$^{65}Cu/^{63}Cu$ fractionation during copper sulphide formation from iron sulphides in aqueous solution

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An important geological mechanism for the formation of copper sulphides (chalcopyrite, covellite, chalcocite) is by the reaction of Cu(II) solutions with Fe sulphides. We report here the first results of an experimental study of the copper isotope ($^{65}Cu/^{63}Cu$) fractionation during copper sulphide formation by the reaction of Cu(II) solution with pyrite and pyrrhotite. The experiments were made by reacting pyrite and pyrrhotite crystals with $CuSO_4$ solution under anoxic conditions at 40ºC for 6 weeks and 100ºC for 2 weeks. After separation of the solid phases by filtration, the residual bulk copper in solution was precipitated by the addition of excess sulphide. Isotopic analyses of both copper fractions were made using MC-ICP-MS using sample standard bracketing. Prior to this, 1 ppm Cu solutions were prepared by dissolving the solid phases in HNO_3 and separating the copper from other solution ions using a chromatigraphic protocol [1].

Pyrrhotite reacts readily at both temperatures, sequentially forming: chalcopyrite, covellite and chalcocite, with covellite being the dominant phase. Pyrite reacts less readily, but sufficient amounts of copper sulphides formed in all experiments for Cu(II)-Cu sulphide isotopic fractionations to be measured. $\Delta^{65}Cu$(Cu(II)–Cu sulphide) values determined in the various experiments are: pyrrhotite starting material, 40ºC 3.02 ± 0.14‰, 100ºC 2.67 ± 0.15‰; pyrite starting material, 40ºC 2.66 ± 0.11‰, 100ºC 2.69 ± 0.16‰. The large fractionations are similar to those determined for the precipitation of covellite from Cu(II) solutions [2], and are consistent with Cu(II) reduction to Cu(I) producing a significant depletion in the heavy isotope. The results are compatible with studies showing that copper is Cu(I) in chalcopyrite and covellite, and that the mechanism of chalcopyrite formation from Fe sulphides involves reduction of Cu(II) to Cu(I)[3].

References

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