Zn and S isotope exchange between sphalerite and hydrothermal fluid

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We carried out a series of experiments to calibrate the zinc (^{66}Zn/^{64}Zn) and multiple sulfur (^{34}S/^{33}S/^{32}S) equilibrium isotope fractionations at elevated temperatures applicable to mid-ocean ridge (MOR) hydrothermal environments, to better understand the dissolved Zn and S mobility and isotopic fractionation processes in the subseafloor.

A long term sphalerite (ZnS)-fluid Zn and S isotope exchange experiment was performed at hydrothermal conditions, 300°C and 500 bar, using gold-cell reactor technology. The exchange experiment implemented an enriched ^{34}S tracer, as H_2S/SO_4, to gauge the extent of exchange between sphalerite and dissolved Zn- and S-species.

Time-series changes in the δ^{34}S and Δ^{33}S composition of sphalerite and dissolved H_2S demonstrated achievement of complete exchange between the mineral and fluid reservoirs within the course of 2716 hours. The experimentally determined equilibrium Zn and S isotope fractionations between sphalerite and dissolved Zn and H_2S at 300° C are small, albeit significant, resulting in -0.08 ± 0.06 and -1.35 ± 0.06 ‰ (2σ), for δ^{66}Zn and δ^{34}S, respectively. Sphalerite is depleted in ^{66}Zn and ^{34}S at equilibrium. These experimentally calibrated equilibrium fractionations are close to theoretical predictions [1, 2, 3] and are similar to a previous experimental S isotope study demonstrating equilibrium [4].

Coupling of the experimental isotope equilibrium Zn and S relations with concentration and isotopic data of hydrothermal fluids and sphalerite mineral separates sampled from MOR hydrothermal environments indicate 1) that the magnitude of Zn isotope fractionation is minor for vent fluids ≥ 300°C and 2) sphalerite is close to S and Zn isotope equilibrium with high temperature hydrothermal fluids. This is in accord with the fast experimentally determined exchange rate, approximately 0.02 hr^{-1} [4]. **Ref:** [1]Black et al., 2011; [2]Ducher et al., 2016; [3]Fujii et al., 2011; [4]Sugaki et al., 1989.