyrite is enriched in heavy iron isotope ($\beta_{py} > \beta_{cpy}$). Quantitatively, iron isotope fractionation between chalcolpyrite and pyrite is very close to equilibrium iron isotope fractionation between chalcolpyrite and FeS phase (mackinawite or troilite). This agrees the mechanism of pyrite formation through intermidient FeS phase if to assume isotopic equilibrium between the FeS phase and dissolved iron and no isotopic effect in the final stage of conversion FeS to FeS_2 (pyrite).

Another iron isotope fractionation was observed between pyrite and chalcopyrite in the case of the Cu-Au porphyry deposit of Crasberg igneous complex (GIC) [8]. In this case, pyrite is enriched in heavy iron isotope relative to chalcopyrite that is in agreement with direction of iron isotope fractionation in equilibrium. Using these data [8] and appropriate iron β-factors obtained from INRXS- and Moessbauer experiments, we estimated temperatures of pyrite and chalcopyrite formation. We obtained reasonable temperatures varying between 180 and 650^{o}C for different intrusions of GIC, which are in agreement with other estimations [9,10]

Conclusions:

1. Iron β-factors for chalcopyrite $CuFeS_2$ were calculated from ^{57}Fe PDOS obtained in INRXS synchrotron radiation experiments [1].
2. Iron β-factors for mackinawite were calculated from the Moessbauer SOD shift based on experiments [4].
3. Using new value of chalcopyrite and mackinawite and/or troilite iron β-factors, it was shown that isotope composition of pyrite in hydrothermal seafloor processes is controlled by equilibrium isotope fractionation between FeS phase (pyrite precursor) and hydrothermal fluid.
4. Fe isotope equilibrium between pyrite and chalcopyrite may be attained in magmatic processes.

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