



Experimental study of copper isotope fractionation during the formation of Cu and Cu-Fe sulfides in aqueous solutions at 40-200 °C.

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Natural Cu and Cu-Fe sulfides show significant Cu fractionation. In order to interpret these data an improved understanding of the major Cu isotope fractionation processes is required. Here we report laboratory experiments aimed at elucidating processes involved in Cu isotope distribution in Cu sulfides.

Progressive replacement of Fe sulfides by Cu-Fe and Cu sulfides has been widely reported from a range of magmatic, hydrothermal and sedimentary deposits, and may sometimes lead to economically relevant Cu accumulations such as in the Kupferschiefer of SW Poland [1]. This replacement sequence is commonly observed in deep sea floor hydrothermal vents where massive Cu-Fe sulfide mineralisation is found [2,3]. Experimental investigations [4,5,6] have demonstrated that this type of mineral replacement is developed during the reaction of Fe sulfides (pyrrhotite and pyrite) with Cu(II)-rich aqueous solutions.

Fractionation of Cu isotopes during the reaction of Fe sulfides (natural crystals of pyrrhotite and pyrite) with Cu(II) sulfate solutions was studied under anoxic conditions. It was observed that the original Fe sulfides were replaced by Cu-Fe and Cu sulfides. The effect of temperature (40-200 °C) and reaction extent (10-100 %) were investigated. Cu isotope ratios were determined in the Cu(II) solutions and in the corresponding mineral phases by sector field multicollector inductively coupled plasma mass spectrometry.

Measured Cu(II) solution–Cu sulfide fractionation factors (in excess of 2 permil) show substantial Cu isotope fractionation accompanying the reaction of Fe sulfides with Cu(II) solutions. The data points to a kinetic fractionation process that favours the transfer of the lighter Cu isotope into the mineral phase. The extent of Cu isotope fractionation resulting from this alteration process is of a similar order to fractionation observed during direct CuS precipitation from Cu(II)aq and S(-II)aq [7]. This suggests that Cu(II)-Cu(I) reduction, that proceeds the formation of Cu-Fe and Cu sulfides, is the most important fractionation process in the studied system. The marked fractionation factors measured in the 200 °C samples are surprising and demonstrate that significant Cu isotope fractionation can occur even at relatively high temperatures. Fractionation factors are related inversely to temperature below 100 °C. The replacement reaction is unidirectional, and this temperature dependence is believed to reflect the kinetics of Cu(II)-Cu(I) reduction, as previously proposed by Ehrlich et al. [7].

[1] Huyck H. L. O. and Chourey R. W. (1991) *Mineral. Deposita* 26, 132-142. [2] Butler I. B. et al. (1998) *J. Geol. Soc. London*, 155, 773-785. [3] Duckworth R. C. et al. (1995) (Edits.: Pearson L. M. et al.) *Geol. Soc. Spec. Pub.* 87, 175-189. [4] Schouten C. (1934) *Econ. Geol.* 7, 611-658. [5] Cowper M. and Rickard D. (1989) *Chem. Geol.* 78, 325-341. [6] Rickard D. and Cowper M. (1994) *Geochim. Cosmochim. Acta* 58, 3795-3802. [7] Ehrlich S. et al. (2004) *Chem. Geol.* 209, 259-269.