The Pennsylvania State University
The Graduate School
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ABIOtic CONTROLS ON COPPER ISOTOPE FRACTIONATION
DURING THE DISSOLUTION OF COPPER SULFIDE MINERALS

A Dissertation in
Geosciences
by
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ABSTRACT

Stable isotope measurements have long been used as a geochemical tool in the Earth sciences, and recent advances in analytical techniques have added intermediate mass stable isotopes (e.g. Cu, Zn, Fe, Ni) to this suite of interpretive methods. The Cu isotope system offers particularly high potential to solve geologic problems due to its large natural isotopic variation (~12 ‰). However, the factors that control the fractionation of Cu isotopes, especially during the dissolution of Cu-sulfide minerals, remain incompletely resolved.

In this dissertation, I explore abiotic controls on Cu isotope fractionation during the dissolution of Cu-sulfide minerals by combining in situ time-resolved X-ray diffraction (TR-XRD) coupled with stable isotope analysis. As a foundational part of this study, I modified a pre-existing design for a TR-XRD flow-through cell in order to remove any metal content and to allow for automated sampling of the eluate fluid. The resulting device (described in Chapter 1) allowed us to correlate Cu isotope fractionation with changes in crystal structure during Cu-sulfide dissolution.

TR-XRD analyses of oxidative dissolution of chalcocite (Cu₂S) and bornite (Cu₅FeS₄) enabled the development of rate equations that describe these reactions and the identification of the reaction sequences as Cu leached from the solid phase (Chapter 2). During chalcocite dissolution, XRD analysis revealed mineral transformations involving the following phases: djurleite (Cu₁.₉₄S), roxbyite (Cu₁.₇₅S), yarrowite (Cu₁.₁₃S), and covellite (CuS). Similarly, the dissolution of bornite by ferric sulfate solutions also produced changes to the mineral structure: a contraction of the bornite unit-cell volume as “non-stoichiometric bornite” formed. XRD results demonstrated that the structure of non-stoichiometric bornite is similar to mooihoekite (Cu₂₂₃Fe₂₂₃S₄). These results clarified the reaction sequences that occur when ferric sulfate solutions dissolve chalcocite and bornite.
By combining time-resolved diffraction data of these Cu sulfide dissolution reactions with real-time sampling and isotopic analysis of the eluates, we were able to discern structural controls on Cu isotope fractionation during dissolution. As described in Chapter 3, 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 ($^{65}\text{Cu}$) relative to the solid, with an average apparent isotope fractionation ($\Delta_{\text{aq-min}} = \delta^{65}\text{Cu}_{\text{aq}} - \delta^{65}\text{Cu}_{\text{min}}$, where $\delta^{65}\text{Cu}_{\text{aq}}$ is the isotope composition of the leached Cu and $\delta^{65}\text{Cu}_{\text{min}}$ is the isotope composition of the beginning mineral powder) of 2.20 ± 0.25‰ (Chapter 3). 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 $\Delta_{\text{aq-min}}$ values ranging from -0.21 ± 0.61‰ to 0.92 ± 0.25‰. We propose that the decrease in the apparent isotope fractionation as the reaction progressed resulted from distillation of isotopically heavy Cu ($^{65}\text{Cu}$) during dissolution or isotope effects associated with the formation of a leached layer on the surfaces of bornite particles.

Similarly, during the initial stages of chalcocite oxidative dissolution (Chapter 4), leached fluids were enriched in heavy Cu ($^{65}\text{Cu}$) with $\delta^{65}\text{Cu}$ values of ~3‰. As the dissolution reaction progressed and chalcocite transformed to covellite, the leached Cu became isotopically lighter and $\delta^{65}\text{Cu}$ values of the leachate decreased to as low as -3.01‰. Isotope box models are consistent with two isotope effects that influence the degree of fractionation observed during the reaction: one due to oxidation ($\alpha \sim 1.003$) and another due to changes in bonding during mineral transformations ($\alpha \sim 1.001$). These results may be useful in interpreting the extent of weathering in Cu ore bodies and the potential for Cu release from acid mine drainage environments.
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PREFACE

This dissertation is comprised of four chapters with two appendices. Chapter 1 is an introduction to the novel methods used to carry out combined Cu isotope/XRD experiments. This chapter has been published in the form presented: Wall A.J., Heaney P.J., Mathur R., Post J.E., Hanson J.C., and Eng P.J. (2011) A flow-through reaction cell that couples time-resolved X-ray diffraction with stable isotope analysis. Journal of Applied Crystallography 44, 429-432. A. J. Wall developed the reaction cell with input from P.J. Heaney and J.E. Post. R. Mathur provided the insight, based on previous experiments, that Cu isotope fractionation was associated with chalcocite dissolution. J.C. Hanson and P.J. Eng assisted with the operation of the synchrotron-based XRD beamlines and the development of an automated sampler.

Chapter 2 is a study of chalcocite and bornite dissolution rates. This chapter will be edited and submitted for publication: Wall A.J., Brantley S.L., Post J.E., Heaney P.J., Investigating the dissolution of chalcocite and bornite by ferric sulfate using time-resolved X-ray diffraction. A.J. Wall conducted the synchrotron-based time-resolved XRD dissolution experiments of chalcocite and bornite with the assistance of P.J. Heaney and J.E. Post. S.L. Brantley collaborated with A.J. Wall in the development of kinetic models.

Chapter 3 explores Cu isotope fractionation during the dissolution of bornite. This chapter has been published in the form presented here: Wall A.J., Mathur R., Post J.E., and Heaney P.J. (In Press) Cu isotope fractionation during bornite dissolution: An in situ X-ray diffraction analysis Ore Geology Reviews. A.J. Wall conducted the synchrotron-based time-resolved XRD dissolution experiments of bornite with the assistance of P.J. Heaney and J.E. Post. A.J. Wall analyzed the Cu isotope composition of leached fluids with helpful input from R. Mathur.
Chapter 4 investigates Cu isotope fractionation during the dissolution of chalcocite and presents isotope box models to assist in data interpretation. This chapter will be edited and submitted for publication: Wall A.J., Fantle, M.S., Mathur R., Kimball B.E., Brantley S.L., Post J.E., Heaney P.J., Cu isotope fractionation during chalcocite dissolution: An in situ X-ray diffraction analysis. The manuscript will be submitted to Geochimica et Cosmochimica Acta.

A.J. Wall conducted the synchrotron-based time-resolved XRD dissolution experiments of chalcocite with the assistance of P.J. Heaney and J.E. Post. A.J. Wall analyzed the Cu isotope composition of leached fluids with helpful input from R. Mathur. M.S. Fantle guided the development of the isotope box models. Through discussions, B.E. Kimball and S.L. Brantley provided insight into modeling Cu isotope fractionation from Cu-sulfide minerals, which led to the development of the current isotope models. A.J. Wall compiled digital files of mineral structures that are necessary for DFT/Bader calculations. J.D. Kubicki and M. Aryanpour carried out the DFT/Bader computation.

Finally, two appendices appear in this dissertation. Appendix A is a study of the Cu isotope systematics of the Butte Mining District, MT. Using these data a manuscript will be submitted for publication: Wall A.J., Gammons C.H., Mathur R., Heaney P.J., Cu isotope systematics of the Butte Mining District, MT. Appendix B is a script of Slices of Time: Time Scales of the Environment. This 3D education movie was written by Tim Fischer, Andy Wall, Susan Anderson, and Charles Anderson. The goal of the Slices of Time was to create a science education outreach project that introduced students to geochemical processes across multiple time scales. It can be found at http://www.ceka.psu.edu/slices_of_time/.
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Thank you to my family and, most importantly, to my wife Heidi. All of this would not have been possible without her sacrifice and support. Thank you.
Chapter 1

A flow-through reaction cell that couples time-resolved X-ray diffraction with stable isotope analysis

1.0 Abstract

Here we describe a non-metallic flow-through reaction cell designed for in situ time-resolved X-ray diffraction coupled with stable isotope analysis. The experimental setup allows us to correlate Cu isotope fractionation with changes in crystal structure during Cu-sulfide dissolution. This flow-through cell can be applied to many classes of fluid-mineral reactions that involve dissolution or ion exchange.

1.1 Introduction

Environmental sample cells for time-resolved powder X-ray diffraction (TR-XRD) have been designed to study catalysis reactions (Andersen et al., 1998; Chupas et al., 2001), hydrothermal precipitation (Evans et al., 1995; Hummer et al., 2008; Hummer et al., 2009), cation exchange (Lee et al., 1998; Lee et al., 2000; Lee et al., 2001; Celestian et al., 2004; Celestian & Clearfield, 2007; Lopano et al., 2007; Lopano et al., 2009), and biomineralization (Fischer et al., 2008), among other applications. These real-time X-ray diffraction techniques allow researchers to quantify kinetic parameters for mineral-fluid and mineral-gas reactions (Andersen et al., 1998; Madsen et al., 2005; Fischer et al., 2008) and to determine reaction mechanisms with high precision at the atomic scale (Evans et al., 1995; Scarlett et al., 2008; Lopano et al., 2009).
Many angle-dispersive TR-XRD investigations have employed capillary-based cell
designs innovated by Norby (1996) and Parise et al. (2000). These cells offer an extremely high
degree of versatility. They serve as autoclaves for closed solid-fluid or solid-gas systems at low
and high temperatures, and can accommodate open-system experiments that involve gas or fluid
flow-through reactions with powdered solids. Moreover, a recent design presented in Chupas et
al. (2008) permits flow-through solid-fluid or solid-gas experiments at high temperatures.

Although previous researchers have measured reaction products in gas-solid flow-
through reactions (Clausen et al., 1991; Chupas et al., 2001), we are unaware of angle-dispersive
TR-XRD flow-through studies that have attempted to correlate real-time measurements of fluid
isotope chemistry with changes in the crystal structure of the solid phase. Coupled studies of
fluid-mineral behavior are particularly challenging with respect to mineral reactions that produce
changes in the stable isotope composition of the ambient fluid, since no in-line methodology
currently can extract the isotopic character of the eluate from a flow-through experiment.

Here we report a novel approach that combines in situ, time-resolved synchrotron X-ray
diffraction with time-resolved stable isotope analysis of dissolved metals. In order to make
accurate and reproducible isotope measurements, we modified flow-through capillary reaction
cells to encompass four key components: 1) a non-metallic sample cell to prevent any
contribution of dissolved metals from the cell; 2) a sample cell that can rotate about phi through
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programmed and operated from outside the protective hutch; and 4) regulated N₂ gas pressure to
control eluent flow. Using this sample cell we can directly monitor crystallographic changes in
the solid phase and correlate those changes with variations in the isotopic chemistry of the
solution.
1.2 Experimental Setup

The flow-through reaction cell includes two commercially available components (union tee and capillary tube) and two machined pieces (stainless steel cap and Teflon® plug) (Fig. 1.1a). A Chemfluor® mini union tee (Saint-Gobain Inc., part No. 1072002) provides the basis for this inert material sample cell. A glass capillary (ID 0.7 to 1.0 mm; Charles Supper Inc., part # 10-QZ), which holds the mineral powder to be interrogated, is affixed to one of the union tee fittings. A milled cap of 316 stainless steel is attached to the union tee that is located at 180° to the capillary tee. This stainless steel cap is milled from a single block, but it contains two sections: a post that serves to attach the cell to the goniometer head, and a cup that closes off the union tee. The post section has a length of 8.15 mm and a diameter of 3.12 mm (Fig. 1.1b). The cup portion is 5.08 mm long, and it has an outer diameter of 11.11 mm with a bore diameter of 5.41 mm and depth of 3.81 mm. To accommodate the Teflon® plug, the stainless steel cap has an additional center bore with a diameter of 5.33 mm and a depth of 0.508 mm. Threads were set using a 1/4” – 28 tap. The Teflon® plug, which is required to isolate the stainless steel cap from the reaction fluids, has a diameter of 1.37 mm with a length of 3.94 mm, and its base has a diameter of 5.31 mm and thickness of 0.508 mm (Fig. 1.1a).

A plug of acid-washed glass wool or cotton is placed at the end of the capillary to prevent solid material from passing into solution collectors. The powdered mineral sample is then deposited into the capillary. Powders that pack densely impede fluid flow, and for some of our experiments we sprinkled the powder onto glass wool, rolled the mixture into a tight wad, and packed the wad into the capillary.

The vertical port on the union tee (marked a, Fig. 1.1a) serves as the fitting for the solution tubing and is not modified. However, the horizontal ports are cut off to be flush with the thread barrel in order to accommodate the capillary fitting and the stainless steel cap. We note
that ferrules are not used for either of these fittings. A bead of 5-minute epoxy is placed around the exterior surface near the flared opening of the quartz glass capillary, and the capillary is inserted into a Chemfluor® fitting that contains an o-ring. Once the capillary is epoxied to the fitting, the flared opening of the capillary is crushed and removed from the fitting using tweezers. An additional o-ring is placed within the threads of the fitting and the fitting is attached to the union tee. The closed tip at the outlet end of the capillary is cut to allow for fluid flow. The union tee is attached to the goniometer head using the stainless steel cap with a Teflon plug (Fig. 1.1b).

The reaction fluid is placed in an HDPE acid-washed bottle that is sealed with a screw cap containing inlet and outlet ports. Nitrogen gas is fed into the inlet port to provide a backpressure on the reaction fluid, and in response the fluid flows through the outlet port to the union tee via 1.50 mm I.D. HDPE tubing. A peristaltic pump can be attached to the reaction fluid tubing to regulate the flow rate. As the fluid reacts with the powdered sample, X-ray diffraction patterns are collected every 2 to 3 minutes using an image plate detector. We obtained high-quality patterns using a MAR345 full-imaging plate detector (beamline X7B, National Synchrotron Light Source, Brookhaven National Lab) and a MAR165 CCD camera (beamline 13-BM-C, Advanced Photon Source, Argonne National Lab). Although integration of the diffraction rings helps minimize preferred orientation, our device allows rotation of the capillary about the phi axis by ±30° to diminish this problem further.

The post-reaction eluate drips through the capillary outlet and is collected in HDPE acid-washed 15 ml bottles that are aligned approximately 3 cm apart on a rotating autosampler stage 10 cm directly below the capillary (Fig. 1.1c). The autosampler stage is a 30-cm diameter stainless steel disk attached to a Newport RTM stage using stepping motor control. The autosampler is controlled from outside the hutch using EPICS Open Source software. Sample bottles rotate under the capillary and can be exchanged during an experimental run if flow-rate is
high or a large number of fractions is desired. For our Cu isotope analysis, we required approximately 100 μg of Cu so the volume of solution that we collected depended on the concentration of Cu in the eluate and the flow-rate of the solution. For a typical experimental run we collected 1 to 2 ml of solution over a five-minute span. Evaporation of the collected fluid would likely not influence the Cu isotope composition of the fluid, but it could potentially affect the metal concentrations. This can be prevented by periodically entering the hutch and capping the collection bottles.

In our experiments, we were targeting the fractionation of Cu isotopes during an oxidative transformation of chalcocite (Cu₂S) to covellite (CuS). For our isotope analysis, the eluate was acidified with ultrapure HNO₃, and the remaining mineral powder in the capillary was digested completely using 1 part HNO₃ and 3 parts HCl. In order to separate Cu from other cations, we employed a wet ion exchange chromatography (IEC) procedure following the protocol adapted from previous work (Marechal & Albarede, 2002; Mathur et al., 2005). After sample purification we measured $^{65}\text{Cu}/^{63}\text{Cu}$ using multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS; Thermo Scientific, Neptune) at Washington State University.

A critically important characteristic of our reaction cell is the absence of any metal components that contact the fluid. Prior to the adoption of our cell design, we ran test experiments using more standard cells that employed metallic fittings. The brief exposure of the reaction fluid to the metal fittings resulted in Zn contamination (~ 1 ppm) in the eluate. Using the non-metallic experimental cell, Zn concentrations in run products dropped below analytical detection limits. Furthermore, our design differs from other cells (e.g., the SECRETS cell of Parise et al., 2000) by incorporating a shortened exhaust port that eliminates solution mixing and minimizes lag time between diffraction collection and eluate sampling.
1.3 Application

We designed and tested our non-metallic reaction cell to collect reaction eluate for Cu isotope analysis during real-time XRD of Cu-sulfide mineral dissolution. During oxidative dissolution, chalcocite (Cu₂S), a common copper ore mineral, undergoes a series of phase transformations as it forms covellite (CuS) (Whiteside et al., 1986). Mathur et al. (2005) observed that dissolution of chalcocite fractionates stable isotopes of Cu, with the heavier $^{65}\text{Cu}$ preferentially partitioning into the fluid. Prior studies had demonstrated that bonding environment can strongly influence Cu isotope fractionation (Marechal & Albarede, 2002; Marechal & Sheppard, 2002), and Mathur et al. (2005) proposed that Cu isotope fractionation during the reaction from Cu₂S to CuS may be controlled by changes in the Cu sulfide structure.

We developed our flow-through cell to correlate changes in mineral structure with the degree of Cu isotope fractionation during Cu-sulfide dissolution. Our experiments have allowed us to monitor changes in crystal structure and mineral phase abundance in real time, and we quantitatively relate crystallographic parameters to the changes in the Cu isotope values of the eluate. In Figure 1.2, time-resolved X-ray diffraction patterns are stacked to reveal the oxidation of chalcocite (Cu₂S) to covellite (CuS). The emergence and disappearance of diffraction peaks between the first and final patterns indicate the formation of transient Cu sulfide phases during this reaction. To the left of the stacked diffraction patterns, we have plotted the variation in the $\delta^{65}\text{Cu}$ values of the eluate. As is standard practice in isotope chemistry, the $\delta$ value is a function that expresses the $^{65}\text{Cu}/^{63}\text{Cu}$ ratio normalized to a standard, and the normalized ratio is expressed in units of per mil (‰). In this experiment, the $\delta^{65}\text{Cu}$ of the starting mineral powder equaled 0 ± 0.14‰. Therefore, $\delta^{65}\text{Cu}$ values of the eluate are positive when $^{65}\text{Cu}$ fractionates preferentially into the solution and negative when $^{65}\text{Cu}$ is preferentially retained in the solid.
Because our experimental protocol allowed us to correlate the variation in isotopic fractionation with the transformation of phases, the two graphs share the same time axis. Thus, we observe that aqueous Cu is initially enriched in isotopically heavy Cu relative to the sample and becomes depleted in heavy Cu over time. Coupling the isotope analysis with TR-XRD reveals that the degree of fractionation was heavily dependent on the Cu sulfide phase in coexistence with the solution. Specifically, fractionation is large and positive when the solid phases are characterized by Cu:S ratios close to 2:1, but as the stoichiometry approaches a 1:1 ratio, the fractionation becomes negative, indicating the preferential release of relatively light $^{63}$Cu into solution.

We note that this sample cell can be applied beyond isotopic fractionation during mineral reactions to any structural transformation that involves the release of ions into solution. Additional applications of this cell thus would include mineral dissolution or ion exchange reactions, and these applications uniquely allow the researcher to couple structural analysis with fluid chemistry. This synergy is ideally suited to studies that attempt to bridge reaction kinetics with crystallographic mechanisms of reaction.
1.4 References


Figure 1.1 Experimental set-up. (a) An exploded view of capillary sample cell; (b) a side view showing the sample cell assembled (dimensions are mm); (c) a view from the top showing the fraction collector and position of X-ray source and imaging plate or CCD camera.
Figure 1.2 Stacked synchrotron X-ray diffraction patterns (right) showing the oxidative dissolution phase reaction of chalcocite (Cc) to covellite (Cv) with the presence of intermediate phases. The isotopic values ($\delta^{65}\text{Cu}$) (left) are of aqueous Cu leached during the reaction. Note the shared time axis.
Chapter 2

Investigating the dissolution of chalcocite and bornite by ferric sulfate using time-resolved X-ray diffraction

2.0 Abstract

A significant portion of the global Cu flux into freshwater occurs from the oxidation of Cu-sulfide minerals through the weathering of ore deposits or the leaching of mine wastes. This study investigates the oxidative dissolution kinetics of the common copper ore minerals chalcocite (Cu2S) and bornite (Cu3FeS4) in ferric-rich, acidic waters. We used synchrotron-based X-ray diffraction coupled with a flow-through cell to study the rates of Cu release and the structural changes to the minerals during dissolution by ferric sulfate solutions.

During chalcocite dissolution, XRD analysis revealed mineral transformations involving the following phases: djurleite (Cu1.94S), digenite (Cu1.8S), anilite (Cu1.75S), spionkopite (Cu1.39S), yarrowite (Cu1.13S), and covellite (CuS). We developed a kinetic model that describes the number of moles of Cu per mole S ([Cu2S]) in the solid phase as Cu was leached from chalcocite and formed covellite:

$$[Cu_2S] = e^{-4.122(Fe(III)_{aq})^{1.07}} t + 1$$

Dissolution of bornite by ferric sulfate solutions also produced changes to the mineral structure: a contraction of the bornite unit-cell volume as “non-stoichiometric bornite” formed. XRD results demonstrated that the structure of non-stoichiometric bornite was similar to mooihoekite (Cu2.25Fe2.25S4). As with chalcocite, we developed a model to describe the number of moles of Cu per mole S ([Cu3FeS4]) in the solid mineral as Cu was leached from bornite during oxidative dissolution:
\[ \text{[Cu}_5\text{FeS}_4\text{]} = e^{-0.52}[\text{Fe(III)}_{aq}]^{0.48}t^{-1.05} + 0.9 \]

These results clarify the reaction sequences that occur when ferric sulfate dissolves chalcocite and bornite. Furthermore, this study quantifies the kinetics of Cu sulfide dissolution at ambient temperatures to assist with acid rock drainage (ARD) mitigation and to assess the potential for economic extraction of Cu from mine waste.

2.1 Introduction

Anthropogenic activities are responsible for the largest mass flux in the global Cu cycle, and an estimated 11,000 Gg of Cu per year are extracted from ore deposits around the world (RAUCH and GRAEDEL, 2007). This flux is approximately 2.3 times larger than the mass flux of Cu, on a yearly basis, between the Earth’s mantle and the crust. Of the mined Cu, roughly 14% is lost to mill or smelter wastes in the form of tailings or slag (GORDON, 2002; RAUCH and GRAEDEL, 2007). These wastes contribute to the additional 1,200 Gg of Cu per year that flows into freshwater over and above the non-anthropogenic flux of Cu from the regolith (2600 Gg/yr) (RAUCH and GRAEDEL, 2007). Weathering of these Cu sulfide ores can produce acid rock drainage (ARD) -- solutions with low pH and high Cu, Fe, SO\(_4\), and trace metal concentrations. The significant mass of Cu present in many mine wastes underscores the need to quantify the kinetics of Cu sulfide dissolution at ambient temperatures to assist in efforts of ARD mitigation as well as to assess the potential for economic extraction of Cu from the waste material.

Researchers have developed comprehensive dissolution rate laws for chalcopyrite (CuFeS\(_2\)), which is the most abundant Cu-bearing sulfide mineral (KIMBALL et al., 2010). Chalcocite (Cu\(_2\)S) and bornite (Cu\(_5\)FeS\(_4\)) also are important Cu ores, and they are more soluble
than chalcopyrite in acidic and ferric-rich waters (NEWTON, 1942). The kinetics of dissolution for chalcocite and bornite, however, have not been as extensively studied.

At low temperatures (<80°C) in ferric sulfate solutions, chalcocite dissolves non-stoichiometrically, and it preferentially releases Cu into solution to form covellite (CuS) (THOMAS et al., 1967). The general reaction can be written as:

\[
\text{Cu}_2\text{S} \; (s) + \text{Fe}_2\text{(SO}_4\text{)}_3 \; (aq) \rightarrow \text{Cu}^{2+} \; (aq) + 2\text{Fe}^{2+} \; (aq) + 3\text{SO}_4^{2-} \; (aq) + \text{CuS} \; (s)
\]  

such that Fe(III) oxidizes Cu(I) in chalcocite to form dissolved Cu(II) (SULLIVAN, 1930). The leaching of Cu from covellite can continue until only sulfur remains:

\[
\text{CuS} \; (s) + \text{Fe}_2\text{(SO}_4\text{)}_3 \; (aq) \rightarrow \text{Cu}^{2+} \; (aq) + 2\text{Fe}^{2+} \; (aq) + 3\text{SO}_4^{2-} \; (aq) + \text{S}_0 \; (s)
\]  

However, this reaction is very slow at low temperatures (Fisher, 1994).

In reality, the complexity of the chalcocite dissolution reaction is not adequately represented by Eq. 1, as several transient Cu$_{2-x}$S phases appear and disappear as chalcocite transforms to covellite. Researchers who have monitored the changes in chalcocite during dissolution have reported the following intermediate phases: djurleite (Cu$_{1.94}$S), digenite (Cu$_{1.8}$S), anilite (Cu$_{1.75}$S), and the minerals formerly known as blaubleiblender or “blue-remaining” covellite - spionkopite (Cu$_{1.39}$S) and yarrowite (Cu$_{1.13}$S) (BRENNET et al., 1974; FISHER et al., 1992; KING et al., 1975; POTTER and EVANS, 1976; WHITESIDE and GOBLE, 1986). Because of the close similarity of the X-ray diffraction patterns generated by these minerals, as well as the variability of the Cu stoichiometry, these studies are inconsistent in their assignment of the phases that are produced when ferric sulfate transforms chalcocite to covellite.

Like chalcocite, bornite (Cu$_5$FeS$_4$) undergoes a structural transformation as it oxidizes. In the initial stages of bornite dissolution by ferric iron, S and Fe remain in the crystal structure while Cu is rapidly leached (DUTRIZAC et al., 1970; PESIC and OLSON, 1983; UGARTE and BURKIN, 1975). This incongruent dissolution results in the formation of “non-stoichiometric bornite” at temperatures below 40°C (DUTRIZAC et al., 1985):
\[
\text{Cu}_3\text{FeS}_4 (s) + 2x\text{Fe}^{3+} \text{ (aq)} \rightarrow \text{Cu}_{(5-x)}\text{FeS}_4 (s) + x\text{Cu}^{2+} \text{ (aq)} + 2x\text{Fe}^+ \text{ (aq)} \quad (3)
\]

The reaction kinetics slow significantly once ~25 to 30 mol% of the Cu is leached from the mineral and Cu$_3$FeS$_4$ persists. As with chalcocite dissolution, published studies disagree regarding the phases that are formed during bornite dissolution at low temperatures. Using XRD data, authors have suggested that chalcopyrite (CuFeS$_2$), covellite (CuS), digenite (Cu$_{1.2}$S), and/or idaite (Cu$_6$Fe$_2$S$_6$) are intermediate reaction products (DUTRIZAC et al., 1985; PESIC and OLSON, 1984; UGARTE and BURKIN, 1975).

To clarify the reaction sequences that occur when ferric sulfate dissolves chalcocite and bornite, in this study we conducted in situ dissolution experiments using synchrotron-based X-ray diffraction coupled with a custom-designed flow-through cell. Synchrotron radiation offers superior data because the high flux and intensity yield a high signal-to-noise ratio for these fluid-solid mixtures, and the synchrotron X-rays can be strongly monochromated. Thus, we were able to detect the appearance and disappearance of phases with high precision as Cu was progressively leached from chalcocite and bornite. Moreover, by collecting eluate fractions from the flow-through cell at known intervals, we could correlate the evolution in mineralogy to changes in the concentration of dissolved Cu (Fig. 2.1). As a result, we were able to extract not only reaction sequences for these dissolution reactions but rate equations as well. Here we report the results of those analyses, and we compare the behaviors of chalcocite and bornite.

2.2 Methods

2.2.1 Material

Naturally occurring chalcocite (Cu$_2$S) purchased from Alfa Aesar (#42532, lot H11J11 and B13R003: Butte, MT, USA) and bornite (Cu$_5$FeS$_4$) from Ward’s Natural Science (#49-V-
5921, Magma Mine, Superior, AZ, USA) were crushed with an acid-washed mortar and pestle and ground to an optimal size of \(<20 \mu m\) for X-ray diffraction analysis. XRD revealed that the chalcocite was phase pure, but patterns of the bornite revealed trace amounts of ZrO\(_2\), which was inert in our experiments. In addition, small peaks that could not be indexed to the orthorhombic structure reported in Koto and Morimoto (1975) were observed; these peaks behaved identically to the bornite peaks during dissolution, suggesting that they may have represented a superstructure.

2.2.2 X-ray diffraction flow-through reaction cells

Mineral 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; the design of this cell is detailed in Wall et al. (2011a). Ferric sulfate \((\text{Fe}_2(\text{SO}_4)_3)\) solutions with a range of \(\text{Fe(III)}\) concentrations (chalcocite experiments \([\text{Fe(III)}] = 0.09 \text{ mM, 0.4, 6.5, 6.6, 6.8, 7.3, 12, 132}\); bornite experiments \([\text{Fe(III)}] = 1.6 \text{ mM, 2.1, 13.2, 14, 130, 815}\) were pumped through the reaction cell at a constant rate (which varied from 0.01 to 1.0 mL min\(^{-1}\) in different experiments) to dissolve the minerals. Solutions were maintained at \(~30^\circ\text{C}\) 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 chemical analysis. We performed the X-ray diffraction experiments 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).

Powdered mineral samples (ranging in mass from 0.005 to 0.02 g) were weighed using a Mettler Toledo XS105DU balance and inserted in a quartz-glass capillary (ID 1.0 mm) within the flow-through apparatus. The initial mass of Cu in the starting mineral was calculated using the
ideal weight percentage of Cu in bornite (63.35 wt%) and chalcocite (79.89 wt%). A plug of acid-washed glass wool or cotton then was placed at the outlet of the capillary to prevent solid material from passing into the solution collector. Nitrogen gas provided backpressure for the reaction fluid. As the mineral powders dissolved during the flow of the ferric sulfate solution, synchrotron X-ray diffraction patterns were collected approximately every 2 to 4 minutes using either an image plate detector (MAR 345) or a CCD camera (MAR 165).

2.2.3 Chemical analysis

Eluate samples from the flow-through reactions were acidified with concentrated ultra-pure HNO₃ to make 2% (v/v) solutions. We measured Cu and Fe concentrations using ICP-MS (Thermo X-Series II) and ICP-AES (Perkin-Elmer Optima 5300DV).

2.2.4 Crystallographic analysis

2.2.4.1 Chalcocite

In order to determine phase abundances during the reaction of chalcocite, X-ray diffraction patterns for each member of the Cu₂₋ₓS compositional series was simulated using CrystalDiffract 1.3 software (CrystalMaker, Inc.). Reference intensity ratios (RIRs) were determined for each of these intermediate phases, and then semi-quantitative phase abundances were obtained by measuring the ratios of the areas for diagnostic peaks in the experimental XRD patterns for each phase using JADE software (MDI, Inc.) and applying the RIRs to these diagnostic peaks. This analysis also yielded an average Cu:S ratio for the reactants as a function of time (Table 2.1).
2.2.4.1 Bornite

We were able to monitor the dissolution of bornite by measuring unit-cell parameters of bornite at sequential stages of dissolution. These parameters were determined first by fitting selected peaks from the X-ray diffraction patterns using a pseudo-Voigt function in MDI JADE 7.0 software to extract d-spacings. The reflections included in the least-squares refinement were as follows: 242, 004, 480, 642, 0.16.0, and 488. Unit-cells for bornite then were determined using UNITCELL, a least-squares refinement program (HOLLAND and REDFERN, 1997). The initial structural parameters used to define reflection indices were based on the orthorhombic structure reported in Koto and Morimoto (1975), with space group \( \text{Pbca} \) and \( a = 10.950 \text{ Å} \), \( b = 21.862 \text{ Å} \), \( c = 10.950 \text{ Å} \).

2.3 Results

2.3.1 Chalcocite leach experiments

2.3.1.1 Cu chemistry

In all of the chalcocite dissolution experiments, the amount of Cu leached into solution increased with time until ~50 mol% Cu had been extracted from the mineral (Table 2.1; Fig. 2.2). Once half the original Cu was leached, covellite persisted throughout the remainder of the run. This phenomenon has been widely observed in chalcocite dissolution experiments using ferric sulfate at low temperatures \((< 40^\circ \text{C})\) (FISHER, 1994; WHITESIDE and GOBLE, 1986). As was also reported, the rates of dissolution increased with higher ferric concentrations.
2.3.1.2 X-ray diffraction patterns: chalcocite - covellite

As can be seen in a time-resolved sequence of X-ray diffraction patterns (Fig. 2.3), as Cu leaches from the starting chalcocite, the solid phase transforms through multiple intermediate phases before the formation of covellite. Individual X-ray diffraction patterns at selected time intervals are displayed in Figure 2.4 in order to reveal the identities of these intermediate phases. As an example, for ferric concentrations of 7.3 mM, after 10 minutes chalcocite transformed into a mixture of djurleite (Cu$_{1.94}$S), roxbyite (Cu$_{1.75}$S), and yarrowite (Cu$_{1.13}$S). Chalcocite may have been present in small concentrations during this stage, but subtle peak shifts in the diffraction pattern indicate that djurleite was the dominant phase. As the reaction progressed ($t$=16 min), peaks associated with roxbyite grew in intensity at the expense of djurleite. Yarrowite continued its presence during this interval. At 27 minutes, the djurleite and roxbyite peaks had decreased in intensity and yarrowite had become the dominant phase. The mixture continued to evolve as the reaction progressed ($t$=35 min), at which point peaks associated with covellite began to appear. Finally, after 47 minutes, the yarrowite reflections were no longer distinct, and covellite persisted throughout the remainder of the reaction (a total of 126 minutes) with no changes in its diffraction pattern.

2.3.2 Bornite leach experiments

2.3.2.1 Cu chemistry

Similar to the chalcocite dissolution experiments, the amount of Cu leached during bornite dissolution increased with time but became limited as the reaction progressed (Table 2.2; Fig. 2.5). When bornite was dissolved using 130 mM Fe$^{3+}$, the rate of Cu release slowed once ~28 mol% Cu was leached, consistent with prior studies of bornite dissolution at temperatures
<40°C (Dutrizac et al., 1985; Dutrizac et al., 1970; Ugarte and Burkin, 1975). On the other hand, when bornite was dissolved using 815 mM Fe<sup>3+</sup>, this trend was disobeyed as the rate of Cu dissolution did not slow until ~46 mol% of the total Cu was leached.

2.3.2.2 X-ray diffraction patterns: bornite

Our X-ray diffraction patterns revealed that the dissolution of bornite by ferric sulfate induces structural changes (Fig. 2.6). Previous authors (Dutrizac et al., 1985; Ugarte and Burkin, 1975) have suggested that peak shifts in the bornite diffraction pattern, particularly with respect to the 480 reflection, signify unit-cell contraction of bornite to form “non-stoichiometric bornite” according to Reaction (3). In these studies, once ~30% of the Cu had leached from the mineral, the reaction kinetics slowed significantly and Cu<sub>3</sub>FeS<sub>4</sub> persisted.

When we analyzed the final reaction product in our experiments (Fig. 2.7), however, we could not definitively identify the phase as Cu<sub>3</sub>FeS<sub>4</sub>. In Table 2.3, we list selected d<sub>hkl</sub>-spacings for the phase produced by 815 mM Fe<sup>3+</sup> following 180 minutes of dissolution at 30°C. The closest match to our final run product was mooihoekite, Cu<sub>9</sub>Fe<sub>9</sub>S<sub>16</sub> (Hall and Rowland, 1973), consistent with the greater degree of Cu leaching measured by our chemical analysis.

2.4 Discussion

2.4.1 Kinetic analysis

2.4.1.1 Chalcocite dissolution: kinetic model

The overall stoichiometry for the chalcocite (Cu<sub>2</sub>S) transformation to covellite (CuS) is
\[
\text{Cu}_2\text{S} (s) \quad + \quad 2\text{Fe(III)} (aq) \quad \rightarrow \quad \text{Cu}^{2+} (aq) \quad + \quad \text{CuS} (s) \quad + \quad 2\text{Fe(II)} (aq)
\]

(4)

The rate of transformation can be defined as

\[
- \frac{d[\text{Cu}_2\text{S}]}{dt} = \frac{d[\text{CuS}]}{dt} = \frac{d[\text{Cu}^{2+}_{aq}]}{dt}
\]

(5)

We will define [Cu$_2$S] as the number of moles of Cu per mole S in the solid phase; therefore [Cu$_2$S] initially is equal to 2 and approaches 1 at reaction completion. Importantly, although we model this transformation of chalcocite to covellite as a solid solution, our XRD patterns indicate that chalcocite disappears early and covellite appears late. Thus the chalcocite and covellite in equation 4 are only theoretical components. With these definitions, at time 0, [Cu$_2$S] = 2 and upon complete transformation, [CuS] = 1. We can calculate [Cu$_2$S] by the following equation:

\[
[\text{Cu}_2\text{S}] = \left(\frac{\mu g \ 	ext{Cu}_{\text{min}} - \sum_{i=1}^{n}(\mu g \ 	ext{Cu}_{aq})_i}{\mu g \ 	ext{Cu}_{\text{min}}^o}\right) \times 2
\]

(6)

where Cu$_{\text{min}}^o$ is the amount of Cu in the starting material and we sum the amount of Cu$_{aq}$ measured in each aliquot that has been leached into solution.

We also assume that the Fe(III) sorbs to the mineral surface and can be described by a Freundlich isotherm (Li and Werth, 2002; Newman et al., 1991). The concentration of sorbed Fe(III), denoted as [Fe(III)$_{\text{sorbed}}$] in mol/L, is a function of Fe(III) in solution, denoted as [Fe(III)$_{aq}$] in mol/L, as follows:

\[
[\text{Fe(III)}_{\text{sorbed}}] = K[\text{Fe(III)}_{aq}]^n
\]

(7)

Here K (in units of liters of solvent per kilograms of solid) is the distribution coefficient related to sorbent capacity and n is an empirical constant related to sorbent heterogeneity.

We hypothesize a rate model equation for which Cu is leached from the mineral:

\[
- \frac{d[\text{Cu}_2\text{S}]}{dt} = k \left(K[\text{Fe(III)}_{aq}]^n \left([\text{Cu}_2\text{S}] - 1\right)\right)
\]

(8)
Here $k$ (in units of kg mol$^{-1}$ min$^{-1}$) is a rate constant describing Cu release from the solid mineral. The term ($[Cu_2S] - 1$) is needed because the reaction slows as $[Cu_2S]$ approaches 1 and this model only assesses the first stage of chalcocite dissolution. Since $[Fe(III)]$ is very high, we assume it remains constant through the experiment. Defining $k' = kK$ and re-arranging, we get

$$-\frac{d[Cu_2S]}{([Cu_2S] - 1)} = k'[\left(Fe(III)_{aq}\right)^n] \ dt \tag{9}$$

Integration yields the following relation:

$$-\ln([Cu_2S] - 1) = k'[\left(Fe(III)_{aq}\right)^n]t - C \tag{10}$$

where $C$ is the constant of integration. When $t = 0$, $[Cu_2S] = 2$, therefore

$$C = \ln 1 = 0 \tag{11}$$

so that Eq. 10 can be rewritten as

$$\ln([Cu_2S] - 1) = -k'[\left(Fe(III)_{aq}\right)^n]t \tag{12}$$

Another form of Eq. 12 is

$$[Cu_2S] = \exp\left(-k'[\left(Fe(III)_{aq}\right)^n]t\right)+1 \tag{13}$$

Following equation 12, we have calculated $\ln([Cu_2S] - 1)$ as a function of time for different concentrations of Fe$^{3+}$, and the results are shown in Figure 2.10. For those experiments in which the concentrations of Fe$^{3+}$ were 12 and 132 mM, we plot only the initial rates because the formation of covellite was approached so rapidly in these experiments, and the rates slowed significantly when $[Cu_2S] \approx 1$.

The resulting rate function yielded a nearly linear dependence on time ($R^2$ ranged from 0.954 to 0.995). The slopes of these lines are summarized in Table 2.5. We define these slopes as $k''$, which incorporates the Freundlich isotherm:

$$k'' = -k'[\left(Fe(III)_{aq}\right)^n] \tag{14}$$
Equation 14 is inverted to yield

\[ \frac{1}{k''} = \frac{1}{-k'[\text{Fe(III)}_{aq}]^n} \]  

(15)

From equation 15, it is apparent that we can calculate a value for \( k' \) by examining the dependence of \( 1/k'' \) on \( 1/[\text{Fe(III)}_{aq}]^n \). For simplicity, we assume an initial value for \( n \) of unity. The resulting line is determined by only three data points, but they provide a linear relationship with \( R^2 = 0.98 \). The slope of this line is equal to \( 1/-k' \) (Fig. 2.11). We now can solve for \( k' \) to obtain a value of 4.122 kg mol\(^{-1}\) min\(^{-1}\), and we can apply this value to Equation 13 to predict \([\text{Cu}_2\text{S}] \) as a function of time and ferric sulfate concentration.

By design, the value for \([\text{Cu}_2\text{S}] \) is also the formula unit \( x \) for Cu in \( \text{Cu}_x\text{S} \). Figure 2.12 and Table 2.6 report the relationship between the model prediction for the leaching of \( \text{Cu}_x\text{S} \) versus experimental measures obtained independently. These experimental values were determined by applying Equation 6 to chemical analyses of the eluate from the time-resolved experiments. To obtain the best fit for Figure 2.12, we allowed \( n \) to vary. Since changes in \( n \) also influence the slope calculated from Equation 15, we varied \( n \) iteratively until a best fit was achieved and \( n \) equaled 1.07 (Table 2.5).

2.4.1.2 Kinetic model results: chalcocite

The kinetic model under-predicts the formula unit of Cu in \( \text{Cu}_x\text{S} \) for one sample from the experiment using 7.3 mM ferric solutions and over-predicts \( x \) for four samples from those experiments run with 12 mM ferric solutions. The model predicts the observed values for \( x \) for the remaining experiments within the 90% confidence interval.

Our kinetic analyses were designed to measure initial rates of dissolution, but our data are consistent with previous work that showed that chalcocite dissolution occurs in two steps. The
amount of Cu release proceeds quickly as chalcocite dissolves and then slows as the mineral transforms into covellite. King et al. (1975) calculated the activation energy of Cu release during chalcocite dissolution by ferric chloride and determined that dissolution kinetics are controlled by diffusion of Cu\(^+\) from the core of the mineral to the surface, where it is oxidized to Cu\(^{2+}\) and released into solution. In a study investigating oxidative dissolution of chalcocite by oxygen, Fisher et al. (1992) also suggest that Cu\(^+\) ions diffuse through the crystal structure from the interior chalcocite to the Cu depleted surface where it is oxidized. Charge balance is maintained by S\(^2-\) also oxidizing to form sulfur dimers: S\(_2^{2-}\). Our X-ray diffraction results are consistent with the proposed reaction mechanism that multiple Cu\(_{2-x}\)S phases coexist during the reaction, thereby allowing the possibility that a Cu concentration gradient could exist within a grain.

2.4.1.3 Bornite dissolution: kinetic model

The rate of bornite dissolution by ferric ions has previously been shown to slow significantly as the concentration of leached Cu approaches ~25 to 30 mol% of the initial concentration in bornite. In our experiments using 815 mM Fe\(^{3+}\) the mol% of Cu leached from bornite exceeded 30% which is inconsistent with previous bornite dissolution studies. Because of this we do not include sample set using 815 mM Fe\(^{3+}\) to develop the following models. Instead, we assume an average molar concentration of Cu in non-stoichiometric bornite to be 28 mol%. Therefore, the overall stoichiometry for the first stage of bornite (Cu\(_3\)FeS\(_4\)) dissolution as it forms non-stoichiometric bornite (Cu\(_{3.6}\)FeS\(_4\)) is:

\[
\text{Cu}_3\text{FeS}_4 \text{(s)} + 1.4\text{Fe(III)} \text{(aq)} \rightarrow 1.4\text{Cu}^{2+} \text{(aq)} + \text{Cu}_{3.6}\text{FeS}_4 \text{(s)} + 1.4\text{Fe(II)} \text{(aq)} \tag{16}
\]

Following the same reasoning as was applied to chalcocite, we can define the rate of transformation of bornite to non-stoichiometric bornite as
\[
-d\left[\text{Cu}_{5}\text{FeS}_4\right] \frac{dt}{dt} = d\left[\text{Cu}_{3.6}\text{FeS}_4\right] \frac{dt}{dt} = \frac{1}{1.4} d\left[\text{Cu}^{2+}\text{aq}\right] \frac{dt}{dt}
\]  

(17)

We will define \([\text{Cu}_5\text{FeS}_4]\) as the moles of \(\text{Cu}\) per mole \(\text{S}\) in the capillary; therefore \([\text{Cu}_5\text{FeS}_4]\) starts at \(5/4\) and approaches \(3.6/4\) at reaction completion. With these definitions, at time 0, \([\text{Cu}_5\text{FeS}_4]\) = \(5/4\) and upon complete transformation, \([\text{Cu}_{3.6}\text{FeS}_4]\) = \(3.6/4\). Assuming that bornite dissolves non-stoichiometrically, we can calculate \([\text{Cu}_5\text{FeS}_4]\) by the following equation:

\[
[\text{Cu}_5\text{FeS}_4] = \left(\frac{\mu g \text{ Cu}_{\text{min}}}{\text{Cu}_{\text{aq}}} \cdot \sum_{i=1}^{n} \left(\frac{\mu g \text{ Cu}_{\text{aq}}}{\text{Cu}_{\text{min}}}ight)\right) \left/ \frac{\mu g \text{ Cu}_{\text{min}}}{\text{Cu}_{\text{aq}}}\right\} \times \frac{5}{4}
\]  

(18)

Following the models discussed for chalcocite dissolution, we assume that the \(\text{Fe}(\text{III})\) sorbs to the mineral surface and can be described by a Freundlich isotherm. Therefore we hypothesize that the rate model for \(\text{Cu}\) leaching from bornite is:

\[
-d\left[\text{Cu}_5\text{FeS}_4\right] = k\left(\text{Fe(III)}_{\text{aq}}\right)^n \left([\text{Cu}_5\text{FeS}_4] - 3.6/4\right)
\]  

(19)

Here \(k\ (\text{Kg} \cdot \text{mo} \cdot \text{l}^{-1} \cdot \text{min}^{-1})\) is a rate constant describing \(\text{Cu}\) release from the solid mineral, \(K\) is related to sorbent capacity, and \(n\) is related to sorbent heterogeneity. The term \(([\text{Cu}_5\text{FeS}_4] - 3.6/4)\) is needed because the reaction slows as \([\text{Cu}_5\text{FeS}_4]\) approaches \(3.6/4\), and this model only assesses the first stage of bornite dissolution. As with the chalcocite model we define \(k' = kK\), and if we collect terms we see that

\[
-\frac{d[\text{Cu}_5\text{FeS}_4]}{\left([\text{Cu}_5\text{FeS}_4] - 3.6/4\right)} = k'\left(\text{Fe(III)}_{\text{aq}}\right)^n dt
\]  

(20)

Upon integration, we see that

\[
-\ln([\text{Cu}_5\text{FeS}_4] - 3.6/4) = k'\left(\text{Fe(III)}_{\text{aq}}\right)^n t - C
\]  

(21)

where \(C\) is the constant of integration. When \(t = 0\), \([\text{Cu}_5\text{FeS}_4]\) = \(5/4\), therefore

\[
C = \ln(0.35)
\]  

(22)

which can be substituted back into Eq. 21, yielding
\[
\ln(\text{[Cu}_5\text{FeS}_4]-3.6/4) = -k'([\text{Fe(III)}]_{\text{aq}})^n t + \ln(0.35) \tag{23}
\]

Another form of Eq. 23 is
\[
\text{[Cu}_5\text{FeS}_4] = \exp(-k'([\text{Fe(III)}]_{\text{aq}})^n t + \ln(0.35) + 0.9 \tag{24}
\]

Following equation 23, we examine the dependence of \(\ln([\text{Cu}_5\text{FeS}_4]-3.6/4)\) on time, as shown in Figure 2.13.

The slopes of the curves from Figure 2.13, which we will call \(k''\), are summarized in Table 2.7 (\(R^2\) ranged from 0.514 to 0.957). Using the equation 23, we can define \(k''\) as
\[
k'' = -k'([\text{Fe(III)}]_{\text{aq}})^n \tag{25}
\]

Re-writing equation 25 we get
\[
\frac{1}{k''} = -\frac{1}{k'([\text{Fe(III)}]_{\text{aq}})^n} \tag{26}
\]

Using equation 26, we can ascertain the dependence of \(1/k''\) on \(1/[\text{Fe(III)}]_{\text{aq}}\) with the initial assumption that \(n=1\). The slope of this curve is equal to \(1/k'\) (Fig. 2.14). We can solve for \(k'\) and apply this value to equation 24 to predict \([\text{Cu}_5\text{FeS}_4]\), or moles of Cu per mole of S in the reacted solid. If we multiply the value for \([\text{Cu}_5\text{FeS}_4]\) by 4, then we can determine the formula unit for Cu in bornite.

Figure 2.15 (Table 2.8) shows the relationship between the predicted formula unit, \(x\), for Cu in the solid phase (\(\text{Cu}_x\text{FeS}_4\)) and the formula unit for Cu measured by chemical analysis assuming non-stoichiometric dissolution. To obtain the best \(R^2\) values for Figure 15, we adjusted the constant \(n\). Since changes in \(n\) also influence the slope in equation 26, we varied \(n\) iteratively until a best fit was achieved when \(n = 0.88\).
2.4.1.4 Kinetic model results: bornite

The kinetic model for bornite dissolution by ferric sulfate predicted the formula unit, $x$, for Cu$_x$FeS$_4$ within the 90% confidence interval for ferric concentrations spanning 1.6 mM to 130 mM. The model did not accurately predict the correct formula unit of Cu for Cu$_x$FeS$_4$ in the experiment in which the powder was leached by 815 mM ferric sulfate. However, our model presumed that the final bornite composition was depleted in Cu by 30 mol%, as was observed for “non-stoichiometric bornite” in previous studies (DUTRIZAC et al., 1985; PESIC and OLSON, 1983; UGARTE and BURKIN, 1975). In none of those studies did the ferric sulfate concentrations exceed 200 mM. When we dissolved bornite using 815 mM ferric sulfate, the bornite leached more Cu at a faster rate than had been previously measured at low temperature. This anomalous behavior relative to leaching experiments with lower concentrations of ferric sulfate may indicate that a different dissolution mechanism dominates when ferric levels are very high, perhaps because the framework Fe and S are also being dissolved.

2.4.2 Mineralogical Analysis

2.4.2.1 Structural changes to chalcocite

Thermodynamic calculations carried out by Woods et al. (1987) indicate that chalcocite passes through a series of intermediate phases before forming covellite (and eventually native S) as the reduction potential (Eh) increases. In Figure 2.16, the stability fields for Cu sulfide phases are calculated with respect to Eh and pH when the formation of S-oxyanions is suppressed. This approach is relevant for short time-scales where sulfate formation can be considered irreversible during sulfide mineral reactions. For our chalcocite dissolution experiments at pH 2 to 2.5, we estimate that the Eh values exceeded 770 mV due to the high ferric concentrations. Thus,
according to these calculations, chalcocite should have passed through a series of Cu sulfide phases with decreasing Cu:S ratios during the reaction with ferric sulfate.

Our time-resolved X-ray diffraction results reflect this thermodynamic prediction (Fig. 4). We observed the formation of djurleite (Cu$_{1.94}$S), roxbyite (Cu$_{1.75}$S), and yarrowite (Cu$_{1.13}$S) before covellite was formed. We did not observe the formation of digenite, anilite, or geerite, as has been suggested by a previous study (WHITESIDE and GOBLE, 1986).

Ours is the first study to identify roxbyite (Cu$_{1.75}$S) as a metastable reaction product for our dissolution experiments. Identification of the entire transition suite is difficult without synchrotron-based XRD, which provides a level of resolution that simply was not available to previous researchers. The presence of roxbyite is not unexpected, as it is observed in natural settings associated with djurleite (MUMME et al., 1988).

### 2.4.2.2 Unit-cell analysis: bornite

As we reported in the isotopic study of Wall et al. (2011b), we conducted least-squares refinements of the unit-cell volumes of bornite at selected intervals during Fe$_2$(SO$_4$)$_3$-mediated dissolution. Here we report the changes in unit-cell dimensions as a function of Fe$^{3+}$ concentration and of time. Our refinements revealed that the unit-cell volume did not vary significantly when bornite was exposed to the less concentrated ferric solutions (1.6 mM and 2.1 mM Fe$^{3+}$). This result seems reasonable because very little Cu was leached within the first 200 minutes of those runs (Table 2.4; Fig. 2.8). However, in experiments with higher ferric concentrations (13 to 815 mM Fe$^{3+}$) and significant Cu loss (5 to 30 mol% Cu), the bornite structure contracted sharply within the first 20 minutes of reaction.

In Wall et al. (2011b), we suggested that this sharp contraction might represent a symmetry-changing phase transition, rather than the gradual reaction to non-stoichiometric
bornite proposed by Dutrizac et al. (1985). For the present study, our analysis of the XRD data for the slower reactions associated with the 1.6 mM Fe$^{3+}$ solutions has yielded a different hypothesis. The higher resolution made possible by the longer reaction rate clearly revealed a coexistence of structurally similar phases when bornite is leached. As seen in Figure 2.9, the primary bornite peak at 1.93 Å disappears, and a separate peak at 1.89 Å emerges first as a shoulder and increases in intensity with time. Rather than showing evidence for a structural phase transition, these data indicate that a distinct Cu-leached phase nucleates and grows when the starting stoichiometric bornite dissolves.

Electron microprobe experiments by Dutrizac et al. (1970) show a decrease in Cu/S and Cu/Fe ratios from bornite cores to reacted surfaces. In our experiments, it is therefore likely that the mooihoekite–type phase nucleates as a surface layer when Cu$^+$ in the mineral oxidizes to Cu$^{2+}$ and dissolves into solution. As Cu is leached into solution, Cu$^+$ from the core diffuses across a concentration gradient to the surface. In this way, bornite dissolution behaves similarly to chalcocite.

2.5 Conclusions

The kinetic models presented here provide a tool to predict the transformation of chalcocite and bornite in ferric-rich waters at low temperatures. These models may be useful in acid mine drainage settings as well as heap leaching operations. Synchrotron X-ray diffraction gives new clarity into which metastable phases are present during chalcocite and bornite dissolution reactions. This will lend insight into how to interpret the environment in which mineralogical assemblages formed in supergene enrichment zones.
2.6 References


Table 2.1. Chemical data from chalcopyrite dissolution experiments

<table>
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<tr>
<th>Sample</th>
<th>Fe$_{avg}$ (mmol/L)</th>
<th>Cu$_{aq}$ (μg/mL)</th>
<th>Cu$_{solid}$ (μg)</th>
<th>Cu$_{leached}$ (%)</th>
<th>Cu$_S$ based on XRD</th>
<th>Phases present by XRD</th>
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Notes:
- Cu$_{solid}$ = (μg Cu$_{min}$) = (μg Cu in solution).
- Cu$_{leached}$ = (1 μg Cu in solid / μg Cu$_{min}$) x 100.
- Cu$_S$ based on XRD = (μg Cu$_{min}$) - (μg Cu in solution) x 2.
- cc = chalcopyrite, dj = digenite, an = ankerite, nr = roxbyte, sp = sphalerite, y = yararite, cv = covellite.

* cc = chalcopyrite, dj = digenite, an = ankerite, nr = roxbyte, sp = sphalerite, y = yararite, cv = covellite.
Table 2.2. Chemical data from bornite dissolution experiments

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*a Cu in solid (\(\mu g\)) = (\(\mu g\) Cu min\(^{-1}\)) - (accum. \(\mu g\) Cu in solution).
*b mo% Cu leached = (1 - (\(\mu g\) Cu in solid / \(\mu g\) Cu min\(^{-1}\)) x 100.
*C Cu formula unit = [(\(\mu g\) Cu min\(^{-1}\)) - (accum. \(\mu g\) Cu in solution)] / (\(\mu g\) Cu min\(^{-1}\)) x 5.
*Previously published, Wall et al. 2010 (Ore Geology Reviews)
Table 2.3. X-ray diffraction data for partially dissolved bornite

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30°C, 180 minutes, 0.82 M [Fe]_{aq}
Table 2.4. Unit cell parameters during bornite dissolution

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- , not measured
Table 2.5. Kinetic model parameters for chalcocite dissolution

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Table 2.6. Kinetic model results, chalcolite

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* Cu formula unit = ([µg Cu min⁻¹] - (accum. µg Cu in solution)/[µg Cu min⁻¹]) x 2
Table 2.7. Kinetic model parameters for bornite dissolution

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Table 2.8. Kinetic model results, bornite

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* Cu formula unit = ([μg Cu min^-1] - (accum. μg Cu in solution)) / (μg Cu min^-1) x 5
Figure 2.1  Time-resolved synchrotron X-ray diffraction (XRD) patterns stacked as a function of time and correlated with aqueous Cu concentrations (µg ml⁻¹) during the oxidative dissolution of chalcocite (vertical axis). XRD patterns reveal a series of intermediate phases as chalcocite transforms to covellite. Each diffraction pattern represents 3 minutes of data collection.
Figure 2.2  The amount of Cu leached from chalcocite (Cu₂S) as the ferric sulfate leaching reactions progressed. The experiments have different ferric concentrations ([Fe] mM = mmol L⁻¹) and initial masses of chalcocite (see Table 2.1). Mol% Cu leached was calculated based on XRD quantification for experiments using 132, and 12 [Fe] mM. For the remaining experiments mol% Cu leached was calculated based on equation in Table 2.1.
Figure 2.3 Selected diffraction patterns during oxidative dissolution of chalcocite when [Fe] = 7.3 mM. Stacked patterns are spaced ~3 minutes apart showing chalcocite transforming to covellite. A mixture of intermediate phases with decreasing Cu:S ratio appear as the reaction progresses. Cc = chalcocite and Cv = covellite.
Figure 2.4 X-ray diffraction patterns showing the phases that occur during chalcocite dissolution. Peaks in the XRD patterns are best fit by powder diffraction files for three intermediate phases (djurleite, roxbyite, and yarrowite) as chalcocite transforms to covellite using [Fe] = 7.3 mM solutions.
Figure 2.5 The amount of Cu leached from bornite (\(\text{Cu}_5\text{FeS}_4\)) as the ferric sulfate leaching reactions progressed. The experiments have different ferric concentrations ([Fe] mM) and initial masses of bornite (see Table 2.2).
Figure 2.6 Stacked time-resolved XRD patterns showing the dissolution of bornite using [Fe] = 815 mM solution. Previous studies suggest that the shift in the $4\overline{8}0$ $hkl$ plane is indicative of bornite unit-cell contraction leading to the formation of non-stoichiometric bornite.
Figure 2.7  X-ray diffraction patterns showing the bornite dissolution using [Fe] = 815 mM solutions.
The variation in the unit-cell volume with time as increasing amounts of Cu are leached from the solid bornite. Unit-cell volume of bornite decreases sharply during the initial stages of Cu dissolution from bornite for all experiments except for when \([\text{Fe}]=2.1\ \text{mM}\). As the reaction progressed, the rate of unit-cell contraction decreased to nearly zero.

**Figure 2.8** The variation in the unit-cell volume with time as increasing amounts of Cu are leached from the solid bornite. Unit-cell volume of bornite decreases sharply during the initial stages of Cu dissolution from bornite for all experiments except for when \([\text{Fe}]=2.1\ \text{mM}\). As the reaction progressed, the rate of unit-cell contraction decreased to nearly zero.
Figure 2.9  Time resolved XRD patterns of bornite dissolution using a ferric sulfate solution where $[\text{Fe}] = 1.6$ mM. At slower reactions rates, and indicative peak of bornite (1) shows that the mineral dissolves as a new phase (2) precipitates as opposed to a peak shift due to unit cell contraction perceived in faster reactions. The gap in the diffraction patterns is due to an interruption in the X-ray beam.
Figure 2.10 Initial rates of chalcocite dissolution using ferric sulfate. $[\text{Cu}_2\text{S}]$ is defined as the number of moles of Cu per mole of S. As $[\text{Cu}_2\text{S}]$ approaches 1 the reaction reaches a pseudo-equilibrium and very little Cu dissolves into solution. The experiments have different ferric concentrations ($[\text{Fe}]$ mM) and initial masses of chalcocite.
Figure 2.11  The inverse of the slopes ($1 / k''$) from chalcocite dissolution experiments (Fig. 2.10) versus the inverse of ferric concentrations to the nth power.
Figure 2.12  Kinetic model prediction of Cu$_x$S, where $x$ is the formula unit of Cu, versus measured Cu$_x$S. Actual Cu$_x$S values are determined either by XRD or chemical analysis (see Table 2.6). Small dashed lines are 90% confidence intervals and the large dashed line is 1:1 relationship. The solid lines is a linear regression of the entire data set.
Figure 2.13 Initial rates of bornite dissolution using ferric sulfate. $[\text{Cu}_5\text{FeS}_4]$ is defined as the number of moles of Cu per mole of S. The experiments have different ferric concentrations ([Fe] mM) and initial masses of bornite.
Figure 2.14  The inverse of the slopes ($1 / k''$) from bornite dissolution experiments (Fig. 2.13) versus the inverse of ferric concentrations to the nth power.
Figure 2.15  Kinetic model prediction of Cu$_x$Fe$_4$S$_4$, where $x$ is the formula unit of Cu, versus measured Cu$_x$Fe$_4$S$_4$. Actual Cu$_x$Fe$_4$S$_4$ values are determined by chemical analysis (see Table 2.8). Small dashed lines are 90% confidence intervals and the large dashed line is 1:1 relationship. The solid line is a linear regression of the entire data set.
Figure 2.16  Eh pH diagram of chalcocite Cu$_2$S considering irreversible sulfate production (after Woods et al., 1987). The grey box indicates the Eh and pH conditions during our chalcocite dissolution experiments.
3.0 Abstract

Low-temperature ore deposits exhibit a large variation in $\delta^{65}\text{Cu}$ (~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 ($^{65}\text{Cu}$) relative to the solid, with an average apparent isotope fractionation ($\Delta_{\text{aq-min}} = \delta^{65}\text{Cu}_{\text{aq}} - \delta^{65}\text{Cu}_{\text{min}}$) of $2.20 \pm 0.25$‰. 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 $\Delta_{\text{aq-min}}$ values ranging from $-0.21 \pm 0.61$‰ to $0.92 \pm 0.25$‰. 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 unit-cell volume, which we identified as a transition from stoichiometric to non-stoichiometric bornite. We propose that the initially high $\Delta_{\text{aq-min}}$ values result from isotopically heavy Cu ($^{65}\text{Cu}$) concentrating within Cu$^{2+}$ during dissolution. The decrease in the apparent isotope fractionation as the reaction progresses occurs from distillation of isotopically heavy Cu ($^{65}\text{Cu}$) during dissolution or kinetic isotope effects associated with the depletion of Cu from the surfaces of bornite particles.
3.1 Introduction

Once it became possible to measure Cu isotope ratios ($^{65}\text{Cu} / ^{63}\text{Cu}$) 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 $\delta^{65}\text{Cu}$ of ~2.5‰ (Fig. 3.1) (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, in press; Rouxel et al., 2004; Zhu et al., 2000). However, an even larger range in Cu isotope values (with variations in $\delta^{65}\text{Cu}$ of ~12‰) has been measured in low-temperature Cu deposits where weathering reactions dominate (Fig. 3.1). 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 et al., 2009a, 2009b, in press; Mathur and Schlitt, 2010) and acid mine drainage (Balistrieri et al., 2008; Borrok et al., 2008; Kimball et al., 2009). Figure 3.1 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 $\delta^{65}\text{Cu}$ values from high-temperature deposits cluster around 0.29‰ and display a near-normal distribution. These values are consistent with $\delta^{65}\text{Cu}$ 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 $\delta^{65}\text{Cu}$ values measured in nature has been attributed principally to isotope fractionation during the oxidative weathering of primary Cu sulfide minerals (Albarede,
Laboratory experiments have shown that changes in the oxidation state of Cu can lead to a large isotope fractionation such that the isotopically heavy isotope ($^{65}\text{Cu}$) 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 $^{65}\text{Cu}$ 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 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 Figure 3.1 shows apparent isotopic fractionation values ($\Delta_{\text{aq-min}}$) as measured in Cu-mineral dissolution experiments such that:

$$\Delta_{\text{aq-min}} = \delta^{65}\text{Cu}_{\text{aq}} - \delta^{65}\text{Cu}_{\text{min}}$$

where $\delta^{65}\text{Cu}_{\text{aq}}$ represents the Cu dissolved in the aqueous phase and $\delta^{65}\text{Cu}_{\text{min}}$ 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$_{\text{aq}}$ is enriched in $^{65}\text{Cu}$ 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), $\delta^{65}\text{Cu}$ values of the solution decrease relative to the starting values. Researchers have proposed several hypotheses to account for the decreasing trend in
Δ_{aq-min}^\alpha 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 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 (CuFeS_4) was selected for this study because it undergoes a structural transformation as it oxidizes, providing a unique opportunity to assess structural controls on Δ_{aq-min}^\alpha 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):

\[
\text{Cu}_5\text{FeS}_4 + 2x\text{Fe}^{3+} \rightarrow \text{Cu}_{(5-x)}\text{FeS}_4 + x\text{Cu}^{2+} + 2x\text{Fe}^{2+}
\] (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 Δ_{aq-min}^\alpha 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.
3.2 Methods

3.2.1 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 (Fe₂(SO₄)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).

Naturally occurring bornite (Cu₅FeS₄) from Ward’s Natural Science was crushed with an acid-washed mortar and pestle and ground to an optimal size of <10 μm for X-ray analysis. Powdered samples (0.007 – 0.015 g) were weighed using a Mettler Toledo XS105DU balance and inserted in the flow-through apparatus described in detail in Wall et al. (2011). The initial mass of Cu in the starting mineral was calculated using the ideal weight percentage of Cu in bornite (63.35%). A plug of acid-washed glass wool or cotton then was placed at the outlet of the capillary to prevent solid material from passing into the solution collector. Nitrogen gas provided backpressure for the reaction fluid. As the bornite powder dissolved during the flow of the ferric
sulfate solution, synchrotron X-ray diffraction patterns were collected approximately every 2 to 4 minutes using either an image plate detector (MAR 345) or a CCD camera (MAR 165).

3.2.2 Crystallographic analysis

Unit-cell parameters of dissolving bornite powders were determined using UNITCELL, a least-squares refinement program (Holland and Redfern, 1997). The initial structural parameters used to define reflection indices were based on the orthorhombic structure reported in Koto & Morimoto (1975), with space group \( P_{bca} \) and \( a = 10.950 \, \text{Å}, \; b = 21.862 \, \text{Å}, \; c = 10.950 \, \text{Å} \). XRD patterns were indexed using MDI JADE 6.0 powder diffraction software. The reflections included for the least-squares refinement were as follows: 242, 004, 480, 642, 0.16.0, 488.

3.2.3 Cu isotope analysis

For the preparation of our samples for isotope analysis we used ultrapure reagent grade acids (J.T. Baker) and deionized water (18.2 M\( \Omega \)/cm; Millipore). Flow-through reaction eluate was acidified with concentrated HNO\(_3\) to make 2\% solutions. The remaining mineral powders in the capillary were completely dissolved in heated (80°C) aqua regia (1 part HNO\(_3\), 3 parts HCl) overnight. We employed a wet ion exchange chromatography (IEC) procedure in order to separate Cu from other cations using anion exchange resin AG MP-1 (Bio-Rad), following the protocol adapted from previous work (Marechal and Albarede, 2002; Mathur et al., 2005). We conducted all IEC in a clean hood (NuAire; NU-156). In cases where [Fe] from the ferric sulfate solution far exceeded [Cu] leached from the mineral, a second ion exchange column was used to further separate the Cu from the matrix solution. We verified complete recovery of Cu from the column procedure (yields = 100± 10\%) using ICP-MS (Thermo X-Series II) and ICP-AES.
(Perkin-Elmer Optima 5300DV) since IEC is known to fractionate Cu isotopes (Marechal and Albarede, 2002). The yield on two samples did not fall within 100±10% with sample 6.6mM_4 having a Cu yield of 88% and 65mM_2 having a Cu yield of 83%.

In light of recent work that showed a potential for isobaric interferences from S (\(^{32}\)S-\(^{14}\)N-\(^{16}\)O-\(^{1}\)H) when $SO_4^{2-}$:Cu ratios exceeded 50 (Pribil et al., 2010), we ensured that the measured S:Cu ratios fell below the suggested cut-off in the post-column solutions. In one case (when $[Fe_2(SO_4)_3] = 6.6 \text{ mmol L}^{-1}$), we were unable to obtain S concentrations for post-column samples, but using the calculated mass of S from the known ferric sulfate concentration, we determined that the maximum possible S:Cu ratio was <15.

We measured $^{65}\text{Cu}/^{63}\text{Cu}$ of both the solutions and the powders using multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) at Washington State University (Thermo Scientific, Neptune) and at the University of Arizona (Micromass Isoprobe). To correct for instrumental mass fractionation, we used a sample-standard-sample bracketing technique with the NIST 976 Cu standard. The concentration of Cu in the samples was diluted to match the standard concentrations within 20%. In addition, samples and standards were spiked with a Johnson-Mattey Zn solution for corrections using the exponential law of mass fractionation of the internal standard (Marechal et al., 1999). However this correction was not used because it did not improve the precision and accuracy of the measurements. We report Cu isotopic compositions using standard delta notation:

$$\delta^{65}\text{Cu} (‰) = \left[\left(\frac{^{65}\text{Cu}}{^{63}\text{Cu}}\right)_{\text{sample}} / \left(\frac{^{65}\text{Cu}}{^{63}\text{Cu}}\right)_{\text{NIST 976}}\right] - 1 \times 1000$$  \hspace{1cm} (3)

The average $\delta^{65}\text{Cu}$ value was 0.04 ± 0.14‰ (2σ) for the NIST 976 measurements (n=320) made over the course of 4 years at both Washington State University and the University of Arizona using two different multi-collector ICP mass spectrometers.
We were able to calculate the starting mineral isotope values to be within the error of the measured values using isotopic mass balance equations (Table 3.1), except for the experiment using 2.8 mmol L\(^{-1}\) Fe\(_2\)(SO\(_4\))\(_3\) for which we were unable to measure \(\delta^{65}\)Cu values for every sample in the set.

### 3.3 Results

#### 3.3.1 Chemistry

In all experiments, the amount of Cu leached from the bornite samples increased with time, and the reaction rates decreased dramatically as 27 to 30 mol% of the total Cu was leached (Fig. 3.2). The retardation in the leach rate is consistent with previous reports that bornite dissolution at 30°C slows when approximately 25 to 30 mol% of Cu has been leached (Dutrizac et al., 1970, 1985; Pesic and Olson, 1983; Ugarte and Burkin, 1975). However, the total amount of Cu leached and the initial rates of leaching did not correlate well with the concentration of the ferric sulfate eluent. Specifically, considerably less Cu was released when [Fe\(_2\)(SO\(_4\))\(_3\)] was 6.6 mmol L\(^{-1}\) in comparison with 2.8 mmol L\(^{-1}\). We attribute this non-linearity to the experimental design. We have observed that achieving internal consistency with respect to reaction kinetics in TR-XRD experiments requires a nearly exact reproducibility in flow rate, sample porosity, and sample permeability from one run to the next. We suspect that the sample that we loaded when [Fe\(_2\)(SO\(_4\))\(_3\)] = 6.6 mmol L\(^{-1}\) was more tightly packed than the other two samples. Nevertheless, the changes in unit-cell parameters and the apparent isotope fractionation as a function of the amount of leached Cu should be unaffected by these differences in flow rate.
3.3.2 Cu Isotope fractionation

At the beginning of each experiment, the leached Cu$_{aq}$ was enriched in $^{65}\text{Cu}$ relative to the initial bornite powder (Table 3.1). When <5 mol% of the total Cu was leached from the mineral, the apparent fractionation between the aqueous and the mineral phases ($\Delta_{aq-min}$ = $\delta^{65}\text{Cu}_{aq}$ - $\delta^{65}\text{Cu}_{min}$) averaged 2.20 ± 0.25‰ (Fig. 3.3). As Cu leaching continued, $\Delta_{aq-min}$ values decreased. When >20 mol% Cu was leached from the solid, the degree of apparent isotope fractionation between the aqueous and mineral phases approached zero, with $\Delta_{aq-min}$ values ranging from -0.21 ± 0.61‰ to 0.92 ± 0.25‰. Thus, while allowing for some scatter ($R^2 = 0.51$), as more Cu was leached from the bornite, the degree of apparent isotopic fractionation between the solid and the fluid phases diminished (Fig. 3.3).

3.3.3 Combined XRD and isotope analysis

Figure 3.4 exhibits a time-resolved series of X-ray diffraction patterns as bornite reacted with a 6.6 mmol L$^{-1}$ Fe$_2$(SO$_4$)$_3$ solution, and the XRD results are temporally correlated with changes to Cu isotope values as measured by MC-ICP-MS. In this experiment, the $\delta^{65}\text{Cu}$ values for Cu$_{aq}$ decreased from 2.00‰ to a low of 1.31‰ with a final increase to 1.73‰. As seen in Figures 3.4 and 3.5, a structural change in response to leaching by ferric sulfate is revealed by the shifting and emergence of X-ray diffraction peaks as the reaction progressed. The changes observed in the peak positions are consistent with the formation of “non-stoichiometric bornite”, represented as Cu$_{5-x}$FeS$_4$ (Dutrizac et al., 1985).

Least-squares refinement of the d$_{hk\ell}$-spacings measured from selected non-overlapping reflections reveals that the bornite unit-cell volume decreased as Cu leached from the structure and the mineral transformed into non-stoichiometric bornite (Table 3.2; Fig. 3.6). Dutrizac et al.
(1985) previously observed this unit-cell contraction, although not as a continuous time series. These authors report that non-stoichiometric bornite terminated as Cu$_3$FeS$_4$ in their room-temperature leaching runs, but that the final product varied widely from one experiment to the next. In our study, the bornite unit-cell volume decreased from an initial value of 2633±12 Å$^3$ to as small as 2431±6 Å$^3$ (Fig. 3.6).

Surprisingly, our time-resolved experiments clearly demonstrate that the contraction of the unit cell was not linear as a function of the amount of Cu leached, as Vegard’s law would suggest (Denton and Ashcroft, 1991). Instead, the structure sharply contracted by nearly 8 vol% during the initial stages of the reaction as the first ~7 mol% of the total Cu was leached from the solid. Further leaching of the Cu up to the terminal ~30 mol% introduced a negligible additional decrease in unit-cell volume (~1 vol%). This behavior, in concert with the abrupt appearance of diffraction peaks in the earliest stages of leaching (Fig. 3.4), strongly implies that a structural symmetry-changing phase transition occurs when the first 7 mol% of total Cu is removed from the bornite structure.

3.4 Discussion

The apparent Cu isotope fractionation ($\Delta_{\text{aq-min}}$) of 2.20 ± 0.25‰ observed during the bornite leaching experiments is similar to $\Delta_{\text{aq-min}}$ values reported by other studies that conducted abiotic oxidative dissolution experiments of sulfide minerals, such as chalcopyrite 1.32 ± 0.23‰, (Mathur et al., 2005); 1.65 ± 0.14‰, (Kimball et al., 2009); 2.07 ± 0.22‰, (Fernandez and Borrok, 2009), enargite (0.92 ± 0.14‰, (Kimball et al., 2009)), and chalcocite (2.74 ± 0.23‰, (Mathur et al., 2005)). Thus, for all of these sulfide phases, $^{65}$Cu is preferentially released into solution while $^{63}$Cu remains in the mineral during the first stages of dissolution. This phenomenon has been explained by equilibrium theory, where isotope fractionation is determined
in part by bond stiffness, which is correlated with high oxidation state (Bigeleisen and Mayer, 1947; Schauble, 2004).

Consistent with the present study, other workers have found that the magnitude of the apparent Cu isotope fractionation ($\Delta_{\text{aq-min}}$) decreases as the amount of Cu leached from the mineral increases. In batch leach experiments, Kimball et al. (2009) reported a reduction in $\Delta_{\text{aq-min}}$ of 0.56‰ after 5.1 mol% Cu was leached from chalcopyrite. Mathur et al. (2005) observed a similar decrease of 0.60‰ after 24 mol% Cu was leached from chalcopyrite and a decline in $\Delta_{\text{aq-min}}$ values of 0.50‰ after 36.4 mol% Cu was leached from chalcocite. In addition, Fernandez & Borrok (2009) report a decrease in $\Delta_{\text{aq-min}}$ of approximately 3‰ after close to 2 mol% Cu was leached from chalcopyrite-rich rock using cyclic experiments in which leachate was completely removed following each elution. Their cyclical experimental design closely approximates the open-system flow-through experimental cell presented here, as both methods eliminate the accumulation of product as occurs in batch experiments. The removal of product accounts for the sharper decrease in $\Delta_{\text{aq-min}}$ values relative to the batch experiments.

The authors of these studies present several hypotheses to explain changes in $\Delta_{\text{aq-min}}$ values during the oxidative dissolution of chalcopyrite and chalcocite. We will evaluate the following hypotheses to assess the apparent fractionation of Cu isotopes measured during bornite dissolution: 1) adsorption on Fe oxides; 2) Cu precipitation from solution as a secondary mineral; 3) air oxidation of a Cu-rich surface layer prior to the dissolution reaction; and 4) fractionation upon dissolution.

The first proposed mechanism -- fractionation due to adsorption onto Fe-oxides -- seems unlikely to explain our experimental results because the pH at which they were run (pH 2 – 2.5) was so low. Adsorption of Cu onto Fe-oxides is negligible below pH 4 (Stumm and Morgan, 1996). In addition, studies by Balistrieri et al. (2008) and Pokrovsky et al. (2008) demonstrated
that although Cu sorption to Fe-oxyhydroxides does fractionate Cu isotopes, no Cu sorbed below pH 3.

Our XRD data provide no evidence to support the second hypothesis, which implies that Cu fractionation accompanies the precipitation of a secondary Cu mineral from solution during bornite dissolution reaction. Our synchrotron diffraction patterns (Fig. 3.5) revealed the emergence of a phase that could be indexed with high confidence to non-stoichiometric bornite, and no other diffraction peaks appeared. Indeed, the oxidizing potential of the solution would preclude the formation of secondary sulfide minerals. Thus, even though the precipitation of sulfide minerals has been shown to induce Cu isotope fractionation (Ehrlich et al., 2004), we are ruling out this possibility.

Regarding the third mechanism, Fernandez & Borrok (2009) have previously argued that air oxidation creates a Cu-rich surface layer prior to the dissolution reaction, which accounts for the apparent Cu isotope fractionation during the leaching of Cu from chalcopyrite. Fernandez & Borrok (2009) argue that in their experiments, isotopic fractionation of Cu in chalcopyrite occurred prior to dissolution through solid-state oxidation. Consequently, the large initial apparent fractionation ($\Delta_{\text{aq-min}}$ ~ 2‰) that they observed in their experiments represents dissolution of a thin Cu(II)-sulfate and/or Cu(II)-oxide phase that coats the surface of the chalcopyrite. As the chalcopyrite (along with the oxidized surface) dissolves, the apparent fractionation factor ($\Delta_{\text{aq-min}}$) decreases as a result of simple mixing between the bulk chalcopyrite ($\delta^{65}\text{Cu} \approx 0$) and the surface layer ($\delta^{65}\text{Cu} \approx 2$). Interestingly, their modeling results suggest that only 0.4% of the total Cu had to be present as an oxidized surface layer to explain their isotope data.

We can test the idea that antecedent solid-state oxidation of a Cu-rich rind was responsible for the apparent isotopic fractionation during dissolution of bornite. We invoke an isotope mass balance equation:
\[
\delta^{65}\text{Cu}_{\text{solution}} = f_{\text{surface layer}} \delta^{65}\text{Cu}_{\text{surface layer}} + f_{\text{bulk}} \delta^{65}\text{Cu}_{\text{bulk}}
\] (4)

where \(\delta^{65}\text{Cu}_{\text{solution}}\) is the Cu isotope value of each aliquot collected in our experiment, \(f_{\text{surface layer}}\) and \(f_{\text{bulk}}\) are the fractions of Cu in the surface layer and bulk respectively, and \(\delta^{65}\text{Cu}_{\text{surface layer}}\) and \(\delta^{65}\text{Cu}_{\text{bulk}}\) are the isotope values of each reservoir. Using the equation

\[
f_{\text{surface layer}} + f_{\text{bulk}} = 1
\]

we can rearrange equation 4 and solve for \(f_{\text{surface layer}}\). We can use our measured values for \(\delta^{65}\text{Cu}_{\text{solution}}\), and we can assume that \(\delta^{65}\text{Cu}_{\text{surface layer}} = 3\%_o\) (fractionation due to redox processes, Ehrlich et al., 2004) and \(\delta^{65}\text{Cu}_{\text{bulk}} = 0\), which is the approximate isotopic value of primary bornite.

We have performed these calculations for those experiments in which [Fe\(_2\)(SO\(_4\))\(_3\)] equals 6.6 and 65 mmol L\(^{-1}\); the remaining dataset was not sufficiently dense to solve these equations. Assuming simple mixing, the results suggest that 7.6 mol\% (when [Fe\(_2\)(SO\(_4\))\(_3\)] = 6.6 mmol L\(^{-1}\)) and 8.0 mol\% (when [Fe\(_2\)(SO\(_4\))\(_3\)] = 65 mmol L\(^{-1}\)) of the total Cu must have been extracted from an oxidized surface layer. These abundances are sufficiently large that synchrotron XRD would detect the Cu-oxide or sulfate products, if they were crystalline. As noted above, no secondary phases were revealed by XRD. Crystalline phases could theoretically be present below the detection limit of powder XRD methods (<2 to 3 wt%), but as our calculations reveal, the isotope mass balance would be incorrect if unidentified phases contributed to the measured isotope value.

Moreover, the X-ray diffraction data provide little support for the idea that Cu from an oxidized surface layer mixes with Cu from the bulk mineral to cause the decrease in the apparent isotope fractionation during bornite dissolution. Figure 3.7 shows the relationship between \(\Delta_{\text{aq-min}}\) and the change in unit-cell volume as leaching progresses. Two regions are highlighted: values for apparent fractionation at the beginning of the reaction (<18 mol\% Cu leached), and values for apparent fractionation at the end of the reaction (18 – 30 mol\% Cu leached). If the higher \(\Delta_{\text{aq-min}}\) values at the beginning of the leaching reactions result from dissolution of a previously oxidized surface layer, we would expect to observe little change in the unit-cell...
volume of bornite. X-ray diffraction interrogates the bulk material, and changes in the surface structure would not be apparent. In fact, we observed the opposite behavior. The largest change in unit-cell volume occurs early in the reaction, and that unit-cell contraction is associated with high $\Delta_{aq-min}$ (Fig. 3.7). We interpret this result as evidence that fractionation occurred during oxidative dissolution of the bulk material and not merely of a surface layer.

This leaves the fourth mechanism, fractionation during oxidative dissolution, as the most plausible explanation of observed isotopic trends during bornite leaching. Mathur et al. (2005) discounted fractionation upon mineral dissolution as an explanation for the apparent Cu isotope fractionation during chalcopyrite and chalcocite dissolution because they observed no apparent fractionation during the initial stages (24 hours) of partial dissolution experiments. However, this mechanism is plausible in the case of bornite dissolution, as the largest apparent fractionation occurred during the first 4 minutes in our experiments ($\Delta_{aq-min} \approx 2\%$). While the handling of bornite powders in ambient conditions would most likely result in the formation of a very thin oxidized film, the X-ray diffraction evidence leads us to conclude that the isotopic fractionation occurs during the aqueous reaction and is not merely simple mixing between two isotope reservoirs (the air oxidized layer and the bulk bornite) as Fernandez and Borrok (2009) suggest.

We propose that high $\Delta_{aq-min}$ values during the initial stages of the reactions result from redox isotope effects. The decrease in the apparent isotope fractionation, as the reaction progresses, is a result of Rayleigh-type processes or kinetic isotope effects. This hypothesis is based on previously proposed reaction mechanisms and the surprisingly fast diffusivity of Cu in bornite.

Previous workers have suggested that as Cu is oxidized and leached from the surface bornite, interior Cu diffuses to the surface to fill the resultant Cu vacancies via solid state processes (Dutrizac et al., 1985; Pesic and Olson, 1983; Ugarte and Burkin, 1975). This outward diffusion changes the bulk structure, transforming the mineral to what Dutrizac et al. (1985)
characterize as “non-stoichiometric bornite”. Additionally, Berger and Bucur (1996) report a component diffusion coefficient of Cu in bornite of $5.3 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ at 25°C. According to this result, the diffusion length of Cu in bornite would be 11 μm over 10 minutes and 48 μm over 181 minutes, our longest experiment. These diffusion lengths exceed our particle size, allowing for solid state diffusive processes to be relevant in our system.

Within the framework of the previously established bornite reaction mechanisms, we speculate that during dissolution the $^{65}\text{Cu}$ preferentially concentrates as $\text{Cu}^{2+}$ at the fluid/interface and rapidly dissolves from the mineral. This scenario is consistent with previous studies that have shown the presence of $\text{Cu}^{2+}$ in areas of blue tarnish on the surface of oxidized bornite (Buckley and Woods, 1983; Pratesi and Cipriani, 2000). That oxidation is the dominant influence on the apparent isotope fractionation is plausible because the magnitude of the apparent fractionation observed in the initial stages of dissolution is consistent with that attributed to equilibrium fractionation due to redox changes ($\Delta_{\text{aq-min}}$ of ~3 to 4 ‰, Ehrlich et al., 2004; Zhu et al., 2002). If our model is correct, then the decrease in apparent isotope fractionation during the reaction might be explained by a Rayleigh-type process with a constant fractionation, resulting in a mineral reservoir depleted in $^{65}\text{Cu}$. Alternatively, diffusion of isotopically light Cu ($^{63}\text{Cu}$) from the interior replacing the Cu vacancies at the surface eventually dominates as the reaction progresses. This is similar to the model presented by Kimball et al. (2009) in that there is preferential diffusion of isotopically light Cu ($^{63}\text{Cu}$) to the surface of the mineral. Following this hypothesis, the subsequent oxidation and release of $^{63}\text{Cu}$ that has concentrated at the surface vacancies could explain the decrease in $\Delta_{\text{aq-min}}$ values. However, the number of isotope measurements of the solid phase was too limited in our data set to adequately test the relative accuracy of these two hypotheses.
3.5 Conclusion

The large range in $\delta^{65}\text{Cu}$ values measured in low-temperature Cu ore deposits is likely a result of isotopic variations induced during sulfide weathering. A new approach that combines time-resolved XRD and Cu isotope analysis can be used to assess nano-and micro-scale processes responsible for the apparent isotope fractionation during low-temperature oxidation reactions. Consistent with other Cu-sulfide weathering experiments, our study has shown that isotopically heavy Cu is preferentially released into solution during bornite dissolution initially, but as the reaction progresses, the dissolved Cu becomes relatively lighter. XRD analysis does not support the hypothesis that the change in the apparent Cu isotope fractionation during dissolution is a result of mixing between a previously oxidized surface layer and the bulk mineral. Instead, we argue that this behavior results from fractionation during the oxidation of Cu(I) in the mineral to Cu(II) in solution and distillation as isotopically heavy Cu is removed preferentially from the mineral. Furthermore, the data suggest a correlation between the magnitude of the apparent isotope fractionation of Cu and the amount of Cu leached from the mineral, which is consistent with previous studies that have reported similar trends during chalcocite and chalcopyrite dissolution.

Since oxidation is an important dissolution mechanism for Cu(Fe)-sulfide minerals (Dutrizac et al., 1985; Fisher et al., 1994; Kimball et al., 2010), redox isotope effects have a potentially large influence on the Cu isotope composition of water and rock during weathering reactions. Trends in the apparent fractionation of Cu isotope during these reactions could be useful in assessing the amount of Cu remaining in an ore body, determining Cu sources in waters, and interpreting the extent of supergene reworking of primary ores.
3.6 References


Mathur R, Mendas M, Tittley S, Phillips A. Patterns in the copper isotopic composition of minerals in porphyry copper deposits in southwestern United States. Econ. Geol. in press.


Table 3.1. Chemistry and isotopic composition of bornite leaching experiments.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Collection (minute)</th>
<th>[Fe$_2$(SO$_4$)$_3$] (mmol L$^{-1}$)</th>
<th>Cu in solid (µg)</th>
<th>Cu in solution (µg/mL)</th>
<th>volume (mL)</th>
<th>mol% Cu leached $^b$</th>
<th>δ$^{65}$Cu$^c$ (%)</th>
<th>n $^d$</th>
<th>mass balance δ$^{65}$Cu$^{aq}$ (%)</th>
<th>Δ$^{65}$Cu$^{min}$ (%)</th>
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<td>2.8mM_min$^f$</td>
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<td>2.8</td>
<td>4561</td>
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<td>-</td>
<td>0.323</td>
<td>2</td>
<td>0.24</td>
<td>-</td>
<td>-</td>
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<td>182</td>
<td>1.19</td>
<td>4.2</td>
<td>2.17**</td>
<td>2</td>
<td>2.46</td>
<td>0.40**</td>
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<td>172</td>
<td>1.48</td>
<td>10.4</td>
<td>1.71**</td>
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<td>-</td>
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<td>-</td>
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<td>1.72</td>
<td>17.0</td>
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$^a$, not measured
$^b$ Cu in solid (µg) = (µg Cu min$^{-1}$) - (accum. µg Cu in solution).
$^c$ mol% Cu leached = (1 - µg Cu in solid / µg Cu min$^{-1}$) x 100.
$^d$ δ$^{65}$Cu values calculated according to Eq (3), with 2n of replicates ≤ 0.18‰.
$^e$ Number of replicated analyses
$^f$ δ$^{65}$Cu$_{\text{aq, undissolved}}$ = Σ (fraction of Cu$_{aq, \delta^{65}Cu_{aq}}$) x (fraction of Cu$_{\text{solid, \delta^{65}Cu_{solid}}}$)
$^g$ Δ$^{65}$Cu$_{\text{min}}$ = δ$^{65}$Cu$_{nor} - \delta^{65}$Cu$_{aq}$, where aq = leached δ$^{65}$Cu values and min$^g$ = δ$^{65}$Cu value for undissolved bornite at time 0.
$^h$ 2n ± 0.25‰.

* 2n of replicates for these samples range between 0.30 - 0.63‰.
** 2n of replicates for these samples range between 0.64 - 0.85‰.
Table 3.2. Crystallographic data during bornite dissolution.

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<th>b (Å)</th>
<th>c (Å)</th>
<th>Volume (Å³)</th>
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<sup>a</sup> Cu formula unit = [(µg Cu min<sup>-1</sup>) - (accum. µg Cu in solution)]/ (µg Cu min<sup>-1</sup>) x 5.

2<sub>σ</sub> errors on unit cell parameters: for samples "a" < 0.06, for "b" and "c" <0.03,
2<sub>σ</sub> errors on unit cell volumes: for samples "a" < 12.0, for "b" and "c" <6.0.
Figure 3.1 Cu isotope measurements ($\delta^{65}$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 ($\Delta_{aq-min}$ ‰) 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 & 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.
Figure 3.2 The amount of Cu leached from bornite as the leaching reactions progressed. The experiments have different ferric sulfate concentrations (mM = mmol L\(^{-1}\)) and initial masses of bornite (see Table 1).
Figure 3.3 The dependence of isotopic fractionation ($\Delta_{\text{aq-min}}$ ‰) on the amount of Cu leached from bornite. Dissolved Cu near the beginning of the reaction was enriched in isotopically heavy Cu ($^{65}$Cu) relative to the mineral. As the reaction proceeded, the dissolved Cu became relatively lighter.
Figure 3.4 Time-resolved synchrotron X-ray diffraction (XRD) patterns stacked as a function of time (~3 minute spacing), correlated with Cu isotope values ($\delta^{65}\text{Cu} \, \%$) of leached Cu$_{aq}$ during the oxidative dissolution of bornite (vertical axis). XRD patterns reveal a transformation of stoichiometric bornite into non-stoichiometric bornite.
Figure 3.5 Selected diffraction patterns for oxidative dissolution experiments when [Fe$_2$(SO$_4$)$_3$] = 65 mmol L$^{-1}$ showing peak shifts indicative of bornite unit-cell contraction during the transformation from stoichiometric to non-stoichiometric bornite.
Figure 3.6 The variation in the unit-cell volume with increasing amounts of leached Cu from the solid bornite. During the initial stages of Cu dissolution from bornite, the unit-cell volume of bornite diminished sharply. As the reaction progressed, the rate of unit-cell contraction decreased to nearly zero.
Figure 3.7  The amount of Cu isotope fractionation as a function of the change in unit-cell volume of bornite.
Chapter 4

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

4.0 Abstract

The oxidative dissolution of Cu-sulfide minerals contributes to the large range of Cu isotope values observed in low-temperature environments (~12‰ for $\delta^{65}$Cu). In an attempt to quantify the isotope effects responsible for this large variation, we examined the fractionation of Cu isotopes during oxidative dissolution of chalcocite (Cu$_2$S) using ferric sulfate. In this study, we used a novel approach combining time-resolved X-ray diffraction (XRD) and Cu isotope analysis. During the initial stages of chalcocite oxidation the leached fluids were enriched in heavy Cu ($^{65}$Cu) with $\delta^{65}$Cu values of ~3‰. As the dissolution reaction progressed and chalcocite transformed to covellite, XRD analysis revealed the formation of a number of intermediate phases: djurleite (Cu$_{1.94}$S), digenite (Cu$_{1.8}$S), anilite (Cu$_{1.75}$S), spionkopite (Cu$_{1.39}$S) and yarrowite (Cu$_{1.13}$S).

As the mineral dissolved, the leached Cu became isotopically lighter and $\delta^{65}$Cu values of the leachate decreased to as low as -3.01‰. Isotope box models imply that two isotope effects influence the degree of fractionation observed during the reaction progress: one due to oxidation ($\alpha \sim 1.003$) and another due to changes in bonding during mineral transformations ($\alpha \sim 1.001$). These results may be useful in interpreting the extent of weathering in Cu ore bodies and the potential for Cu release from acid mine drainage environments.
4.1 Introduction

Since the advent of high-precision intermediate mass stable isotope measurements (MARECHAL et al., 1999; ZHU et al., 2000), geochemists have measured isotopic distributions for Cu in low- and high-temperature ore deposits, as well as a variety of surface waters. Low-temperature Cu ore deposits, where oxidative weathering reactions dominate, display the largest variation in Cu isotope values (with a range of ~12‰ in $\delta^{65}$Cu). Albarede (2004b) has attributed the breadth of this range to the alteration of primary Cu sulfide minerals. The variation is evident in Figure 4.1, which represents a compilation of the ~1000 published $\delta^{65}$Cu values for solids from Cu ore deposits. Copper isotope values from high-temperature primary Cu ore bodies display a near-normal distribution with a range of ~2.5‰ and a mean value of 0.29‰ (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; LI et al., 2010; MAHER and LARSON, 2007; MARECHAL et al., 1999; MARKL et al., 2006; MASON et al., 2005; MATHUR et al., in press; MATHUR et al., 2005; MATHUR et al., 2009a; MATHUR et al., 2009b; ROUXEL et al., 2004; ZHU et al., 2000). These values are generally consistent with the $\delta^{65}$Cu values of 0.01±0.30‰ measured in granites (LI et al., 2009), 0.07±0.08‰ for basalts (ARCHER and VANCE, 2004), and 0.01±0.13‰ in loess (LI et al., 2009).

In comparison, $\delta^{65}$Cu values measured for rocks in low-temperature environments are skewed negatively (median = -0.17‰) and have a wide distribution. Included in this cohort are samples from sedimentary deposits (ASAEL et al., 2007; ASAEL et al., 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 et al., in press; MATHUR and SCHLITT, 2010; MATHUR et al., 2009a; MATHUR et al., 2009b), and acid mine drainage environments (BALISTRIERI et al., 2008; BORROK et al., 2008; KIMBALL et al., 2009).
Measurements from black smokers are included in this figure because the authors have identified significant low-temperature alteration in these environments (Rouxel et al., 2004; Zhu et al., 2000).

Similarly, surface water samples collectively display a wide variation in $\delta^{65}$Cu (Fig. 4.1). The Cu isotope composition of stream water affected by acid mine drainage (AMD) exhibits the largest variation (-1.41 to 1.78‰) (Balistrieri et al., 2008; Borrok et al., 2008; Borrok et al., 2007; Kimball et al., 2007), whereas rivers have a smaller range of $\delta^{65}$Cu values between -0.04 and 1.55‰ with a discharge weighted average of 0.68‰ (Vance et al., 2008). Estuaries and seawater samples have smaller isotopic variability but have higher average $\delta^{65}$Cu values of 0.69 and 1.09‰ respectively (Vance et al., 2008).

Researchers have identified multiple processes that fractionate Cu isotopes, such as Cu sorption to mineral surfaces (Balistrieri et al., 2008; Pokrovsky et al., 2008), changes in bonding coordination (Marechal and Albarede, 2002; Zhu et al., 2002), microbial interactions (Kimball et al., 2009; Mathur et al., 2005), and complexation with organic ligands (Bigalke et al., 2010; Vance et al., 2008). The largest isotope fractionation, however, occurs when Cu changes its oxidation state (Ehrlich et al., 2004b; Zhu et al., 2002). During redox reactions, the 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., 2004b; Zhu et al., 2002). This phenomenon also has 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).

To explain the wide variation in Cu isotope values in waters and low-temperature ore deposits, researchers have explored the Cu isotope fractionation that occurs during oxidative dissolution of Cu sulfides. The bottom panel of Figure 4.1 shows apparent isotopic fractionation values ($\Delta_{aq-min}$) as measured in these experiments such that:
where $\delta^{65}\text{Cu}_{\text{aq}}$ represents the Cu dissolved in the aqueous phase and $\delta^{65}\text{Cu}_{\text{min}}$ reflects the Cu in the unreacted mineral. Leached Cu$_{\text{aq}}$ is enriched in $^{65}$Cu relative to the solid by $\sim 1$ to 3.5‰ during the initial stages of dissolution reactions involving chalcocite (MATHUR et al., 2005), bornite (WALL et al., 2011b), and chalcopyrite (FERNANDEZ and BORROK, 2009; KIMBALL et al., 2009; MATHUR et al., 2005). This degree of fractionation can be attributed to changes in the Cu oxidation state, since many studies indicate that aqueous Cu at high Eh and at pH below 6 exists as Cu$^{2+}$ (WOODS et al., 1987). As minerals release Cu during oxidative dissolution, however, the $\delta^{65}\text{Cu}$ values in the leached fluids diminish sharply with time. The mechanism responsible for this apparent change in isotopic fractionation during weathering is largely unexplored, but understanding this behavior may explain the wide range of Cu isotope values observed in low-temperature environments.

For this study, we explored mechanisms responsible for the decrease in the apparent isotope fractionation ($\Delta_{\text{aq-min}}^o$) that has been observed during Cu-sulfide dissolution by using a technique that combines time-resolved X-ray diffraction and multi-collector ICP mass spectrometry. With this approach, we monitored changes in the crystal structure of a Cu mineral, chalcocite (Cu$_2$S), in real time, and we coupled those observations to the evolution of the Cu isotope composition of the fluid simultaneously. In addition, we have developed isotopic fractionation models to account for our observations.

Chalcocite was selected for this analysis because it undergoes sequential structural transformations as it oxidizes, providing a unique opportunity to assess the structural controls on Cu fractionation between solid and aqueous phases. We dissolved chalcocite using ferric sulfate (Fe$^{3+}(\text{SO}_4)_3$) solutions of varying molarity. Ferric sulfate is a common component in acid mine drainage waters and can oxidatively dissolve chalcocite by the following reaction (SULLIVAN, 1930):
\[
\text{Cu}_2\text{S} \text{ (s)} + \text{Fe}_2\text{(SO}_4\text{)}_3 \text{ (aq)} \rightarrow \text{Cu}^{2+} \text{ (aq)} + 2\text{Fe}^{2+} \text{ (aq)} + 3\text{SO}_4^{2-} \text{ (aq)} + \text{CuS} \text{ (s)}
\]

Chalcocite (Cu₂S) dissolves incongruently as Cu is leached from the mineral, eventually reacting to covellite (CuS) or even native sulfur (S) if reaction times are sufficiently long. As Cu is leached, the mineral transforms into a series of intermediate phases: djurleite (Cu₁.ₙ₄S), digenite (Cu₁.₃₅S), anilite (Cu₁.₇₅S), and the minerals formerly known as blauliebleiblender or “blue-remaining” covellite - spionkopite (Cu₁.₃₉S) and yarrowite (Cu₁.₁₃S) (BRENNET et al., 1974; FISHER et al., 1992; KING et al., 1975; POTTER and EVANS, 1976; WHITESIDE and GOBLE, 1986). The reaction kinetics slow considerably once covellite is formed, after which point the rate of Cu release is slower by one order of magnitude in comparison with that during chalcocite dissolution (GRIZO et al., 1982; WALSH and RIMSTIDT, 1986).

Chalcocite is an ideal candidate to assess controls of Cu isotope fractionation during dissolution for another reason: The mechanism by which Cu is leached into solution has been very well characterized. Previous workers have suggested that as Cu is oxidized and leached from the surface of chalcocite, interior Cu diffuses to the surface to fill the resultant Cu vacancies (BRENNET et al., 1974; FISHER et al., 1992; KING et al., 1975; RUIZ et al., 1998; THOMAS et al., 1967) As a result, a compositional gradient develops within each mineral grain such that the Cu:S ratio decreases from the core to the surface layer. This structural feature – the development of intermediate Cu₂₋₅S phases as a leached layer - will allow us to assess the influence of changing bonding environment on Cu isotope fractionation during dissolution of the mineral grains.
4.2 Methods

4.2.1 Materials

Naturally occurring research grade chalcocite (Cu₂S) from Alfa Aesar (#42532, lot H11J11 and B13R003: Butte, MT, USA) was ground in an acid-washed mortar and pestle to a size of < 20 μm. Powdered samples (0.009 – 0.021 g) were weighed using a Mettler Toledo XS105DU balance and inserted in the flow-through apparatus described in detail in Wall et al. (2011a). The initial mass of Cu in the starting mineral was calculated using the ideal weight percentage of Cu in chalcocite (79.85 wt%).

4.2.2 X-ray diffraction flow-through reaction cells

Chalcocite 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., 2011a). A plug of acid-washed glass wool or cotton then was placed at the outlet of the capillary to prevent solid material from passing into the solution collector. Nitrogen gas provided backpressure for the reaction fluid. As the chalcocite powder dissolved during the flow of the ferric sulfate solution, synchrotron X-ray diffraction patterns were collected approximately every 2 to 4 minutes using either an image plate detector (MAR 345) or a CCD camera (MAR 165).

Ferric sulfate (Fe₂(SO₄)₃) solutions in a range of concentrations ([Fe³⁺] = 0.09, 0.42, 6.55, 6.56, 6.8, 7.3, 12, and 132 mM) were pumped through the reaction cell at a constant rate (0.02 to 0.48 mL min⁻¹) to dissolve the chalcocite. 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 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 synchrotron X-ray diffraction depends on the material but it is generally accepted to be 2 to 3 wt % (BISH and POST, 1993).

In order to determine phase abundances during the reaction sequence, an X-ray diffraction pattern for each member of the Cu$_{2-x}$S compositional series was simulated using CrystalDiffract 1.3 software (CrystalMaker, Inc.). Reference intensity ratios (RIRs) were determined for each of these intermediate phases, and then semi-quantitative phase abundances were obtained by measuring the ratios of the areas for diagnostic peaks in the experimental XRD patterns for each phase using JADE software (MDI, Inc.) and applying the RIRs to these diagnostic peaks. This analysis also yielded an average Cu:S ratio for the reactants as a function of time; the Cu:S ratio was determined by combining our X-ray analysis with the known stoichiometry of each Cu$_{2-x}$S phase.

### 4.2.3 Cu isotope analysis

For the preparation of our samples for isotope analysis, we used ultrapure reagent grade acids (J.T. Baker) and deionized water (18.2 MΩ/cm; Millipore). Flow-through reaction eluate was acidified with concentrated HNO$_3$ to make 2% solutions. The remaining mineral powders in the capillary were completely dissolved in heated (80°C) aqua regia (1 part HNO$_3$, 3 parts HCl) overnight. We employed a wet ion exchange chromatography (IEC) procedure in order to separate Cu from other cations using anion exchange resin AG MP-1 (Bio-Rad), following the protocol adapted from previous work (MARECHAL and ALBAREDE, 2002; MATHUR et al., 2005). We conducted all IEC in a clean hood (NuAire; NU-156). In cases where [Fe] from the ferric sulfate solution far exceeded [Cu] leached from the mineral, a second ion exchange column was
used to further separate the Cu from the matrix solution. We verified complete recovery of Cu from the column procedure (yields = 100± 10%) using ICP-MS (Thermo X-Series II) and ICP-AES (Perkin-Elmer Optima 5300DV) since IEC is known to fractionate Cu isotopes (MARECHAL and ALBAREDE, 2002). Ten samples had yields of 100± 15% (6.8mM_2, 6.56mM_res, 6.55mM_1 – 3, 6.55mM_6 – 8; see Table 4.1). For five samples the yields were 100± 20% (6.55mM_5, 6.55mM_9 – 10, 0.42mM_2, 0.09mM_4; see Table 4.1). Additionally, four samples exhibited yields of 100± 30% (6.55mM_min^a, 6.55_res, 0.09mM_min^a, and 0.09_res; see Table 4.1).

In light of recent work that showed a potential for isobaric interferences from S when SO_4^{2-}:Cu ratios exceed 50 (PRIBIL et al., 2010), we ensured that the measured S:Cu ratios fell below the suggested cut-off in the post-column solutions. We note that in three samples SO_4^{2-}:Cu ratios did exceed 50 (132mM_4, 12mM_5, 12mM_8; see Table 4.1). We were unable to obtain these ratios for two samples (12mM_6 and 12mM_7; see Table 4.1).

We measured $^{65}$Cu/$^{63}$Cu of both the solutions and the powders using multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) at Washington State University (Thermo Scientific, Neptune) and at the University of Arizona (Micromass Isoprobe). To correct for instrumental mass fractionation, we used a sample-standard-sample bracketing technique with the NIST 976 Cu standard. The concentration of Cu in the samples was diluted to match the standard concentrations within 20%. In addition, samples and standards were spiked with a Johnson-Mattey Zn solution in the event that corrections would be required using the exponential law of mass fractionation of the internal standard (MARECHAL et al., 1999). However, this correction did not improve the precision and accuracy of the measurements, and it was not utilized. We report Cu isotopic compositions using standard delta notation:

$$\delta^{65}\text{Cu} (\text{‰}) = \left[\left(\frac{^{65}\text{Cu}}{^{63}\text{Cu}}\right)_{\text{sample}} / \left(\frac{^{65}\text{Cu}}{^{63}\text{Cu}}\right)_{\text{NIST 976}}\right] - 1 \times 1000$$  (3)
The average $\delta^{65}\text{Cu}$ value was $0.04 \pm 0.14\%_\text{RSD}$ for the NIST 976 measurements ($n=320$) taken over the course of 4 years between the two laboratories at Washington State University and the University of Arizona and using two different multi-collector ICP mass spectrometers.

Using an isotopic mass balance equation (Table 4.1), our calculations of $\delta^{65}\text{Cu}$ for starting mineral samples agreed with the actual starting mineral values (min°) within the external precision ($\pm 0.14\%_\text{RSD}$) or the standard error of the mean of replicate analyses, whichever was larger. The experiments for which $[\text{Fe}^{3+}] = 6.8 \text{ mM and 0.09 mM}$ were exceptions to this rule. In these experiments, however, the differences in $\delta^{65}\text{Cu}$ between the actual starting mineral and the calculated values did not exceed 0.30\%.

4.2.4 Scanning Electron Microscopy

Scanning electron microscopy (SEM) analysis of chalcocite powders reacted with 0.01 $M$ ferric sulfate for 2.5 min and for 85 min was carried out with an FEI-Philips XL 20 scanning electron microscope at 20 kV in order to measure the development of leached zones. The powders and solutions were mixed in beakers and agitated during reaction using a shaker table, and at the designated times the powders were filtered and rinsed with H$_2$O to halt the reaction. The powders then were air dried and mounted in epoxy and polished for SEM analysis. Although back-scattered electron images revealed variations in image intensity, efforts to obtain compositional energy dispersive x-ray spectroscopy (EDS) maps were complicated by the roughness of the partially dissolved particle surfaces.
4.2.5 Density functional theory and Bader calculations

Crystal structure parameters used for density functional theory (DFT) calculations were derived from the following studies: chalcocite (Cu$_2$S) (EVANS, 1979), covellite (CuS) (EVANS and KONNERT, 1976), chalcopyrite (CuFeS$_2$) (HALL and STEWART, 1973), villamaninite (CuS$_2$) (KING and PREWITT, 1979), tenorite (CuO)(Wyckoff, 1963), and paramelaconite (CuCu$_2$O$_3$)(Wyckoff, 1963). Atom positions and lattice parameters were held constant during calculations which were performed using the planewave pseudopotential implementation of density functional theory (DFT) as written into the VASP code (Kresse and Furthmuller, 1996; Kresse and Furthmuller, 2003). Exchange and correlation were treated within the Perdew-Burke-Ernzerhof (PBE) functional (Perdew et al., 1996). Additionally, ionic cores were described by the projector-augmented wave (PAW) method (Blochl, 1994; Kresse and Joubert, 1999).

For Cu and Fe, pseudopotentials in which the semicore states (3p, 4s, and 3d) were treated as valence electrons were used. Similarly, the valence shell of S included the 3s and 3p states, while for O the 2s and 2p states were used. The calculations employed a Monkhorst-Pack 2 × 2 × 2 grid for the Brillouin zone sampling in bulk crystal calculations (Monkhorst and Pack, 1976). Energy minimizations were carried out until all forces on atoms were less than 0.0001 eV/Å. Lastly we used Bader analysis to assign charge density to each atom (Henkelman et al., 2006).
4.3 Results

4.3.1 Dissolution experiments: Cu concentrations

In all experiments the amount of Cu leached into solution increased with time, and the rate of Cu release generally increased with higher concentrations of ferric sulfate solutions (Table 4.1). In three of the eight experiments, the reaction proceeded until ~50 mol% Cu was leached from the mineral. In the remaining experiments, the reactions were terminated at different extents of reaction. When the amount of Cu leached approached 50 mol%, the reaction rates significantly slowed (Fig. 4.2). This result is consistent with previous studies demonstrating a decrease in dissolution rates as chalcocite transforms into covellite at ambient temperatures (Walsh and Rimstidt, 1986; Whiteside and Goble, 1986).

4.3.2 Cu isotope results

In each experiment, we measured the Cu isotope compositions ($\delta^{65}$Cu$_{measured\_values}$) of the aqueous eluates as a function of reaction time and of the residual mineral solids (e.g. 12_res) after the conclusion of the run. These data are presented in Table 4.1. Because we did not use the same chalcocite powders for every experiment, we adjusted the Cu isotope values in order to compare one experiment to another ($\delta^{65}$Cu$_{adjusted}$). To do this we assigned the starting $\delta^{65}$Cu value of the mineral powder (min$^\circ$) to be 0‰. The offset between 0‰ and the measured isotope value of min$^\circ$ was then added to the remaining values in the sample set. For the aqueous samples, the $\delta^{65}$Cu$_{adjusted}$ values are the apparent fractionation values ($\Delta_{aq\_min}$). The Cu isotope results, henceforth, will refer to $\delta^{65}$Cu$_{adjusted}$ values, as listed in Table 4.1.
Because our experimental design allowed us to correlate time-resolved X-ray diffraction results with our Cu isotope analyses, we could monitor with high precision the Cu isotope values of the reaction eluate as chalcocite transformed to covellite during dissolution. In Figure 4.3, the X-ray diffraction patterns and the Cu isotope compositions share a temporal axis. As can be seen in Fig. 4.3, $\delta^{65}{\text{Cu}}$ values of the leachate decreased sharply and nonlinearly as chalcocite transformed to covellite through the series of intermediate Cu$_{2-x}$S phases.

Changes in the Cu isotope composition of the leachates were measured for different Fe$^{3+}$ concentrations. For clarity, Fig. 4.4 displays only a sub-sample of the results from experiments using three Fe$^{3+}$ concentrations (12 mM, 6.55 mM, and 0.42 mM). In all cases, $\delta^{65}{\text{Cu}}$ values for the first aliquots of the reactant solution were 2 to 3 ‰ higher than the isotope values of the starting mineral (min$^o$). Thus, as is consistent with prior chalcocite leaching experiments (Mathur et al., 2005), the mineral initially dissolves in the ferric sulfate solution by preferentially leaching $^{65}$Cu rather than $^{63}$Cu. For the lowest concentration of ferric sulfate (0.42mM Fe$^{3+}$), the isotope value for the leached Cu remained constant at ~3‰ for the duration of the experiment. Higher concentrations of ferric sulfate induced a faster rate of Cu release, and when [Fe$^{3+}$] was 12 mM, $\delta^{65}$Cu values of the eluate decreased by more than 3‰ within the first 50 min, becoming negative and settling at -3‰. These results indicate that following the strong pulse of the heavy Cu isotope into the solution, lighter Cu was then preferentially leached by ferric sulfate. For intermediate concentrations of [Fe$^{3+}$] (6.55 mM), $\delta^{65}$Cu in the leachate decreased to negative values but not as quickly as with higher [Fe$^{3+}$] concentrations.

4.3.3 Time-resolved X-ray diffraction

The fractionation of Cu isotopes between the mineral powder and the ferric sulfate solution depended not only on time but on the composition of the solid, as demonstrated in Figure
4.3. The assemblages of co-existing phases for the time-intervals over which eluate aliquots were isotopically analyzed are included for each experiment in Table 4.2. In six of the eight experiments, covellite was generated as the final run product. X-ray diffraction patterns from the two slowest reactions (with 0.42 mM Fe^{3+} and 0.09 mM Fe^{3+}) revealed the presence only of chalcocite and djurleite after 474 min and 167 min of reaction time, respectively. Diffraction patterns collected at sequential time intervals for an experiment in which [Fe^{3+}] = 7.3 mM reveal the complexity of the phase assemblages at any given point in the reaction (Fig. 4.5).

A comparison of the Cu:S ratios calculated using the effluent chemistry with those determined by XRD analysis of the solid reveals a rough correlation (R^2=0.73; Table 4.2). By far the poorest agreement between these independently computed analyses was observed for [Fe^{3+}] = 7.3 mM; in this experiment, the XRD results indicated that only covellite (CuS) was present for most of the reaction interval even though the Cu:S ratio calculated for the eluate was greater than 1:1. We interpret the discrepancy as an experimental error, such that the X-ray beam was not impinging upon the entire sample. In light of the difficulties involved in extracting quantitative measures of the co-existing solid phases, we expect that the Cu:S ratios measured directly from the eluate are significantly more accurate than the diffraction-derived values. Nevertheless, the parallel trends in these analyses support the notion that the transition of the solid phases through the Cu_{2-x}S series is systematically linked to the evolution in solution chemistry.

4.3.4 SEM

SEM analysis revealed that the starting chalcocite powders in our experiments consisted of grains whose diameters ranged from 20 μm to 100 μm. Figure 4.6 shows representative mineral grains after reaction times with ferric sulfate solutions of 2.5 min to 85 min. Even after brief reaction times, the surfaces of the grains exhibited irregular dissolution fissures that
extended from the grain surfaces into the interiors. Consequently, our SEM analyses imply that a concentric “onion-skin” model for Cu diffusion may be overly simplistic.

4.3.5 DFT/Bader results

DFT and Bader calculations were carried out to elucidate the change in valence of Cu as chalcocite transforms to covellite. In the conventional assignment of charge, Cu in chalcocite is monovalent and in covellite is divalent, and the reaction is thus considered to involve an oxidation of Cu. Our Bader calculations, however, indicate that the average atomic charge for Cu in chalcocite is 0.40, whereas that for covellite is 0.51 (Table 4.3). Consequently, these results suggest that each Cu loses only 0.11 electrons as chalcocite transforms into covellite. Furthermore, the charge of Cu in covellite is similar to that of other Cu-sulfide minerals that are thought to consist of reduced Cu (Table 4.3). In Cu oxides (such as tenorite and parameleaconite), our Bader calculations suggest that the formal charge on Cu is close to 1 rather than 2.

4.4 Discussion

4.4.1 Apparent fractionation as a function of extent of reaction

When the fractionation of Cu isotopes was treated simply as a function of time (as in Fig. 4.4), the trends in $\delta^{65}$Cu for experiments with different concentrations of dissolved Fe$^{3+}$ revealed inconsistent behaviors suggesting that time alone was not the critical factor. In contrast, Cu isotopes values of the leachate showed strong agreement between experiments when plotted in terms of reaction progress (Fig. 4.7). We determine the extent of reaction based on the fraction of Cu remaining in the solid. Thus, at the start of the reaction, when only chalcocite is present, the
Cu occupancy in the solid phase is 100%, and the fraction of Cu is assigned a value of 1. Since covellite contains half the starting concentration of Cu in the original chalcocite, once the reaction has proceeded to the point that only covellite is present, the fraction of Cu remaining is designated as 0.5. If all the remaining Cu were leached from covellite, the fraction of Cu remaining would be 0, but due to the extremely slow kinetics of covellite dissolution, our experiments were halted once an extent of reaction of 0.5 was reached. Thus, intermediate phases were assigned a value for fraction of Cu remaining between 1 and 0.5, based on the stoichiometry of the mineral.

For all concentrations of Fe$^{3+}$, at the outset of the experiment $\delta^{65}$Cu in the leachate was approximately 3‰ higher than that of the starting mineral, indicating that relatively heavy Cu ($^{65}$Cu) was preferentially leached into solution. As the reaction progressed and chalcocite transformed into covellite, the $\delta^{65}$Cu values of the leached Cu decreased and eventually became negative by the end of the reaction when only covellite was detected. Beyond this point, relatively lighter Cu ($^{63}$Cu) was preferentially leached into solution. Overall, the $\delta^{65}$Cu values for the residual Cu sulfide powders started at 0‰ and decreased to no less than ~1.50‰ during the reaction.

The apparent isotope fractionation ($\Delta_{\text{aq-min}}^\circ$) measured at the beginning of our leaching experiments (when less than 10 mol% Cu had been leached) ranged from 3.13 ‰ to ~2.00 ‰ (with an error of ±0.25‰). These values are similar to $\Delta_{\text{aq-min}}^\circ$ values from chalcocite dissolution experiments by Mathur et al. (2005), who report an apparent fractionation between abiotically leached Cu and the mineral of 3.40±0.14 ‰. This apparent fractionation of approximately 3 ‰ is consistent with that attributed to the equilibrium fractionation for redox reactions by Ehrlich et al. (2004b) and Zhu et al. (2002), who report that $\Delta_{\text{aq-min}}^\circ$ varies from ~3 to 4‰ when Cu sulfides are oxidized. The isotope data reported here, along with results from previous studies, suggest that during oxidative dissolution of Cu-sulfide minerals, $^{65}$Cu is preferentially released into the
solution while $^{63}\text{Cu}$ remains in the mineral during the first stages of the dissolution. Equilibrium isotope theory provides an explanation for this phenomenon, where isotope fractionation is determined in part by bond stiffness, which is correlated with high oxidation state (Bigeleisen and Mayer, 1947; Schauble, 2004). Based on our DFT and Bader calculations, $\text{Cu}^{2+}$ is less stable within the $\text{Cu}_{2-x}\text{S}$ solids than $\text{Cu}^{1+}$, and we speculate that heavy Cu ($^{65}\text{Cu}$) is thus preferentially released into the solution as $\text{Cu}^{2+}_{\text{aq}}$, since $^{65}\text{Cu}$ is more likely to be associated with the higher valence state, even as a hydrated cation.

4.4.2 Mechanisms for isotope fractionation

While it appears that oxidation strongly influences $\Delta_{\text{aq-min}}$ values when chalcocite is initially leached of Cu, redox effects do not account for the decrease in the apparent fractionation when the reaction progresses beyond its initial stages – in our experiments, when more than 10 mol% of the Cu is leached from chalcocite. Researchers have offered several hypotheses to explain the decrease in apparent Cu isotope fractionation during Cu-sulfide dissolution. These include: 1) adsorption (or co-precipitation) of Cu to secondary phases, such as Fe-oxides; 2) oxidation of the mineral surface by air prior to dissolution; 3) Rayleigh-type distillation processes of the solid, and 4) a complex interplay of several superimposed fractionation events.

The first mechanism – isotope fractionation due to adsorption reactions – seems unlikely to explain our results because of the Eh and pH conditions at which the experiments were run. Isotope fractionation due to adsorption of Cu on to a mineral surface, such as an Fe-oxide, is unlikely during our experiments because of the low pH (pH 2 to 2.5). Studies by Balistrieri et al. (2008) and Pokrovsky et al. (2008) demonstrated that Cu isotopes do fractionate during sorption to Fe-oxyhydroxides; however no Cu was observed in these experiments to sorb below pH 3. In
fact, adsorption of Cu onto Fe-oxides has been shown to be negligible below pH 4 (STUMM and MORGAN, 1996).

Fernandez & Borrok (2009) have argued that the second mechanism -- air oxidation on the mineral surface prior to dissolution -- accounts for the apparent Cu isotope fractionation observed during the leaching of Cu from chalcopyrite. They argue that the isotope fractionation of Cu occurs during the formation of a thin Cu(II)-sulfate and/or Cu(II)-oxide phase that coats the surface of the chalcopyrite prior to the experiment. As the surface layer dissolves, $\Delta_{\text{aq-min}}$ values decrease as a result of simple mixing between the bulk chalcopyrite ($\delta^{65}\text{Cu} \approx 0$) and the diminishing surface layer ($\delta^{65}\text{Cu} \approx 2$).

Our X-ray diffraction data as well as the negative $\delta^{65}\text{Cu}$ values of the leachate lead us to eliminate this hypothesis. First, no secondary oxide or sulfate phases were revealed by XRD. Crystalline phases could theoretically be present below the detection limit of powder XRD methods (2 to 3wt%); however, because 50 mol% Cu was removed when chalcocite transformed to covellite in our experiments, the contribution of Cu from any superficial surface rind would be overwhelmed by Cu from the bulk mineral. Lastly, and perhaps most significantly, a simple mixing model for Cu isotope fractionation in our experiments suggests that the “bulk” mineral $\delta^{65}\text{Cu}$ value would have to be close to -2.5‰ in order to explain the negative $\Delta_{\text{aq-min}}$ values that we observed. Our starting chalcocite, like most primary Cu ore minerals, had an average $\delta^{65}\text{Cu}$ close to 0‰.

With regard to the third mechanism proposed above, the inverse dependence of $\delta^{65}\text{Cu}$ on the fraction of Cu remaining in the solid (Fig. 4.7) might seem suggestive of a Rayleigh-type distillation process. Since the flow-through experimental cell was an open system, removal of heavy Cu ($^{65}\text{Cu}$) with a constant fractionation would have caused continual depletion of heavy Cu from the solid reservoir. Thus, the $\delta^{65}\text{Cu}$ values measured in the leachate over time also would
have decreased as the reaction proceeded. A typical Rayleigh-type model is expressed by the following equations (SHARP, 2007):

$$
\delta_{\text{solid}} = (1000 + \delta_{s}^0) (F^{(\alpha - 1)} - 1) + \delta_{s}^0 \quad (3)
$$

$$
\delta_{\text{liquid}} = (1000 + \delta_{s}^0) (F^{(\alpha - 1)} - 1) + \delta_{l}^0 \quad (4)
$$

where $\delta_{\text{solid}}$ and $\delta_{\text{liquid}}$ are the isotopic compositions of the solid and fluid, $\delta_{s}^0$ and $\delta_{l}^0$ are the initial isotope values of the solid and fluid, $F$ is the fraction of solid reacted, and $\alpha$ is the fractionation factor.

We applied this Rayleigh-type model to our data, however, and it yielded a poor match between the predicted and observed values of $\delta^{65}\text{Cu}$ as a function of residual Cu in the solid. In Figure 4.8, we present calculated curves for $\delta^{65}\text{Cu}$ values produced by Rayleigh distillation in an open system using fractionation factors of 1.002, 1.003, and 1.004 -- values within the range attributed to redox isotope effects (EHRlich et al., 2004b; ZHU et al., 2002). We include data from four representative leachates along with measured $\delta^{65}\text{Cu}$ values for the solid residues calculated for each aliquot. The residue isotope values were calculated based on a mass balance for each time step (Table 4.4):

$$
\delta^{65}\text{Cu}_{\text{residual solid}} = \frac{(\delta^{65}\text{Cu}_{\text{min}} - f_{\text{aq}} \delta^{65}\text{Cu}_{\text{aq}})}{f_{\text{res}}} \quad (5)
$$

where $\delta^{65}\text{Cu}_{\text{min}}$ is the isotopic composition of the initial solid (0‰), $f_{\text{aq}}$ and $f_{\text{res}}$ are the fractions of Cu in the fluid and residual solid, and $\delta^{65}\text{Cu}_{\text{aq}}$ is the measured isotopic composition of the fluid.

As can be seen clearly in Figure 4.8, $\delta^{65}\text{Cu}$ values for the fluid decreased more rapidly than is predicted by a Rayleigh-type model. Furthermore, when the extent of reaction approached 0.5, the measured $\delta^{65}\text{Cu}$ value for the fluid actually was lower than that of the solid for higher [Fe$^{3+}$] concentrations and faster reaction rates. A Rayleigh-type model would require that, in such cases, $\delta^{65}\text{Cu}$ values for the solid must be more negative than those for the fluid throughout
the entire reaction. Consequently, a constant isotope fractionation combined with distillation cannot fully capture the behavior that we observed in our experiments.

The elimination of the first three hypotheses leaves the fourth possibility: the Cu isotope fractionation that occurs when chalcocite dissolves is the effect of multiple processes whose effects are superimposed. Previous workers have suggested that as Cu is oxidized and leached from the surface of chalcocite and that Cu from the interior diffuses to the surface to fill the resultant Cu vacancies (BRENNET et al., 1974; FISHER et al., 1992; KING et al., 1975; RUIZ et al., 1998; THOMAS et al., 1967). Thus, as Cu is leached from a crystal of chalcocite, the mineral develops a compositional gradient with respect to Cu such that the Cu:S ratio in the core is higher than that of the leached surface layer. When ferric sulfate oxidatively dissolves chalcocite, we assume that Fe$^{3+}$ adsorbs to the surface of the mineral grain. Cu$^{+}$ is oxidized to Cu$^{2+}$, which is released into solution. Monovalent Cu from the interior diffuses to fill the vacancy, creating non-stoichiometric compositions within the crystal, such that a Cu$_{2-x}$S series of intermediate phases appears, with x decreasing towards the rim. Once the entire crystal is transformed to covellite (CuS), the reaction slows. Whereas previous authors have proposed this concentric “onion skin” as a conceptual model, in reality it is more complex. Based on the solution fractures of reacted grains observed in our SEM results, we propose that individual grains exhibit geometrically convoluted reaction zones, as shown diagramatically in Figure 4.9. Nevertheless, during the reaction, each crystal represents a composite of multiple phases.

4.5 Model

Box models have proved useful in simulating geochemical fluxes and changes in isotope ratios in many geological systems (DE LA ROCHA and DEPAOLO, 2000; DEPAOLO, 2004; FANTLE, 2010; FANTLE and DEPAOLO, 2005). We have used the STELLA software package to
simulate the time-dependent dissolution flux of Cu during chalcocite dissolution in terms of mass and isotopic composition (HANNON and RUTH, 1994; PETERSON and RICHMOND, 1996). A time-dependent model, instead of a steady-state approach, is preferred in this situation due to the nature of the reaction: most of the Cu is released into solution during the transformation of transient mineral phases. Differential equations were developed to incorporate the combined effects of multiple fractionation processes, such as solid-state diffusion and surface oxidation. These equations are presented below and were solved within STELLA using Euler’s method.

4.5.1 Box model definitions

The conceptual framework for the dissolution mechanism and development of leached layers involves three distinct reservoirs: a solid, a residual solid, and fluid (Fig. 4.10). At $t = 0$, all of the Cu is located in the solid reservoir. As the model runs, the Cu flows into either the fluid reservoir or the residual solid reservoir. The flux of Cu from the solid into the fluid ($J_{s,f}$) represents the Cu that is leached into solution from the mineral grain.

At the same rate, Cu moves from the solid into residual solid ($J_{s,rs}$). This flux represents the movement of Cu that occurs during the mineral phase transformation when Cu diffuses throughout the mineral to form new Cu-S bonding arrangements. The reconfiguration of Cu-S bonds occurs as chalcocite forms into transitional phases and eventually into covellite (GOBLE, 1985).

The reaction stops once the solid reservoir is depleted. At this point half the total Cu has moved into the fluid and the other half has formed as a new mineral in the residual solid. As a simplifying assumption, we presume that each reservoir is associated with a distinct Cu isotope composition expressed as a ratio of $^{65}$Cu to $^{63}$Cu ($R_i$) and mass of Cu ($m_i$ in $\mu$g).
The isotopic composition in each reservoir can be expressed in terms of the moles of nuclides ($N$).

$$R = \frac{N^{65}}{N^{63}}$$ (6)

The isotope ratio of the solid is represented by $R_s$, that for the residual solid by $R_{rs}$, and that for the fluid reservoir by $R_f$. The mass flux of Cu from the solid to the fluid also has an associated ratio of $^{65}$Cu to $^{63}$Cu, called $R_{s-f}$. Similarly, the mass flux of Cu from the solid to the residual solid has an associated isotope ratio: $R_{s-rs}$ . Lastly, the terms $\alpha_{s-f}$ and $\alpha_{s-rs}$ describe the isotopic fractionation of Cu during oxidation of Cu from the solid into solution and the isotopic fractionation during the solid state processes that occur as the solid transforms into the leached layer. The relationships among these terms is expressed in the following equations.

$$\alpha_{s-rs} = \frac{R_{s-rs}}{R_s}, \quad R_{s-rs} = \alpha_{s-rs} R_s, \quad \text{with} \quad R_{s-rs} = \left( \frac{J^{65}_{s-rs}}{J^{63}_{s-rs}} \right)$$ (7, 8, 9)

and

$$\alpha_{s-f} = \frac{R_{s-f}}{R_s}, \quad R_{s-f} = \alpha_{s-f} R_s, \quad \text{with} \quad R_{s-f} = \left( \frac{J^{65}_{s-f}}{J^{63}_{s-f}} \right)$$ (10, 11, 12)

Because there is no dominant nuclide among the stable isotopes of Cu, we must consider the flux of both $^{65}$Cu and $^{63}$Cu during dissolution and precipitation. We will need to rewrite the nuclide specific equations involving the flux of $^{63}$Cu ($J_{i}^{63}$) in order to consider the total flux of both Cu nuclides ($J_{i}^{Tot}$) as follows:

$$\frac{J_{i}^{Tot}}{J_{i}^{63}} = \frac{N^{63} + N^{65}}{N^{63}} = 1 + \frac{N^{65}}{N^{63}} = 1 + R_i$$ (13)
Therefore,

\[ J_{s \rightarrow r_s}^{63} = \frac{J_{s \rightarrow r_s}^{Tot}}{1 + R_{s \rightarrow r_s}} \]  \hspace{1cm} (14)

and

\[ J_{s \rightarrow f}^{63} = \frac{J_{s \rightarrow f}^{Tot}}{1 + R_{s \rightarrow f}} \]  \hspace{1cm} (15)

We also consider equations that describe the total Cu in each reservoir \( N_{i \, Tot} \) that we derive from the nuclide specific equations.

\[ \frac{N_{i \, Tot}^{63}}{N_{i}^{63}} = \frac{N_i^{63} + N_i^{65}}{N_i^{63}} = 1 + \frac{N_i^{65}}{N_i^{63}} = 1 + R_i \]  \hspace{1cm} (16)

The goal of this analysis is to model the elemental and isotopic composition of the fluid, residual solid, and solid \((R_i)\). We define our isotope ratios as the following

\[ R_i = \frac{N_i^{65}}{N_i^{63}} = \frac{f}{g} \]  \hspace{1cm} (17)

and use the quotient rule to derive our differential equations.

\[ \left( \frac{f}{g} \right)' = \frac{g f' - f g'}{g^2} \]  \hspace{1cm} (18)

4.5.1.1 Differential equation for \( R_s \): the Solid

The nuclide-specific differential equations that describe the change in the isotope ratio \((R_s)\) of the solid over time are:

\[ \frac{dN_i^{63}}{dt} = -J_{s \rightarrow f}^{63} - J_{s \rightarrow r_s}^{63} \quad \text{and} \quad \frac{dN_i^{65}}{dt} = -J_{s \rightarrow f}^{65} - J_{s \rightarrow r_s}^{65} \]  \hspace{1cm} (19, 20)
We substitute equations 9 and 12 into 20 and get:

\[
\frac{dN_{65}^s}{dt} = -(R_{s \rightarrow f} J_{s \rightarrow f}^{63}) - (R_{s \rightarrow r3} J_{s \rightarrow r3}^{63}) \tag{21}
\]

Expressing the change in the isotopic ratio of the reservoir \( R_s \) with time as

\[
\frac{dR_s}{dt} = \left( \frac{N_{65}^s}{N_{63}^s} \right) \tag{22}
\]

we then use equation 18 to write the following:

\[
\frac{dR_s}{dt} = \frac{dN_{65}^s}{dt} \frac{N_{63}^s}{N_{65}^s} = \frac{dN_{65}^s}{dt} \frac{dN_{63}^s}{dt} \tag{23}
\]

Equation 23 simplifies to the following:

\[
N_{65}^s \frac{dR_s}{dt} = \frac{dN_{65}^s}{dt} - R_s \frac{dN_{63}^s}{dt} \tag{24}
\]

Using the relationships in equation 19 and 20, and then again in 7, 8, 9, and 10, 11, 12 we can rewrite equation 24 as:

\[
N_{65}^s \frac{dR_s}{dt} = \left( \alpha_{s \rightarrow f} R_s J_{s \rightarrow f}^{Tot} \right) - \left( \alpha_{s \rightarrow r3} R_s J_{s \rightarrow r3}^{Tot} \right) - R_s \left( \frac{J_{s \rightarrow f}^{Tot}}{1 + \alpha_{s \rightarrow f} R_s} - \frac{J_{s \rightarrow r3}^{Tot}}{1 + \alpha_{s \rightarrow r3} R_s} \right) \tag{25}
\]

Finally, we account for the total flux \( J_{i \rightarrow f}^{Tot} \), and total number of nuclides in a reservoir \( N^i_{Tot} \) by substituting the proper equations:

\[
\frac{dR_s}{dt} = \left[ \left( \alpha_{s \rightarrow f} R_s J_{s \rightarrow f}^{Tot} \right) - \left( \alpha_{s \rightarrow r3} R_s J_{s \rightarrow r3}^{Tot} \right) - R_s \left( \frac{J_{s \rightarrow f}^{Tot}}{1 + \alpha_{s \rightarrow f} R_s} - \frac{J_{s \rightarrow r3}^{Tot}}{1 + \alpha_{s \rightarrow r3} R_s} \right) \right] \frac{1 + R_s}{N^i_{Tot}} \tag{26}
\]

\[
\frac{dR_s}{dt} = \left[ \left( \frac{R_s J_{s \rightarrow f}^{Tot}}{1 + \alpha_{s \rightarrow f} R_s} \right) - \left( \alpha_{s \rightarrow f} R_s J_{s \rightarrow f}^{Tot} \right) \right] \frac{1 + R_s}{N^i_{Tot}} \tag{27}
\]

and
\[
\frac{dR_s}{dt} = \left[ \left( R_s J_{s \rightarrow r\bar{s}}^{\text{Tot}} \right) + \left( \alpha_{s \rightarrow r\bar{s}} R_s \frac{J_{s \rightarrow r\bar{s}}^{\text{Tot}}}{1 + \alpha_{s \rightarrow r\bar{s}} R_s} \right) \right] \left[ 1 + \frac{R_s}{N_s^{\text{Tot}}} \right] \quad (28)
\]

This results in a time-dependent equation describing the isotope ratio of the solid.

### 4.5.1.2 Differential equation for \(R_{rs}: the\ Residual\ Solid\)

Using a similar treatment we can solve for a time-dependent equation describing the isotope ratio of the residual solid.

\[
\frac{dN_r^{63}}{dt} = J_{s \rightarrow r\bar{s}}^{63} \quad \text{and} \quad \frac{dN_r^{65}}{dt} = J_{s \rightarrow r\bar{s}}^{65} \quad (29, 30)
\]

\[
N_r^{63} \frac{dR_{rs}}{dt} = \frac{dN_r^{63}}{dt} - R_{rs} \frac{dN_r^{63}}{dt}
\]

\[
N_r^{63} \frac{dR_{rs}}{dt} = \alpha_{s \rightarrow r\bar{s}} R_s \left( \frac{J_{s \rightarrow r\bar{s}}^{\text{Tot}}}{1 + \alpha_{s \rightarrow r\bar{s}} R_s} \right) - R_{rs} \left( \frac{J_{s \rightarrow r\bar{s}}^{\text{Tot}}}{1 + \alpha_{s \rightarrow r\bar{s}} R_s} \right) \quad (32)
\]

This gives a time-dependent equation describing the Cu isotope ratio of the residual solid:

\[
\frac{dR_{rs}}{dt} = \left[ \alpha_{s \rightarrow r\bar{s}} R_s \left( \frac{J_{s \rightarrow r\bar{s}}^{\text{Tot}}}{1 + \alpha_{s \rightarrow r\bar{s}} R_s} \right) - R_{rs} \left( \frac{J_{s \rightarrow r\bar{s}}^{\text{Tot}}}{1 + \alpha_{s \rightarrow r\bar{s}} R_s} \right) \right] \left[ 1 + \frac{R_{rs}}{N_{rs}^{\text{Tot}}} \right] \quad (33)
\]

### 4.5.1.3 Differential equation for \(R_f: the\ Fluid\)

Finally, we can also develop an equation that describes the change in isotopic ratio of the fluid over time using a similar treatment:

\[
\frac{dN_f^{63}}{dt} = J_{s \rightarrow f}^{63} \quad \text{and} \quad \frac{dN_f^{65}}{dt} = J_{s \rightarrow f}^{65} \quad (34)
\]
\[
N_f^{65} \frac{dR_f}{dt} = dN_f^{65} \frac{dN_f}{dt} - R_f dN_f^{65} 
\]

(35)

\[
N_f^{65} \frac{dR_f}{dt} = J_{s \rightarrow f}^{65} - R_f J_{s \rightarrow f}^{65} 
\]

(36)

\[
N_f^{65} \frac{dR_f}{dt} = R_{s \rightarrow f} J_{s \rightarrow f}^{65} - R_f J_{s \rightarrow f}^{65} 
\]

(37)

\[
N_f^{65} \frac{dR_f}{dt} = R_{s \rightarrow f} \left( \frac{J_{s \rightarrow f}^{\text{Tot}}}{1 + R_{s \rightarrow f}} \right) - R_f \left( \frac{J_{s \rightarrow f}^{\text{Tot}}}{1 + R_{s \rightarrow f}} \right) 
\]

(38)

\[
N_f^{65} \frac{dR_f}{dt} = \alpha_{s \rightarrow f} R_s \left( \frac{J_{s \rightarrow f}^{\text{Tot}}}{1 + \alpha_{s \rightarrow f} R_s} \right) - R_f \left( \frac{J_{s \rightarrow f}^{\text{Tot}}}{1 + \alpha_{s \rightarrow f} R_s} \right) 
\]

(39)

\[
\frac{dR_f}{dt} = \left[ \alpha_{s \rightarrow f} R_s \left( \frac{J_{s \rightarrow f}^{\text{Tot}}}{1 + \alpha_{s \rightarrow f} R_s} \right) - R_f \left( \frac{J_{s \rightarrow f}^{\text{Tot}}}{1 + \alpha_{s \rightarrow f} R_s} \right) \right] \left[ 1 + R_f \right] 
\]

(40)

The STELLA model configuration is designed as a closed system where the fluid reservoir accumulates Cu. In order to compare the model result to a flow-through geometry, consistent with our experimental protocol, we must instead calculate the \( \delta^{65} \text{Cu} \) of the experimental results as though the experiments were conducted in a closed, batch-style reaction using the following equation:

\[
\delta^{65} \text{Cu}_{\text{fluid batch}} = \sum_{i=1}^{n} \left( f_{aq} \delta^{65} \text{Cu}_{aq} \right)_{\text{aliquot } i} 
\]

(41)

where \( f_{aq} \) is the mass fraction of Cu leached into solution compared to the accumulated Cu in solution at each time step (Table 4.4).
4.5.1.4 Model inputs

In our modeling, we used five inputs: 1) initial mass of Cu, 2) a rate constant for the release of Cu from the solid into fluid, 3) a rate constant for Cu moving from the solid into the residual solid, 4) a fractionation factor controlling isotope fractionation between the solid and the fluid, and 5) a fractionation factor describing the isotope fractionation between the solid and the residual solid.

In order to model isotopic composition of the fluid and residual solid we constrained the Cu fluxes by modeling the total Cu leached into the fluid over time. We used the following equation to describe the flux of Cu from the solid:

\[ J = k \cdot m \]  

(42)

where the \( k \) is the rate constant and \( m \) is the mass of Cu in the solid reservoir. We set \( m \) to be the initial mass of Cu in the solid that we measured (Table 4.1). During the model runs, we then varied both \( m \) and \( k \) in each experiment until the model fit the measured values for accumulated Cu (\( \mu \)g) in the fluid and for the Cu:S ratio in the solid (e.g. Fig. 4.11 a and b). Once we constrained the fluxes, we varied the fractionation factors in the model. We assume that fractionation factor between the solid and fluid (\( \alpha_{s,f} \)) is due to redox isotope effects so we set those values close to 1.003 (EHRLICH et al., 2004a; ZHU et al., 2000). We then adjust the fractionation factor between the solid and the residual solid (\( \alpha_{s,rs} \)) until the model achieves a good fit by visual inspection for the \( \delta^{65} \)Cu of the fluid and of the bulk solid (e.g. Fig. 4.11 c and d).
4.5.2 Box model results

4.5.2.1 Model results: Cu fluxes

We present the results of our box models in Figures 4.11 to 4.18. Each figure includes four graphs that compare our measured values with two types of model results – first, a model in which fractionation is based only on the oxidation of Cu and thus employs a simple Rayleigh distillation between solid and fluid; and second, as described in the preceding section, a model that additionally incorporates a residual solid reservoir (or leached layer), which mediates the isotopic fractionation of Cu as the leached layer develops. The graphs represent the time-dependent behavior of: a) the accumulated mass of Cu in the solution; b) the Cu:S ratio of the bulk solid; c) the δ⁶⁵Cu values of the solution; and d) the δ⁶⁵Cu values of the bulk solid.

Table 4.5 lists the model parameters that were used to best fit the Cu mass flux and Cu:S composition of the solid. To optimize the fit, we adjusted the initial mass of Cu in the solid. In some cases the modeled initial mass values differed slightly (<7 wt%) from those we report in Table 4.1; this discrepancy most likely arises from analytical error. In addition, we adjusted the model constants controlling the rate of Cu release from the solid to the fluid ($k_{s-f}$) and the solid to the residual solid ($k_{s-rs}$). We set these rate constants to be equal because the rate of Cu release from the solid into the fluid is equal to the rate of mineral transformation within the solid (i.e. decreasing Cu:S). By visual inspection, we were able to achieve good model fits for data for the accumulated mass of Cu and the Cu:S ratio of the solid over time (Fig. 4.11(a,b) to 4.18(a,b)).
4.5.2.2 Model results: Cu isotope fractionation factors

Once the mass of Cu and the Cu:S composition of the solid were accurately modeled, we adjusted the fractionation factor associated with dissolution Cu from the solid into the fluid (\(\alpha_{s-f}\)) and the fractionation of Cu associated with the transformations within the leached layer, or residual solid (\(\alpha_{s-rs}\)), until the model best fit the measured values for \(\delta^{65}\)Cu of the fluid and of the bulk solid (Figure 4.11 (c, d) to 4.18 (c,d)). The actual \(\delta^{65}\)Cu values are for the fluid and solid are listed in Table 4.4.

The solid lines in Figures 4.11(c,d) to 4.18 (c,d) are the model results that represent the contribution of two isotope effects: 1) redox fractionation during the dissolution of Cu from the solid to the fluid (\(\alpha_{s-f}\)); and 2) fractionation that accompanied the transformation of the starting solid to the residual solid (\(\alpha_{s-rs}\)). Data were best fit with \(\alpha_{s-f}\) values between 1.0022 and 1.00325 (Table 4.4). This range is consistent with reported fractionation factors that are associated with changes in oxidation state (EHRLICH et al., 2004a; ZHU et al., 2000). The fractionation factors associated with the flux of Cu from the mineral phase transition (\(\alpha_{s-rs}\)) varied between 1.001 to 1.003 (Table 4.4).

To test whether fractionation due to redox processes alone could model the data, we set \(\alpha_{s-rs}\) equal to 1.0000, meaning that no additional fractionation occurred during the transformation from the starting chalcocite to the \(\text{Cu}_{2-x}\text{S}\) intermediate phases that characterize the leached layer. These results are represented by a dashed line in Figures 4.11(c,d) to 4.18 (c,d), and these model results diverged from the previous model results (solid line) in all cases but three. We interpret this disparity as indicating that redox fractionation alone, or any mechanism for which constant fractionation is combined with distillation, cannot completely describe the data that we measured. To achieve the best fit of the model to our data, we were constrained to include in our model a
fractionation associated with the flux of Cu from the solid to the residual solid, and the fractionation factor for this flux had to be slightly greater than 1.

4.5.3 Model interpretation

If our models are correct, then the apparent isotope fractionation of Cu during the oxidative dissolution of chalcocite represents the sum of several fractionation mechanisms. The overall decrease in $\delta^{65}\text{Cu}$ values as measured in aliquots of solution sampled at distinct time intervals following reaction with chalcocite can be explained by preferential oxidation of $^{65}\text{Cu}$ at the surface of the mineral grain, thereby depleting the reservoir of $^{65}\text{Cu}$ within the CuS solid. In order for redox isotope effects to be relevant during chalcocite/covellite dissolution the valence of Cu in the solid must be 1+ throughout the entire reaction. The DFT/Bader calculations provide support for previous studies that suggest that the valence of Cu in covellite (CuS) is 1+ (GOH et al., 2006; LUTHER et al., 2002). While the DFT/Bader results do not assign an integer charge to Cu in covellite, the results do suggest that there is little difference between the charge of Cu in chalcocite and in covellite. This supports the idea that redox isotope effects can influence Cu isotope fractionation as chalcocite transitions into covellite.

However, Raleigh-type processes alone cannot account for the high rapidity with which $\delta^{65}\text{Cu}$ diminished as a function of reaction progress. To explain the anomalously rapid decrease, we suggest that as vacancies develop when Cu is leached from the mineral, $^{65}\text{Cu}$ preferentially forms bonds with S as the structure reconfigures in the transforming leached layer, thus leaving $^{63}\text{Cu}$ to become available to dissolve into solution. In terms of the box model, when $\alpha_{rs-rs}$ is $\sim 1.001$, $^{65}\text{Cu}$ preferentially moves into the residual solid leaving behind a lighter Cu in the reservoir to then leach into solution. The magnitude of this alpha value is close to what has been reported for fractionation attributed to bonding in Cu chloro-complexes ($\alpha = 1.00075$, (ZHU et al., 2011).
Calculations by Seo et al. (2007) suggest a theoretical range for $\alpha$ between 1.00073 to 1.00195 at 25°C when fractionation occurs between $^{65}$Cu$^+$ and $^{63}$Cu$^+$ in chloro- and sulfo-complexes.

### 4.6 Implications

The results from the isotope and XRD analysis combined with modeling suggest that Cu isotopic fractionation during chalcocite dissolution is intrinsic to properties of the mineral itself. Consequently, as the mineralogy changes during the reaction, the $\delta^{65}$Cu values of the leached fluid will change in a predictable manner (Fig. 4.7). These results are consistent with experiments monitoring the dissolution of bornite and sulfide-rich rock (Fig. 4.19), suggesting that the large variation of $\delta^{65}$Cu values measured in low-temperature environments can in part be attributed to multiple fractionation processes that control isotope behaviors during oxidative dissolution. Indeed, the relationship between apparent fractionation and reaction progress may prove useful as a field indicator for determining the extent to which Cu has leached from an ore body or from mine tailings.

### 4.7 References


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Table 4.1. Chemistry and isotopic composition of chalcocite leaching experiments.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Collection (minutes)</th>
<th>[Fe] (mM)</th>
<th>Cu(III) solid (ppm)</th>
<th>Cu(I) w. pyrite (ppm)</th>
<th>volume (L)</th>
<th>mass% Cu leached</th>
<th>Cu (%)</th>
<th>extent of reaction</th>
<th>$\delta^{13}$Cu (‰) measured values</th>
<th>$\Delta^{13}$Cu (‰)</th>
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<td>1.25</td>
<td>3.07</td>
<td>0.28</td>
<td>0.14</td>
<td>3</td>
<td>0.03</td>
<td>-0.60</td>
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Table 4.2. XRD results.

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<td>0.6_6</td>
<td>cc, di</td>
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</table>

\(^a\) cc=chalcedonite, di=bideite, dg=diopside, an=anhydrite, rj=ronzolite, s=spallanstrumite, p=pyroxenite, cv=cyonmorevitite

\(^b\) Cu S = [µg Cu min\(^{-1}\)] - v-bottom, µg Cu in solution/µg Cu min\(^{-1}\) x 2.

\(^c\) see methods for Cu S calculation.
Table 4.3. Average atomic charge.

<table>
<thead>
<tr>
<th>Mineral name</th>
<th>Crystallographic information file</th>
<th>Chemical formula</th>
<th>Cu</th>
<th>Fe</th>
<th>S</th>
<th>Cu</th>
<th>Cu</th>
<th>O</th>
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</tr>
<tr>
<td>sulfides</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>chalcocite</td>
<td>(Evans, 1979)</td>
<td>CuS</td>
<td>0.40</td>
<td>-</td>
<td>-0.81</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
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<td>(Evans and Konnert, 1976)</td>
<td>CuS</td>
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<td>-</td>
<td>-0.51</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>(Hall and Stewart, 1973)</td>
<td>CuFeS&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.57</td>
<td>0.96</td>
<td>-0.77</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>(King and Prewitt, 1979)</td>
<td>CuS&lt;sub&gt;2&lt;/sub&gt;</td>
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<td>oxides</td>
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<td>tenorite</td>
<td>(Wyckoff, 1963)</td>
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<td>-</td>
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<tr>
<td>parameilaconite</td>
<td>(O'Keefe and Bovin, 1978)</td>
<td>CuCu₂O₃</td>
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<td>-</td>
<td>-</td>
<td>0.56</td>
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Table 4.4. Calculating batch and solid $\delta^{65}\text{Cu}$ values

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\delta^{65}\text{Cu}$ (%o HDO) batch</th>
<th>$\delta^{65}\text{Cu}$ (%o solid calculated)</th>
<th>$\delta^{65}\text{Cu}$ (%o solid adjusted)</th>
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* not measured
1 see Eq. 41
2 see Eq. 6
3 see Table 1
Table 4.5. Isotope model parameters.

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<tr>
<th>Sample Set</th>
<th>$k_{(s-f)}$</th>
<th>$k_{(s-rs)}$</th>
<th>$\alpha_{(s-f)}$</th>
<th>$\alpha_{(s-rs)}$</th>
<th>Initial solid Cu mass (µg)</th>
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<td>132_mM_Fe(III)</td>
<td>0.070</td>
<td>0.070</td>
<td>1.0030</td>
<td>1.00125</td>
<td>7174</td>
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<tr>
<td>12_mM_Fe(III)</td>
<td>0.050</td>
<td>0.050</td>
<td>1.0030</td>
<td>1.0010</td>
<td>3432</td>
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<td>7.3_mM_Fe(III)</td>
<td>0.007</td>
<td>0.007</td>
<td>1.0030</td>
<td>1.0010</td>
<td>5300</td>
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<td>6.8_mM_Fe(III)</td>
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<td>0.012</td>
<td>1.0025</td>
<td>1.0010</td>
<td>3000</td>
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<td>0.012</td>
<td>1.0030</td>
<td>1.0030</td>
<td>5000</td>
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<tr>
<td>6.55_mM_Fe(III)</td>
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<td>0.010</td>
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<td>1.0010</td>
<td>3900</td>
</tr>
<tr>
<td>0.42_mM_Fe(III)</td>
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<td>0.00035</td>
<td>1.00325</td>
<td>1.0010</td>
<td>11000</td>
</tr>
<tr>
<td>0.09_mM_Fe(III)</td>
<td>0.00011</td>
<td>0.00011</td>
<td>1.0030</td>
<td>1.0010</td>
<td>16700</td>
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</table>
Figure 4.1  Published Cu isotope measurements (δ⁶⁵Cu ‰, n = 981). Two histograms display Cu isotope measurements of solids from high-temperature (see text for citations) and low-temperature Cu deposits (see text for citations). Below, appear Cu isotope measurements of waters from acid mine drainage (AMD) streams (a=BALISTRIERI et al., 2008; BORROK et al., 2008; BORROK et al., 2007; KIMBALL et al., 2007), rivers, estuaries, and seawater (b= VANCE et al., 2008) Laboratory dissolution experiments appear on the lower panel showing the range of apparent fractionation factors (Δaq-min ‰) measured between dissolved Cu and the initial solid mineral in several experiments (c = (WALL et al., 2011b); d = (FERNANDEZ and BORROK, 2009); e =(KIMBALL et al., 2009); f = (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.
Figure 4.2 The mol% Cu leached from chalcocite vs. time using different concentrations of Fe(III).
Figure 4.3 Time-resolved synchrotron X-ray diffraction (XRD) patterns display as a function of time, correlated with Cu isotope values ($\delta^{65}$Cu ‰) of leached Cu$_{aq}$ during chalcocite oxidative dissolution using 12mM Fe(III). XRD patterns reveal chalcocite transforming first into intermediate phases and then to covellite.
Figure 4.4 $\delta^{65}\text{Cu}$ values of leached Cu over time. The term “min$^o$” is the Cu isotope value of the starting mineral.
Figure 4.5 X-ray diffraction patterns showing the phases that occur during chalcocite dissolution. Peaks in the XRD patterns are best fit by powder diffraction files for three intermediate phases (djurleite, roxbyite, and yarrowite) as chalcocite transforms to covellite using [Fe] = 7.3 mM solutions.
Figure 4.6 SEM images of chalcocite grains reacted with 0.01M ferric sulfate solutions. The grain in panel $a$ was reacted for 2.5 minutes, while the grains in panel $b$ and $c$ were reacted for 85 minutes.
Figure 4.7 Isotope composition of leached Cu (symbols) and mineral residues (dash) versus the fraction of Cu remaining in the solid.
Figure 4.8 Cu isotope values of leachate and residues from experiments that ended at covellite. Rayleigh-type models are plotted for the fluid (dashed lines) and solid (solid lines) with various fractionation factors ($\alpha$).
Figure 4.9 Chalcocite dissolution mechanism. The diagram on the left show the development of a leached layer of intermediate Cu-sulfide phases and covellite as Cu$^{+}$ is oxidized to Cu$^{2+}$ and dissolves. We speculate that the actual leached layer that develops is more complex as represented by the reaction sequence (right).
Figure 4.10 Isotope box model schematic.
Figure 4.11 Box model results for experiment using 132 mM Fe(III). Actual data appear as symbols, the solid and dashed lines are model results.

Model fractionation factors

\[ \alpha_{(S-f)} = 1.0030 \quad \alpha_{(S-rS)} = 1.00125 \]
Figure 4.12 Box model results for experiment using 12 mM Fe(III). Actual data appear as symbols, the solid and dashed lines are model results.

\[ \alpha_{(S - f)} = 1.0030 \quad \alpha_{(S - r_S)} = 1.00100 \]
Figure 4.13 Box model results for experiment using 7.3 mM Fe(III). Actual data appear as symbols, the solid and dashed lines are model results.

\[
\alpha_{(S-f)} = 1.0030 \quad \alpha_{(S-rS)} = 1.00100
\]
Figure 4.14 Box model results for experiment using 6.8 mM Fe(III). Actual data appear as symbols, the solid and dashed lines are model results.
Figure 4.15 Box model results for experiment using 6.56 mM Fe(III). Actual data appear as symbols, the solid and dashed lines are model results.
Figure 4.16 Box model results for experiment using 6.55 mM Fe(III). Actual data appear as symbols, the solid and dashed lines are model results.
Figure 4.17 Box model results for experiment using 0.42 mM Fe(III). Actual data appear as symbols, the solid and dashed lines are model results.

\[ \alpha_{(S - f^*)} = 1.00325 \quad \alpha_{(S - rs)} = 1.00100 \]
Figure 4.18 Box model results for experiment using 0.09 mM Fe(III). Actual data appear as symbols, the solid and dashed lines are model results.
Figure 4.19 The apparent fraction of Cu isotopes between aqueous and mineral phases during the dissolution of chalcocite, bornite, and sulfide-rich rocks.
## Appendix A

### Butte, MT Cu Isotope Study

**Table A.1.** Cu isotope data from Butte, MT

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<th>Sample</th>
<th>$\delta^{65}$Cu (%) $^a$</th>
<th>sample type</th>
<th>Latitude</th>
<th>Longitude</th>
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<tr>
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<td>water</td>
<td>46.016</td>
<td>-112.510</td>
</tr>
<tr>
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<td>water</td>
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<td>BP - 250'</td>
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<td>BP - 500'</td>
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<td>water</td>
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<td>BP - 650'</td>
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<td>water</td>
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<td>BP - 780'</td>
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<tr>
<td>Water adjacent to Berkeley Pit</td>
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$^a$ $\delta^{65}$Cu = \frac{[65Cu/64Cu]_{sample}}{([65Cu/64Cu]_{standard})} \times 1000, \ 2\sigma = \pm 0.14\% \ $
Figure A.1 Location of sampling sites from the Butte Cu isotope study.
Figure A.2 Cross section of Butte Mining District. Cu isotope values are express as $\delta^{65}$Cu (see Table A.1). Mineral specimens are from the Anaconda ore collection.
Figure A.3  Cu isotope values from the Berkeley Pit and surrounding ground water. Isotope values are expressed as $\delta^{65}\text{Cu} \text{‰}$ (see Table A.1). The ground water divide is located between the Berkeley Pit and Silver Bow Creek. Ground water contours are adapted from Gammons and Madison 2006.
Figure A.4 Cu isotope values downstream of the Butte Mining District. Isotope values are expressed as $\delta^{65}$Cu ‰ (see Table A.1).
Appendix B

“Slices of Time: Time Scales of the Environment” Script

The following is the script from the 3-D movie developed by the Center for Environmental Kinetics Analysis. This script was co-written by Tim Fischer, Andy Wall, Susan Anderson, and Charles Anderson. The movie can be downloaded at the following web site:

http://www.ceka.psu.edu/slices_of_time/

Slices of Time

1: Western Pennsylvania coal country.
A pristine stream flows through the forested landscape…
2:
Cut of just stream
…Wait…pristine? The rocks are orange
1:
Yeah… This stream has been affected by something call Acid Mine Drainage.
… actually it’s quite toxic.
2:
That’s what I thought. In abandoned coal mines water flows over rocks producing acidic water. This releases iron into the stream…
1:
…and that explains the orange. But that’s only a small part of the story…there is much more than meets the eye.
2:
To help understand this polluted stream we are going to take a journey through time. We will explore processes in our environment that take millions of years to occur as well as those that happen millions of times a second… all of which are related, in some way, to this scene.
1:
On our journey, we will use THESE clocks to help us keep track of time. Each of these clocks accurately represents time. Even the clocks that appear to be still are in fact moving…
2:
…while some clocks are moving so quickly, they are blurred.
1:
Let’s highlight the seconds clock
The seconds clock is rotating one revolution per second.
2:
The microsecond clock is moving 1 million times faster… that’s why it’s blurred.
1:
Nanoseconds…
Each clock is rotating 1000 times faster than the one before it.…
2:
Picoseconds….Femtoseconds…
1:
and
Attoseconds.
2:
This clock is revolving 1 trillion million times per second. That’s a 1 with 18 zeros after it. That’s really fast.
1:
Now that we know about the clocks, let’s go back to the stream. We’ll start by zooming into the source of acid mine drainage pollution, the mineral pyrite. You might know this as fools gold. It’s common in coal country.
2:
The break down of pyrite causes the pollution. So what we are going to do is to slow things down and take a really close look at how that happens. The first step is to take a microscopic look at the surface of the pyrite crystal.

Microseconds
1:
Here is the surface of the mineral pyrite breaking down. This happens over microseconds. Viewed at this slower speed we can actually see pits form and grow larger.
2:
But to really see what’s going on we need to look even closer. We need to see what’s going on with the atoms.
1:
And to do this we have to zoom in again and slow down things even more. We need to slow down another 1000 times. Notice the changing clocks.

Nanoseconds
2:
Here we’re looking at a group of atoms, the red and white water molecules are attacking the surface of the pyrite.
1:
It only takes nanoseconds to release an Fe atom from the pyrite. That’s really fast, a billionth of a second. But because atoms are so small, this has to happen over and over, to break down enough of the surface to cause the pits that we just saw. This eventually leads to the orange rocks in our polluted stream.
2:
In order to attack the pyrite the water has to get to the mineral surface. To understand this we need to slow things down another 1000 times and take a wider view.

Picosecond
1:
At picoseconds, a 1 trillionth of a second, we can see the water moving around the pyrite. Remember we have slowed things down so we can actually see it.
2:
The water molecules need to move to and from the pyrite surface to keep dissolving it.
…..(space)
But believe it not, there are things going on here that are even faster. Let’s focus on a single water molecule.

*Femtoseconds*
1: We have slowed things down another 1000 times to look at the motion of this water molecule, this is H – 2 - O.
…. (space)
2: The white hydrogen atoms vibrate around the red oxygen atom. This oscillation happens in mere femtoseconds… or a quadrillionth of a second.

*Attoseconds*
1: Finally we reach attoseconds, our fastest time step! We now have slowed down 1 trillion million times. Remember that’s a 1 with 18 zeros!!!
2: Electrons are swarming around an atom’s nucleus. We are looking at the fundamental building block of every THING, including you.

*Zooming back to seconds*
1: As we speed back up to normal time…we are reminded that these activities go unnoticed, but still lead to our polluted stream… they just happen too fast for us to observe.
1: Attoseconds…
The motion inside atoms
2: Femtoseconds…
The vibration of water molecules
1: Picoseconds…
The motion of water around pyrite
2: Nanoseconds…
Water’s assault on pyrite
1: Microseconds…
Growing pits on the surface
2: And finally, what we CAN see, the flowing of the polluted stream… but our journey is only half over.

*Clocks highlighted again*
1: To know the full story… we must look at things that take place over minutes, years, thousands of years, …pause…, even hundreds of millions of years.
2: But wait most of these clocks aren’t even moving!
1: They are! But they’re just moving very slowly. If we sat and watched this clock for a hundred millions years, it would only go around once.
That’s a lot of sitting.

Yeah… So then we just need to speed things up to see what happens. But before we do that, there is one more part of the story that we can watch at normal speed.

*Minutes*

In just minutes, we can significantly change the Earth…

*“fire in the hole, BOOM”.*

At this coal mine they use a large digger to get at the coal. This digging also uncovers pyrite that was formed along WITH the coal. And when that happens, the pyrite becomes open to attack by water and air. Modern coal mining operations like this one, work hard to prevent pollution.

In the past, old coal mines were not as careful to prevent pollution from pyrite. That’s why we have things like our polluted stream.

*Transition*

Ok, so now we’ll need to speed up things up. Let’s speed it up about 100 thousand times to see what happens over years.

*Years*

Once pollution is released, it can move in streams, lakes, oceans….. or even in the water underground.

True! But that can happen much more slowly. This red plume of pollution takes years of move through the ground. Even though it moves more slowly, sometimes it can be a big problem because it’s hard to see where the pollution is.

*Thousand years*

If we don’t dig up the pyrite, it gets uncovered slowly through the natural break down of rocks. That takes 1000’s of years to happen, so we need to speed things up again to actually see it.

*Spin clocks, fade into rock*

Over thousands of years rocks breakdown naturally. We call this weathering.

Weathering starts at the surface and works towards the inside. Over time you see the core of original rock get smaller and smaller. Though you don’t see it, pyrite minerals in this rock slowly breakdown with the rest of the rock.

*100 Thousand years*

We just saw how one rock breaks down. Over time weathering combines with erosion to drastically change whole landscapes.

But this happens ever slower still. Though this landscape seems unchanging, when we speed things up, we see that things ARE changing as weathering and erosion carves into land.
transition
1:
Let’s take a closer look, now.
2:
Good idea, that way we can see where coal and pyrite comes from in the first place.
1:
But we’ll also speed things up AGAIN, because it takes millions of years for this to happen.

Millions of years
1:
The formation of a coal bed can takes millions of years. Here we see a swamp where plants live and die… building up layers and layers of dead plant material. Over millions of years, drastic changes to the earth’s surface can cause the swamp to get flooded and buried.

(pause)
2:
Once it’s buried, the dead plant material gets heated and squeezed changing it into coal. And often pyrite is formed right along with the coal.

100’s of millions of years
1:
We are going to speed things up 100 times. This takes us to the other end of our story. At this speed we see the entire surface of the Earth change.
2:
Over 100’s of millions of years, the Earth’s surface, which to you or me appears stable… changes quickly. Watch how North America evolves over time.

(pause)
1:
This is what we call plate tectonics and it is ultimately responsible for the shape of the world you see around you.

Zoom back to …
2:
As we slow back down to normal time, we are reminded of all the things that happen too slowly to notice.
1:
100’s of millions of years.
Movement of the earth’s plates
2:
Millions of years
Formation of coal beds
1:
100 of thousands of years
The carving of landscapes
2:
Thousand of years
Weathering of rocks
1:
Years
Pollution moving through the ground.

2: Minutes
Human changes to the landscape
_Stream shot_
1: What seemed like a simple stream, we now know is much more complex. It is a result of many things. Some too fast to see…
2: And some too slow to notice. It’s all a matter of how you think about time.
Andrew J. Wall  
Curriculum Vita

Education
- **PhD Geosciences**, Pennsylvania State University, Aug. 2011
- **BA Geology**, with Honors, Middlebury College, 2000
  
  *Thesis:* Trace metal speciation in wetland soils with amphibian malformities.

Selected Awards and Honors
- Edward H. Kraus Crystallographic Research Grant  
  *Mineralogical Society of America*  
  2009
- Outstanding Graduate Student Research Grant Award  
  *Geological Society of America*  
  2008
- Arnulf I. Muan Graduate Fellowship for Academic Excellence  
  *Penn State University*  
  2007
- American Federation of Mineralogical Societies Scholarship  
  *AFMS- Eastern Federation*  
  2007

Selected Professional Experience
- ORISE Postdoctoral Fellow  
  *National Energy Tech. Lab./Univ. of Pittsburgh, Pittsburgh, PA*  
  2011 - present
- Graduate Research Assistant, Dept. of Geosciences  
  *Pennsylvania State Univ., Univ. Park, PA*  
  2005 - 2011
- Teaching Assistant, Dept. of Geosciences  
  *Pennsylvania State Univ., Univ. Park, PA*  
  2005 - 2009
- Atmospheric Chemist  
  *Mount Washington Observatory, N. Conway, NH*  
  2002 - 2004
- Ski Patroller/EMT, 2002 Winter Olympics  
  *Deer Valley Resort, Park City, UT*  
  2002
- Research Geochemist / Mineralogist  
  *Middlebury College, Middlebury, VT*  
  1999 and 2002

Selected Publications