Origins of Chalcocite Defined by Copper Isotope Values

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The origin of chalcocite is explored through a comparison of the copper isotope values of this mineral from supergene enrichment, sedimentary copper/red bed, and high-temperature hypogene mineralization around the world. Data from the literature and the data presented here reveal that chalcocite from high-temperature mineralization has the tightest cluster of values of $\delta^{65}$Cu = 0 ± 0.6 in comparison to sedimentary copper/red bed $\delta^{65}$Cu = −0.9 ± 1.0 and supergene enrichment $\delta^{65}$Cu = +1.9 ± 1.8. Although the errors of the means overlap, large portions of the data lie in different values, allowing for distinguishing ranges for $\delta^{65}$Cu of <−1‰ for sedimentary copper/red bed, between −1 and +1 for high-temperature hypogene, and >+1 for supergene enrichment chalcocite. The copper isotope values of sedimentary copper/red bed and supergene enrichment chalcocite are caused by redox reactions associated with the dissolution and transport of copper, whereas the tighter range of copper isotope values for hypogene minerals is associated with processes active with equilibrium conditions.

1. The Importance of Chalcocite

Chalcocite is an economically important mineral of copper. Crystallographic, trace element, mineral assemblage, and textural observations and measurements have been used to understand the origin of this mineral [1–3]. Models regarding the genesis of chalcocite vary substantially, with conditions ranging from the highest temperature hydrothermal systems to ambient temperature weathering solutions, and no single model can be used to constrain how all of the occurrences of this mineral formed.

To contribute to the understanding of how chalcocite forms and what geologic processes lead to its concentration, this study analyzes copper isotope values from the literature and from new data presented here. The data are used to distinguish different types of mineral deposits ultimately related to the geological processes that lead to the generation of this essential economically significant mineral.

2. Types of Chalcocite Considered and Deposits Analyzed

The genesis of chalcocite can be categorized into three general models: (1) hypogene hypothermal ores that precipitate from hydrothermal fluids (>150°C), (2) red bed and stratiform “sedimentary” ores that precipitate from fluids that circulate through sedimentary basins at temperatures <150°C, and (3) supergene enrichment ores that precipitate from low to ambient temperature oxidative fluids in near-surface environments.

The copper isotope composition of chalcocite in these deposits varies due to several factors. In general, the primary source of most copper deposits is a large body of magmatic rock with an isotopic composition of approximately $\delta^{65}$Cu‰ = 0‰ (where $\delta^{65}$Cu‰ = ((65Cu/63Cu) sample/(65Cu/63Cu) Nist 976 − 1) * 1000) [4–6]. However, the relatively minor variations in the isotopic composition of Cu of the dominantly magmatic source material...
## Table 1: Summary of deposits analyzed and sources of data considered.

| Deposit          | Type of chalcocite | Data source                                      |
|------------------|--------------------|--------------------------------------------------|
| Butte, Montana   | Hypogene           | Mathur et al. 2009, Wall et al. 2011              |
| Canarico, Peru   | Hypogene           | Mathur et al. 2010                               |
| Rippoldsau, Germany | Hypogene           | Markl et al. 2006                               |
| Coates Lake, Canada | Sedimentary Cu     | This document                                    |
| Coppermine, Canada | Sedimentary Cu     | This document                                    |
| Dikulushi, DRC    | Sedimentary Cu     | Haest et al. 2009                               |
| Kupferschiefer, Germany | Sedimentary Cu | Asael et al. 2009                               |
| Cu, Michigan      | Sedimentary Cu     | This document, Larson et al. 2003, Mathur et al. 2014 |
| Timna, Israel     | Sedimentary Cu     | Asael et al. 2007, Asael et al. 2009, Asael et al. 2012 |
| Udokan, Russia    | Sedimentary Cu     | This document                                    |
| Bayugo, Philippines | Supergene          | Braxton et al. 2012                             |
| Chuquicamata, Chile | Supergene          | Mathur et al. 2009                               |
| Collahuasi, Chile | Supergene          | Mathur et al. 2009                               |
| El Salvador, Chile | Supergene          | Mathur et al. 2009                               |
| Inca de Oro, Chile | Supergene          | Mathur et al. 2014                               |
| PCDs, Iran        | Supergene          | Mirenjad et al. 2010, Asadi et al. 2012           |
| Morenci, Arizona  | Supergene          | Mathur et al. 2010                               |
| Ray, Arizona      | Supergene          | Mathur et al. 2010, Larson et al. 2003            |
| Silver Bell, Arizona | Supergene          | Mathur et al. 2010                               |
| Spence, Chile     | Supergene          | Palacios et al. 2010                             |

In contrast to hypogene chalcocite, the copper associated with red bed and stratiform types of chalcocite is derived from leaching of sandstones and shales at low temperatures by residual brines. The source rocks contain Cu$^{2+}$ that is hosted within detrital mafic minerals or is absorbed onto Fe hydroxides which are formed as products of weathering and diagenesis. A redox shift is thought to occur during transport of copper in these formational waters because the initial state of copper in the weathered source material is Cu$^{2+}$ but the copper is mobilized in the Cu$^{+}$ state as CuCl$_0$, or similar aqueous species [13, 14]. Thus, the reaction required to mobilize copper for sedimentary deposits involves the reduction of copper, which would be expected to induce isotopic fractionation favoring $^{65}$Cu, assuming that copper extraction from the source material was incomplete. Dissolved copper remains unchanged until it encounters organic material or other reductants within the sediment, where Cu$^{1+}$ is fixed by sulfide or by reaction with preexisting pyrite [15].

Six locations at which chalcocite occurs within "sedimentary" copper deposits (a total of 161 samples) are considered herein (Table 1). Literature sources that reported chalcocite as the major phase present in the copper isotope analyses were used [16–19] along with new data from Coates Lake, Copper Mine, Michigan, and Udokan. Data from Kupferschiefer [20], Michigan [21, 22], and Coates Lake [23] provide classic examples of sedimentary copper deposits along with the prospect, Coppermine [24]. Data from each of these deposits is compiled in Table 2.

The copper for supergene-type chalcocite is derived by oxidative weathering of rocks or ores containing Cu sulfide...
Table 2: Copper isotope data from sedimentary copper type deposits where cc means chalcocite and some samples reported trace bn (bornite).

| Sample | Location                | Phase | $\delta^{65}\text{Cu}$ (per mil) |
|--------|-------------------------|-------|---------------------------------|
| 1      | Udokan, Russia          | cc    | −0.32                           |
| 2      | Udokan, Russia          | cc    | −0.04                           |
| 3      | Udokan, Russia          | cc-bn | 0.4                             |
| 4      | Udokan, Russia          | bn-cc | −0.34                           |
| 5      | Udokan, Russia          | bn-cc | −1.33                           |
| 6      | Udokan, Russia          | cc-bn | −0.61                           |
| 7      | Udokan, Russia          | cc    | −0.18                           |
| 8      | Udokan, Russia          | cc    | −1.82                           |
| 9      | Udokan, Russia          | cc    | −0.13                           |
| 10     | Udokan, Russia          | cc    | −1.61                           |
| 11     | Udokan, Russia          | cc    | −1.07                           |
| 12     | Udokan, Russia          | cc    | −0.57                           |
| 13     | Udokan, Russia          | cc    | −0.68                           |
| 14     | Udokan, Russia          | cc    | −1.27                           |
| 15     | Udokan, Russia          | cc    | −0.53                           |
| 16     | Udokan, Russia          | cc    | −0.77                           |
| 17     | Udokan, Russia          | cc    | −0.04                           |
| 18     | Udokan, Russia          | cc    | −0.07                           |
| 19     | Udokan, Russia          | cc    | −1.07                           |
| 20     | Udokan, Russia          | cc    | −0.66                           |
| 21     | Udokan, Russia          | cc    | −0.74                           |
| 22     | Udokan, Russia          | cc    | −0.16                           |
| 23     | Udokan, Russia          | cc    | −0.66                           |
| 24     | Udokan, Russia          | cc    | −0.41                           |
| 9098   | Coates Lake, Canada     | cc    | −3.67                           |
| 9110   | Coates Lake, Canada     | cc    | −0.40                           |
| 9430   | Coates Lake, Canada     | cc    | −1.22                           |
| NWT 743 BI/5 | Coates Lake, Canada     | cc    | −0.28                           |
| JP77 7X1 2122 R2 #42 | Coates Lake, Canada    | cc    | 0.08                            |
| JP77 36984-4 3381.5 #38 | Coates Lake, Canada    | cc    | −0.31                           |
| NWT JP77 74121225 #45 R8 | Coates Lake, Canada    | cc    | −0.27                           |
| JP77 COATES 36984-1 1638 #36 | Coates Lake, Canada    | cc    | −0.72                           |
| NWT 7371 | Coates Lake, Canada     | cc    | −0.26                           |
| NWT 7Y3 BI/11 | Coates Lake, Canada    | cc    | −0.49                           |
| NWT JP77 644 3379 #39 | Coates Lake, Canada    | cc    | −0.20                           |
| JP77 781 422 #43 R4 | Coates Lake, Canada    | cc    | −0.38                           |
| 9097 cc | Coates Lake, Canada     | cc    | −2.01                           |
| 7371   | Coates Lake, Canada     | cc    | 0.43                            |
| #41    | Coates Lake, Canada     | cc    | 0.96                            |
| 45 r8  | Coates Lake, Canada     | cc    | 0.62                            |
| 43 r4  | Coates Lake, Canada     | cc    | 0.90                            |
| 7352   | Coates Lake, Canada     | cc    | 0.70                            |
| 7358 A | Coates Lake, Canada     | cc    | 0.14                            |
| #38    | Coates Lake, Canada     | cc    | 0.36                            |
| NWT 7356 | Coates Lake, Canada     | cc    | −0.24                           |
| NWT 7361A | Coates Lake, Canada     | cc    | −0.78                           |
| JP77 36984.2 2289 #37 | Coates Lake, Canada    | cc    | −0.54                           |
| NWT 9410 | Coates Lake, Canada     | cc    | −0.60                           |
| 9410   | Coates Lake, Canada     | cc    | 0.28                            |
| NWT KQ 74-11964 | Coates Lake, Canada    | cc    | −0.78                           |
| CM32619 | Baltic Mine, Michigan, USA | cc  | 0.47                            |
Table 2: Continued.

| Sample  | Location                  | Phase | δ$^{65}$Cu (per mil) |
|---------|---------------------------|-------|----------------------|
| CM32620 | Baltic Mine, Michigan, USA | cc    | −0.18                |
| CM32621 | Baltic Mine, Michigan, USA | cc    | 0.03                 |
| CM32622 | Baltic Mine, Michigan, USA | cc    | −0.05                |
| jk 10 h2 | Coppermine, Canada        | cc    | −0.69                |
| cool rock | Coppermine, Canada        | cc    | −1.35                |
| ly 03 h16 | Coppermine, Canada       | cc    | 0.07                 |
| dn 04   | Coppermine, Canada        | cc    | −1.11                |
| nr 02   | Coppermine, Canada        | cc    | −0.51                |
| h13     | Coppermine, Canada        | cc    | −0.55                |
| dt 02 h8 | Coppermine, Canada        | cc    | −0.07                |
| rd 04   | Coppermine, Canada        | cc    | −1.23                |
| rd 04-2 | Coppermine, Canada        | cc    | −1.24                |
| h23     | Coppermine, Canada        | cc    | −0.01                |
| ct 02 h3 | Coppermine, Canada        | cc    | −1.49                |
| ly03    | Coppermine, Canada        | cc    | −0.10                |
| h16     | Coppermine, Canada        | cc    | −0.25                |
| jk01    | Coppermine, Canada        | cc    | −0.02                |

(e.g., chalcopyrite CuFeS$_2$). The oxidized copper is transported downward toward the water table, where it is reprecipitated [25]. Near-surface oxidation zones in porphyry copper deposits are a classic example of this process. Commonly, some Cu remains in the leached capping. This incomplete oxidation reaction results in fractionated copper through the weathered profile. A reduction reaction of copper at the water table where fresh metallic surfaces of pyrite and other sulfides are present results in the precipitation of the reduced copper. Due to the increased pH at the water table and effective removal of copper via precipitation onto sulfide minerals, a majority of the copper is thought to be recovered from the oxidative solutions [26]. Late stage covellite (CuS) normally accompanies supergene chalcocite, further demonstrating the reductive nature of the reaction. Since reduction at the water table is essentially complete, fractionation preserved in the chalcocite from supergene enrichment will be due to the oxidation stage weathering and so would be expected to favor $^{65}$Cu. Continual reworking of the previous supergene enrichment layers due to uplift and erosion has been modeled [27, 28] to illustrate how larger degrees of fractionation would evolve.

A total of 182 samples from 10 locations are considered (Table 1). Any data from the following sources that had listed chalcocite as an analyzed phase was included [27, 29–36]. Data from Morenci, Ray, Chuquicamata, and Spence provide type examples of supergene enrichment in classic porphyry copper deposits.

3. The Behavior of Copper Isotopes and Predicted Differences for Redox Reactions

While many reactions can result in a shift in copper isotope values, redox reactions have been documented to produce the most substantial changes; redox reactions that result in oxidized copper favor the $^{65}$Cu isotope, whereas reactions that result in reduced copper favor the $^{63}$Cu isotope due to stronger bonding environments for each isotope [33, 37–39]. Experimental and empirical data support the magnitude and direction of copper isotope fractionation during the redox reactions [33, 38, 39].

In the case of oxidative reactions, the weathering of copper sulfide in supergene enrichment environments has been studied in the greatest detail. Solutions that leach copper during oxidation from the copper sulfide mineral become enriched in the $^{65}$Cu isotope due to a stronger bonding environment [33, 38, 39]. Although the degree of enrichment (fractionation factor) is different for a variety of copper sulfides (chalcopyrite, chalcocite, bornite, and enargite), in each case, the reactions produce cupric copper (Cu$^{2+}$) in solution which always has greater $^{65}$Cu‰ than the starting mineral. This phenomenon has been traced in natural aqueous solutions such as rivers, lakes, groundwater, and seawater [28, 40–43].

Reduction reactions involving copper have not been as thoroughly studied. Laboratory experiments that reduce copper from oxidized solutions have resulted in precipitated solids that have lower $^{65}$Cu‰ values than the starting solutions [38]. Modeling of copper isotopes in sedimentary copper deposits by Asael et al. [16] showed that the reduction of copper during transfer to solution should favor the lighter copper isotope. Thus, the available data indicate that reduction reactions favor the lighter copper isotope and that the products of the reduction have lower $^{65}$Cu‰ values than the starting materials. Furthermore, current models of copper behavior during redox reactions would predict that supergene enrichment copper mineralization would be associated with higher copper isotope values than that of sedimentary copper deposits.
4. Methods for Cu Isotope Data Presented

A total of 68 new Cu isotope measurements from chalcocite are presented. The chalcocite samples were handpicked from veins or disseminations. X-ray diffraction techniques were used to identify mineral species present and those methods are described by Mathur et al. (2005). Approximately 30–40 milligrams of powdered chalcocite was dissolved in 15 ml Teflon jars containing 4 ml of heated aqua regia for 12 hours. Complete dissolution was visually confirmed. The solutions were dried and copper was separated using ion exchange chromatography described by Mathur et al. (2009).

Isotope measurements were conducted on ICP-MS multicollectors at the University of Arizona and the Pennsylvania State University. Solutions were measured at 100 ppb and mass bias was corrected for by standard-sample-standard bracketing using the NIST 976 standard. Instrumentation setup and run conditions are described in detail by Mathur et al. (2005). Errors for the analyses presented are 0.1‰ and 2σ and error calculation is described by Mathur et al. (2005). Internal cent standards were measured at both locations during the analytical sessions and the 1838 cent $\delta^{65}$Cu = 0.02 ± 0.1 (2σ, n = 14).

5. Data and Its Implications

The histogram in Figure 1 compares the distribution of copper isotope values of 361 chalcocite samples from three distinct environments of formation: supergene enrichment (182 samples), sedimentary copper deposits (161 samples), and hypogene ores (18 samples). Each datum has an error on the order of ±0.1‰ and data are binned at 0.5‰ increments. All data reported here were compared to the NIST 976 standard with mass bias controlled by standard bracketing.

The mean values and 1-sigma variations for supergene enrichment chalcocite are $\delta^{65}$Cu = +1.9 ± 1.8‰ (n = 182), for sedimentary copper chalcocite are $\delta^{65}$Cu = −0.9 ± 1.0‰ (n = 161), and for hypogene chalcocite is $\delta^{65}$Cu = −0.001 ± 0.6‰ (n = 18). Although the three populations show considerable overlap in the weakly fractionated range, 64% of the sedimentary copper measurements are less than −0.8‰, and
suggests that the processes that lead to copper isotope variations at elevated temperature are broadly similar regardless of the resulting copper mineral assemblage. Several studies [44–46] suggest that the range of copper isotope values may be related to changes in pH or Eh or the partitioning of Cu between liquid and vapor phases as the hydrothermal solution cools. Overprinting high-temperature events could potentially lead to greater degrees of fractionation; however, none of the samples here have petrographic evidence to suggest this. Additional experimental work is needed to resolve the roles of different mechanisms that lead to these small but measurable copper isotope variations and to decide whether they vary systematically throughout a deposit as suggested by Mathur et al. (2012) and Li et al. [10].

6. Transportation of Copper and Precipitation of Chalcocite in Lower Temperature Solutions

The hydrothermal systems being considered involve metal migration at <$150^\circ$C in mixtures of brine, diagenetic, and meteoric fluids associated with typical sedimentary copper and supergene enrichment processes [15, 25]. Geochemical modeling of reaction kinetics and equilibrium of the observed mineral assemblages greatly enhanced our understanding of how and why metals move in these environments. In general, these studies identify the controls of copper transfer and precipitation in these systems as complicated and impacted by many interrelated variables such as pH, Eh, salinity, temperature, bulk chemistry of the solution, and bulk chemistry of the substrate that initiates precipitation [47–50]. Coupled with isotopic studies of these ores and host rocks, the reaction sources and pathways can be identified.

The copper in chalcocite (Cu$_2$S) from supergene enrichment and sedimentary copper deposits is hypothesized to be mobilized and transported by two different redox reactions. For supergene enrichment, copper is oxidized from preexisting copper minerals, which are exposed to meteoric fluids during uplift and erosion. These fluids are dominantly strongly acidic due to oxidation of pyrite accompanying the Cu sulfides. The acid allows ready transport of Cu$_2$+ within sandstones. The following two reactions (Davies, 1978) describe how copper adheres to the adsorption sites of Fe-oxide surfaces (see (1)) and how it is transported (see (2)) from adsorption sites:

$$\text{SOH} + \text{Cu}^{2+} (\text{aq}) \rightarrow \text{SO-Cu}^{2+} + \text{H}^+$$  \hspace{1cm} (1)

$$\text{H}^+ + \text{SO-Cu}^{2+} + 2\text{Cl}^- + e^- \rightarrow \text{CuCl}_2^- (\text{aq}) + \text{SOH}.$$  \hspace{1cm} (2)
With regard to the associated fractionation of copper isotopes, it is important to note that copper is transported in two different redox states. In these near-neutral solutions, Cu$^{2+}$ is soluble, and transport is as CuCl or related complex ions [13]. Although many different copper molecules are likely formed in association with carbonates, sulfates, and organic ligands, it is the isotopic proportioning potential of the two redox reactions and the likelihood of partial extraction that will control the measured variations in the copper isotopes. As shown in Figures 1 and 2, the supergene enrichment chalcocite preserves a heavier copper isotope value, which most likely represents the transportation and concentration of oxidized copper in the supergene. In contrast, the reduction reactions that led to the transport of copper in the sedimentary copper resulted in chalcocite that has significantly lower copper isotope values.

The data presented here indicate that redox reactions associated with copper transport are the primary means by which copper fractionates in low-temperature systems. At the deposition site, precipitation processes appear to have a negligible contribution to the degree of isotopic differentiation through fractionation. For supergene enrichment copper deposits, the oxidized copper molecule is reduced during the formation of chalcocite when the oxidized waters interact with the water table and hypogene sulfide minerals. This reduction process is highly effective in removing copper from solution [47], and the essentially complete precipitation of dissolved copper results erases the record of redox fractionation in this process. In sedimentary copper deposits, copper that is transported via CuCl complexes (such as CuCl$_2$ and CuCl$_3^{-}$) does not change redox state upon precipitation. Thus, fractionation due to electron transfer during precipitation is not thought to occur in the sedimentary copper chalcocite.

7. Conclusions

Despite the chemical complexity of the systems from which chalcocite is produced, copper isotope values in chalcocite provide a means by which the three major sources of chalcocite may be differentiated: (1) $\delta^{65}$Cu values less than $-1.0$ are most likely associated with sedimentary copper deposits; (2) $\delta^{65}$Cu values greater than $-1.0$ are most likely associated with supergene enrichment; and (3) a tightly clustered population of $\delta^{65}$Cu at 0.0 is most consistent with hypogene ores. These distinct variations in $\delta^{65}$Cu values in chalcocite are controlled predominantly by redox reactions at low temperature and equilibrium type reactions at high temperatures. Therefore, copper isotope values in chalcocite can provide insights into the genesis of chalcocite and can be used to develop improved mineralization models.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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