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Cu isotope fractionation during bornite dissolution: An in situ X-ray diffraction analysis

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ABSTRACT

Low-temperature ore deposits exhibit a large variation in $\delta^{65}Cu$ (~12‰), and this range has been attributed, in part, to isotope fractionation during weathering reactions of primary minerals such as chalcocite and chalcopyrite. Here, we examine the fractionation of Cu isotopes during dissolution of another important Cu ore mineral, bornite, using a novel approach that combines time-resolved X-ray diffraction (XRD) and isotope analysis of reaction products. During the initial stages of bornite oxidative dissolution by ferric sulfate (<5 mol% of total Cu leached), dissolved Cu was enriched in isotopically heavy Cu (^{65}Cu) relative to the solid, with an average apparent isotope fractionation ($\Delta_{aq-min} = \delta^{65}Cu_{aq} - \delta^{65}Cu_{min}{}^{0}$) of 2.20 ± 0.25‰. When >20 mol% Cu was leached from the solid, the difference between the Cu isotope composition of the aqueous and mineral phases approached zero, with $\Delta_{aq-min}{}^{0}$ values ranging from -0.21 ± 0.61‰ to 0.92 ± 0.25‰. XRD analysis allowed us to correlate changes in the atomic structure of bornite with the apparent isotope fractionation as the dissolution reaction progressed. These data revealed that the greatest degree of apparent fractionation is accompanied by a steep contraction in the unit-cell volume, which we identified as a transition from stoichiometric to non-stoichiometric bornite. We propose that the initially high Δ_{aq-min} values result from isotopically heavy Cu (^{65}Cu) concentrating within Cu^{2+} during dissolution. The decrease in the apparent isotope fractionation as the reaction progresses occurs from the distillation of isotopically heavy Cu (^{65}Cu) during dissolution or kinetic isotope effects associated with the depletion of Cu from the surfaces of bornite particles.

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1. Introduction

Once it became possible to measure Cu isotope ratios ($^{65}Cu/^{63}Cu$) with high precision and accuracy (Marechal et al., 1999; Zhu et al., 2000), researchers began exploring this intermediate-mass isotope system for its insights into geochemical processes of ore deposit formation and Cu mobilization. For example, Cu isotope fractionation has been shown to reveal the source and mineralization pathways of high-temperature (hypogene) Cu deposits with variations in $\delta^{65}Cu$ of ~2.5‰ (Fig. 1) (Asael et al., 2007; Fernandez and Borrok, 2009; Graham et al., 2004; Ikehata et al., 2008; Kimball et al., 2009; Larson et al., 2003; Li et al., 2007, 2010; Maher and Larson, 2007; Marechal et al., 1999; Markl et al., 2006; Mason et al., 2005; Mathur et al., 2005, 2009a, 2009b, 2010; Rouxel et al., 2004; Zhu et al., 2000). However, an even larger range in Cu isotope values (with variations in $\delta^{65}Cu$ of ~12‰) has been measured in low-temperature Cu deposits where weathering reactions dominate (Fig. 1). These include sedimentary deposits (Asael et al., 2007, 2009; Ikehata et al., 2008; Marechal et al., 1999; Zhu et al., 2000), supergene enrichment zones (Haest et al., 2009; Larson et al., 2003; Marechal et al., 1999; Markl et al., 2006; Mathur and Schlitt, 2010; Mathur et al., 2009a, 2009b, 2010) and acid mine drainage (Balistrieri et al., 2008; Borrok et al., 2008; Kimball et al., 2009). Fig. 1 represents a compilation of ~1000 published Cu isotope values of solids from high-temperature Cu deposits, low-temperature deposits, and modern black smokers and massive sulfides. The $\delta^{65}Cu$ values from high-temperature deposits cluster around 0.29‰ and display a near-normal distribution. These values are consistent with $\delta^{65}Cu$ values of 0.01 ± 0.30‰ measured in granites (Li et al., 2009). Cu isotope values from low-temperature deposits, on the other hand, are more varied and are skewed to more negative values (median = −0.17‰).

The variation of $\delta^{65}Cu$ values measured in nature has been attributed principally to isotope fractionation during the oxidative weathering of primary Cu sulfide minerals (Albarede, 2004). Laboratory experiments have shown that changes in the oxidation

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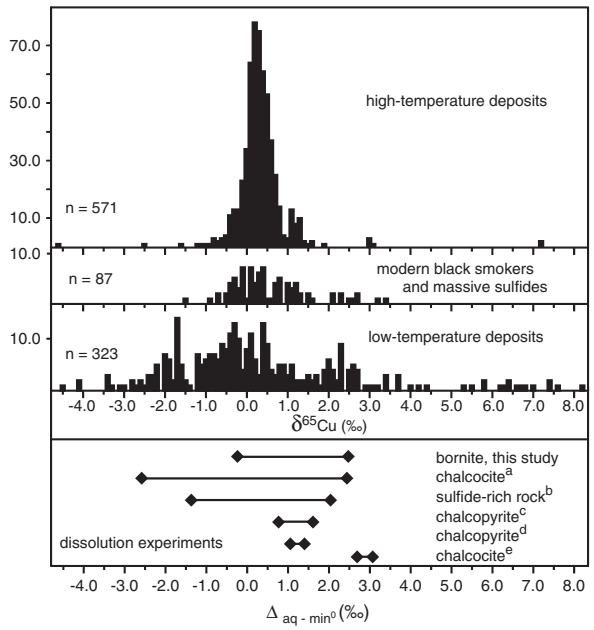

Fig. 1. Cu isotope measurements (δ^{65}Cu ‰, n = 981) of solids from high-temperature Cu deposits (see text for citations), modern black smokers and massive sulfides (Rouxel et al., 2004; Zhu et al., 2000), and low-temperature Cu deposits (see text for citations). High-temperature deposits are defined where mineralization is thought to be >150 °C and low-temperature deposits are <150 °C or where authors note significant supergene alteration. Modern black smokers and massive sulfides are separated because the authors suggest the presence of both high- and low-temperature processes. Laboratory dissolution experiments appear on the lower panel showing the range of apparent fractionation factors $\Delta_{aq-min}{}^{0}$(‰) measured between dissolved Cu and the initial solid mineral in several experiments (a = (Wall et al., 2007); b = (Fernandez and Borrok, 2009); c = (Kimball et al., 2009); d and e = (Mathur et al., 2005)). Note: one sample (<−5‰) does not appear on the high-temperature histogram, and nine samples (<−5‰) do not appear on the low temperature histogram because they fall outside the range of these graphs.

state of Cu can lead to a large isotope fractionation such that the isotopically heavy isotope (^{65}Cu) preferentially concentrates in the Cu^{2+}-rich phase by ~3 to 4‰ relative to the reduced Cu^{1+}-bearing phase (Ehrlich et al., 2004; Zhu et al., 2002). This phenomenon has also been observed in the field; Cu(II)-hydroxide/carbonate minerals are typically enriched in ^{65}Cu relative to co-existing Cu(I)-sulfides (Asael et al., 2007; Markl et al., 2006). In addition, processes other than redox reactions can influence Cu isotope ratios, such as changes in bonding coordination (Marechal and Albarede, 2002; Zhu et al., 2002), Cu sorption to Fe-oxides (Balistrieri et al., 2008; Pokrovsky et al., 2008), microbial interaction (Kimball et al., 2009; Mathur et al., 2005), and complexation with organic ligands (Bigalke et al., 2010). The magnitude of fractionation reported for these processes, however, is much smaller than that associated with the redox reactions.

Consequently, in an attempt to explain the large variations in Cu isotope values observed in mine waters and low-temperature ore deposits, researchers have conducted laboratory oxidative dissolution experiments with Cu sulfide minerals. The lower panel of Fig. 1 shows apparent isotopic fractionation values ($\Delta_{aq-min}{}^{\circ}$) as measured in Cu–mineral dissolution experiments such that:

$$\Delta_{aq-min}{}^{\circ} = \delta^{65}Cu_{aq} - \delta^{65}Cu_{min}{}^{\circ} \quad (1)$$

where $\delta^{65}Cu_{aq}$ represents the Cu dissolved in the aqueous phase and $\delta^{65}Cu_{min}{}^{\circ}$ reflects the Cu in the unreacted mineral. Dissolution experiments involving chalcocite (Mathur et al., 2005; Wall et al., 2007) and chalcopyrite (Fernandez and Borrok, 2009; Kimball et al., 2009; Mathur et al., 2005) show that at the beginning stages of the reaction, leached Cu_{aq} is enriched in ^{65}Cu relative to the solid by ~1 to 3.5‰. Interestingly, as more Cu is leached from the mineral (i.e., as the extent of reaction progresses), δ^{65}Cu values of the solution decrease relative to the starting values. Researchers have proposed several hypotheses to account for the decreasing trend in $\Delta_{aq-min}{}^{\circ}$ values during oxidative dissolution, but no studies have monitored changes in the crystal structure of a Cu mineral in real time and coupled those observations with the evolution in the Cu isotope composition of the fluid simultaneously. Here, we examine the apparent fractionation of Cu isotopes during the dissolution of the Cu sulfide bornite using a novel combination of time-resolved X-ray diffraction and multi-collector ICP mass spectrometry of the fluid and solid fractions over time.

Bornite (Cu_5FeS_4) was selected for this study because it undergoes a structural transformation as it oxidizes, providing a unique opportunity to assess structural controls on $\Delta_{aq-min}{}^{\circ}$ values. Multiple studies have shown that during the oxidative dissolution of bornite by ferric iron, in the initial stages of the reaction Cu is rapidly leached from the bornite with Fe and S remaining in the crystal structure (Dutrizac et al., 1970, 1985; Pesic and Olson, 1983; Ugarte and Burkin, 1975). At temperatures below 40 °C this incongruent dissolution results in the formation of "non-stoichiometric bornite" (Dutrizac et al., 1985):

$$Cu_5FeS_4 + 2xFe^{3+} \rightarrow Cu_{(5-x)}FeS_4 + xCu^{2+} + 2xFe^{2+} \quad (2)$$

Once ~30% of the Cu is leached from the mineral, the reaction kinetics slow significantly and Cu_3FeS_4 persists.

To help explain the variation of Cu isotope values in low-temperature Cu deposits, in this study we used a custom-designed flow-through reactor cell to monitor changes to the bornite crystal structure and the formation of additional precipitates using X-ray diffraction. By collecting eluate fractions at known time intervals for subsequent isotope analysis, we were able to correlate mineralogical changes with isotope composition directly. The objective of the study was to elucidate the atomic-scale mechanisms responsible for the variation in $\Delta_{aq-min}{}^{\circ}$ values during sulfide weathering. Insights gained from this approach will allow us to better use Cu isotope signatures measured in the field to assess Cu sources in waters, the extent of weathering in ore bodies, and the degree of supergene reworking of primary ores.

2. Methods

2.1. X-ray diffraction flow-through reaction cells

Bornite dissolution experiments were conducted using a custom-designed flow-through reaction cell compatible with synchrotron X-ray diffraction to allow us to monitor reaction progress and crystallographic variations during dissolution (Wall et al., 2011). Ferric sulfate ($Fe_2(SO_4)_3$) solutions in a range of concentrations (2.8 mmol L^{-1}, 6.6 mmol L^{-1}, and 65 mmol L^{-1}) were pumped through the reaction cell at a constant rate (0.01 to 0.34 mL min^{-1}) to dissolve the bornite. Experiments were carried out at approximately 30 °C and at pH 2–2.5. Eluates from the reaction cell were acquired in time-resolved aliquots using an automated fraction collector and saved for multi-collector ICP-MS analysis. We carried out the X-ray diffraction experiments at synchrotron facilities at the National Synchrotron Light Source, Brookhaven National Lab (beamline X-7b) and at the Advanced Photon Source, Argonne National Lab (beamline 13-BM-C). The detection limit for resolving phase abundance using X-ray diffraction depends on the material but it is generally accepted to be 2 to 3 wt.% (Bish and Post, 1993).

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