Experimental study of Cu isotope fractionation during the reaction of aqueous Cu(II) with Fe(II) sulphides at temperatures between 40 and 200 °C

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ABSTRACT

We present results of an experimental study on Cu isotope fractionation during the reaction of aqueous Cu(II) with Fe(II) sulphides: pyrrhotite and pyrite. The reaction was investigated under a range of experimental conditions, including time, temperature, initial Cu concentration in the solution, presence of a complexing ligand (acetate), and mineral to solution ratio.

The reaction develops a series of mixed Cu–Fe and Cu sulphides. Cu isotope composition of reacted solutions and minerals determined by MCICP-MS attests to significant isotope fractionation that accompanies this reaction. The measured $\Delta^{65}Cu_{solution-minerals}$ values range from 1.97 to 3.23‰ $\delta^{65}Cu$, with an average of 2.64‰ $\delta^{65}Cu$. Observed shifts in Cu isotopic composition with reaction progress are explained by preferential transfer of the lighter Cu isotope, ^{63}Cu, from solution into the mineral. It is proposed that Cu(II) to Cu(I) reduction step is the key control of the magnitude of observed isotope fractionation, while other factors, such as presence of complexing ligands, play minor role. This kinetic fractionation process is, however, affected by some degree of isotopic exchange and equilibration between Cu in the neoformed minerals and in the solution, at least in samples representing higher reaction extent. The results from 150 and 200 °C runs suggest that significant isotope fractionation occurs even at these elevated temperatures ($\Delta^{65}Cu_{solution-minerals}$ above 2‰ $\delta^{65}Cu$).

The results of this study suggest that that the reaction of aqueous Cu(II) with Fe(II) sulphides may be an important process in generating depleted $\delta^{65}Cu$ signatures found in Cu-rich sulphides formed at low temperatures, such as seafloor hydrothermal vents or sediment-hosted stratified copper deposits.

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1. Introduction

Stable Cu isotopes are known to undergo significant fractionation in nature spanning at least 10‰ as $\delta^{65}Cu$ (Walker et al., 1958; Shields et al., 1965; Gale et al., 1999; Zhu et al., 2000). The advent of multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) over the last decade has reduced analytical uncertainties on $\delta^{65}Cu$ to below 0.1‰ (2σ). As a consequence of this increased precision, Cu isotope systematics may provide new insights into the complex processes associated with metal cycling in the crust and the formation of metalliferous ore deposits. However, fractionation mechanisms responsible for the observed spread in natural Cu isotope compositions are still poorly understood, and need to be identified and quantified.

Primary Cu-rich sulphide minerals formed at high temperatures in igneous, skarn and high-temperature hydrothermal deposits, for example, are characterised by a relatively restricted range of Cu isotope compositions clustering about $\delta^{65}Cu = 0‰$ ($\pm 1‰$ — calculated with respect to the NIST SRM-976 standard), which is believed to represent the bulk Earth composition (Zhu et al., 2000; Larson et al., 2003; Mason et al., 2005; Markl et al., 2006; Mathur et al., 2009; Weiqiang et al., 2009). In contrast, lower temperature, secondary Cu-rich sulphides from hydrothermal vent deposits and stratified sediment-hosted deposits are typically depleted in ^{63}Cu with $\delta^{65}Cu$ values as low as $-3.4‰$ (Rouxel et al., 2004; Markl et al., 2006; Asael et al., 2007).

A commonly observed mineralogical feature in low-temperature Cu–Fe and Cu sulphides is the progressive replacement by mineral phases increasingly rich in Cu. This type of mineral replacement is well documented in both hydrothermal (Duckworth et al., 1995; Knott et al., 1995; Butler et al., 1998) and stratified sediment-hosted (Huyck and Chorey, 1991; Sawlowicz, 1992; Bechtel et al., 2001; McGowan et al., 2006) Cu deposits. Because of their economic importance, the formation of Cu-rich sulphides at low temperatures has been a subject of experimental studies over the last century (Young and Moore, 1916; Zies et al., 1916; Schouten, 1934; Roberts, 1961, 1963; Rickard, 1970, 1972, 1973; Walker and Rimstidt, 1986;

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Cowper and Rickard, 1989; Rickard and Cowper, 1994; Luther et al., 2002). The results of recent experiments (Cowper and Rickard, 1989; Rickard and Cowper, 1994) suggest that the reaction of Cu(II) solutions with Fe(II) sulphides (pyrrhotite, mackinawite and pyrite) at low and moderate temperatures is an important pathway for the formation of mixed Cu–Fe and Cu sulphides. By reacting aqueous Cu (II) (at pH between 2 and 4.5) with Fe(II) monosulphides (pyrrhotite and mackinawite) (Cowper and Rickard, 1989) produced a succession of mixed Fe–Cu and Cu mineral phases (cubanite, chalcopyrite, bornite, covellite and digenite) characterised by increasing Cu content. In fact, these workers failed to synthesise chalcopyrite by any other previously reported reaction, such as direct precipitation form solution (Roberts, 1963), solid-state diffusion (Roberts, 1961), or the reaction of solid CuS with iron solutions (Walker and Rimstidt, 1986).

Because of the potential importance of the reaction of Cu(II) solutions with Fe(II) sulphides in the formation of Cu–Fe and Cu sulphides at low temperatures, and their occurrence in Cu rich deposits with depleted $\delta^{65}Cu$ signatures, we investigated the Cu isotope fractionation associated with this reaction in laboratory under controlled experimental conditions.

2. Experimental methods

Natural crystals of pyrrhotite (from Brazil) and pyrite (from Spain) were used in the experiments. Crystals were crushed, ground, and sieved into two fractions: 1 mm-250 μm and above 1 mm. The pyrite contained small inclusions of hornblende (considered unreactive) and carbonate, which was removed by washing in 10% HCl. The pyrrhotite was separated from impurities magnetically.

All chemical reagents used were analytical reagent grade. The water used was deoxygenated Milli-Q™ ($\sim$18 M$\Omega\cdot$cm). Deoxygenation of water was achieved by vigorously sparging it with oxygen-free grade N_2 for at least 45 min in order to replace dissolved O_2. Cu(II) sulphate pentahydrate was used for the preparation of 3175 ppm (0.050 M) and 500 ppm (0.008 M) Cu solutions. The solutions were prepared in a N_2-filled anoxic glove box with either water or 0.20 M Na-acetate buffer at pH = 4.00. Prior to the start of the experiment the material was immersed in a 1:1 acetone-petroleum ether mixture to remove grease from the mineral surfaces. This was followed by a brief wash with deoxygenated, concentrated HCl in order to dissolve iron oxides. The acid wash was conducted in the glove box so as to minimise the potential for re-oxidation of the mineral surfaces.

The experimental set-up differed between lower-temperature runs (40, 80 and 100 °C) and higher-temperature runs (150 and 200 °C). For the lower-temperature experiments, 250 or 500 mg of the mineral material was weighed into glass ampoules (see (Rickard, 1997) for original reference), and 10 or 20 ml of Cu solution was added with an automatic pipettor. The glass ampoules were closed using Swagelok® valves and attached to a gas-manipulation manifold (see (Rickard, 1997)). The ampoule atmosphere was further purged with oxygen-free grade N_2 and sealed using a blow-torch. Sealed ampoules were left in an oven for the duration of the experiment at a constant ($\pm$2 °C) temperature, their contents being occasionally (typically once a day) agitated. In case of the higher-temperature runs, the material was weighed into an O-ring-sealed teflon vessel. The vessel was placed inside a steel pressure-vessel and filled with appropriate amount of water so as to assure pressure equalisation between the insides of the teflon vessel and the steel vessel. The temperature of the steel vessel was raised to target temperature within a period of up to 2 h and controlled ($\pm$1 °C) throughout the experiment using an assembly of thermocouples, heating tape and a digital (PID) controller. Throughout the experiment the content of the vessel was allowed to mix on a shaking table. At the end of the run, the steel bomb was quenched to room temperature with cold water within 10–15 min.

The reacted crystals were separated from the solution by vacuum filtration using 0.45 μm cellulose nitrate Whatmanperscript® filters. The collected mineral material was washed with water, dried and collected for Cu isotope analysis. The filtrate was quantitatively transferred into a 100 ml volumetric flask, acidified to pH$\approx$2 with HNO_3, and made up to volume. 10 ml of the solution was sub-sampled for the determination of Cu and Fe. Slight molar excess of sulphide (as Na_2S solution) was added to the remainder to quantitatively precipitate the metals. The solution was filtered through the 0.45 μm membrane. Full recovery of Cu and Fe was assured by the addition of a few extra drops of sulphide solution while the experimental solution remained colourless. The membrane with Cu-Fe sulphide was freeze-dried and the precipitate was collected for Cu isotope analysis. The collection of aqueous Cu as solid mackinawite was chosen for easier and safer transport between the UK and Israel, where the Cu isotope measurements were conducted.

Procedural blanks for the experimental procedure were conducted with 500 ppm and 3000 ppm Cu solutions giving complete recovery of Cu within instrumental errors (3% relative error — see section 3).

In the experiments the type of reacted mineral (pyrrhotite and pyrite), mineral mass (250 and 500 mg), reaction temperature (40, 80 and 100 °C), Cu concentration in the initial solution (500 and 3175 ppm), volume of the initial Cu solution (10 and 20 ml), and the duration of the experiment (7, 10, 14, 21, and 42 days) were varied. In addition, selected solutions were buffered to pH = 4.50 with 0.20 M Na-acetate. All samples were run as duplicates under the same experimental conditions. Table 1 gives a summary of the experimental run conditions for all experiments.

3. Analytical techniques

Final Cu and Fe concentrations were measured in experimental solutions. Cu was determined spectrophotometrically using a modified procedure adopted from (Zaki and Alqasmi, 1981), by Atomic Absorption Spectrometry using a Varian SpectraAA-300, and by EDTA titration (0.01 M) at pH=5.5 (1 M Na-acetate buffer) using glycine cresol red as an indicator (magenta to green endpoint). Fe was measured by Atomic Absorption Spectrometry. The relative precision of Cu and Fe concentrations in the analysed solutions is $\pm$3%.

The reacted mineral grains were mounted in an epoxy resin and polished to provide smooth cross-sectional surfaces. These were studied by reflected light optical microscopy to determine the produced mineral phases. Reaction zones on a μm-scale were investigated by scanning electron microscopy with a Philips XL30CP energy dispersion system.

Experimental Cu(II) solutions precipitated as covellite, and their corresponding minerals were dissolved in 10 ml of 0.1 M HNO_3. Prior to mass spectrometric measurement, samples were column purified using the procedure of (Maréchal et al., 1999). The solutions were analysed for Cu and Fe contents by ICP-AES. Cu isotopic composition was determined using a Nu Plasma™ MC-ICP-MS at the Geological Survey of Israel in Jerusalem, Israel. Depending on the current sensitivity of the instrument, samples were introduced as 0.2–1 ppm Cu solutions in 0.1 M HNO_3 using an Aridus sample introduction system with aerosol desolvation. The instrumental drift and mass discrimination were monitored and corrected for relative to the external SRM NIST 976 Cu standard with standard-sample-standard bracketing technique, and by using Ni internal standard. Each measurement consisted of one block of 25 analyses, where precision was routinely tested by running the SRM NIST 976 Cu standard. Details of the mass spectrometric measurement and solution matrix corrections are given in (Asael et al., 2007). It should be noted, that occasional isotopic shifts were encountered during the analytical work; these shifts are discussed in the Results section.