

Research Article

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 ($n = 361$) reveal that chalcocite from high-temperature mineralization has the tightest cluster of values of $\delta^{65}\text{Cu} = 0 \pm 0.6$ in comparison to sedimentary copper/red bed $\delta^{65}\text{Cu} = -0.9 \pm 1.0$ and supergene enrichment $\delta^{65}\text{Cu} = +1.9 \pm 1.8$. Although the errors of the means overlap, large portions of the data lie in different values, allowing for distinguishing ranges for $\delta^{65}\text{Cu}$ 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 ($>150^\circ\text{C}$), (2) red bed and stratiform “sedimentary” ores that precipitate from fluids that circulate through sedimentary basins at temperatures $<150^\circ\text{C}$, 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 $\delta^{65}\text{Cu}\text{‰} = 0\text{‰}$ (where $\delta^{65}\text{Cu}\text{‰} = ((65\text{Cu}/63\text{Cu})_{\text{sample}}/(65\text{Cu}/63\text{Cu})_{\text{Nist 976}} - 1) * 1000$) [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

will influence the possible values of Cu within the ore solution and the associated chalcocite. More importantly, the initial isotopic composition can be affected by fractionation during leaching of Cu from the source, as well as during precipitation of secondary chalcocite. The nature of the fractionation is dependent upon the specific dissolution and precipitation processes (e.g., bonding within the solid or in solution) and the physical and chemical conditions (e.g., temperature, redox), with redox processes leading to stronger bonding environments for ^{65}Cu in oxidized products and ^{63}Cu in reduced products. In addition, the extent of extraction of copper from the source and the fraction of copper that is reprecipitated in the ore-forming processes affect fractionation. If 100% of the Cu is extracted and precipitated, then no evidence of fractionation will be preserved. However, if the chemical transfer is incomplete, then the various phases (primary mineral, solution, and secondary mineral) may have differing isotopic compositions based on the degree of fractionation.

Copper in chalcocite that is associated with hypogene hydrothermal ores is derived from a magmatic hydrothermal fluid or is extracted from country rocks at high temperatures. Moreover, extensive studies showed that hypogene hydrothermal copper minerals such as chalcopyrite and bornite do not display appreciable fractionation ($>\pm 1\%$) [7–11]. Similarly, chalcocite that precipitated from these high-temperature fluids is not anticipated to contain copper that has undergone significant copper isotope fractionation. This study includes 18 chalcocite samples from three hypogene deposits (Table 1), including an archetypal example of hypogene chalcocite at Butte, Montana [12].

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 ^{63}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 B1/5	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 B1/11	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	$\delta^{65}\text{Cu}$ (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 h12	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 $\delta^{65}\text{Cu}\%$ 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 $\delta^{65}\text{Cu}\%$ 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 $\delta^{65}\text{Cu}\%$ 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.

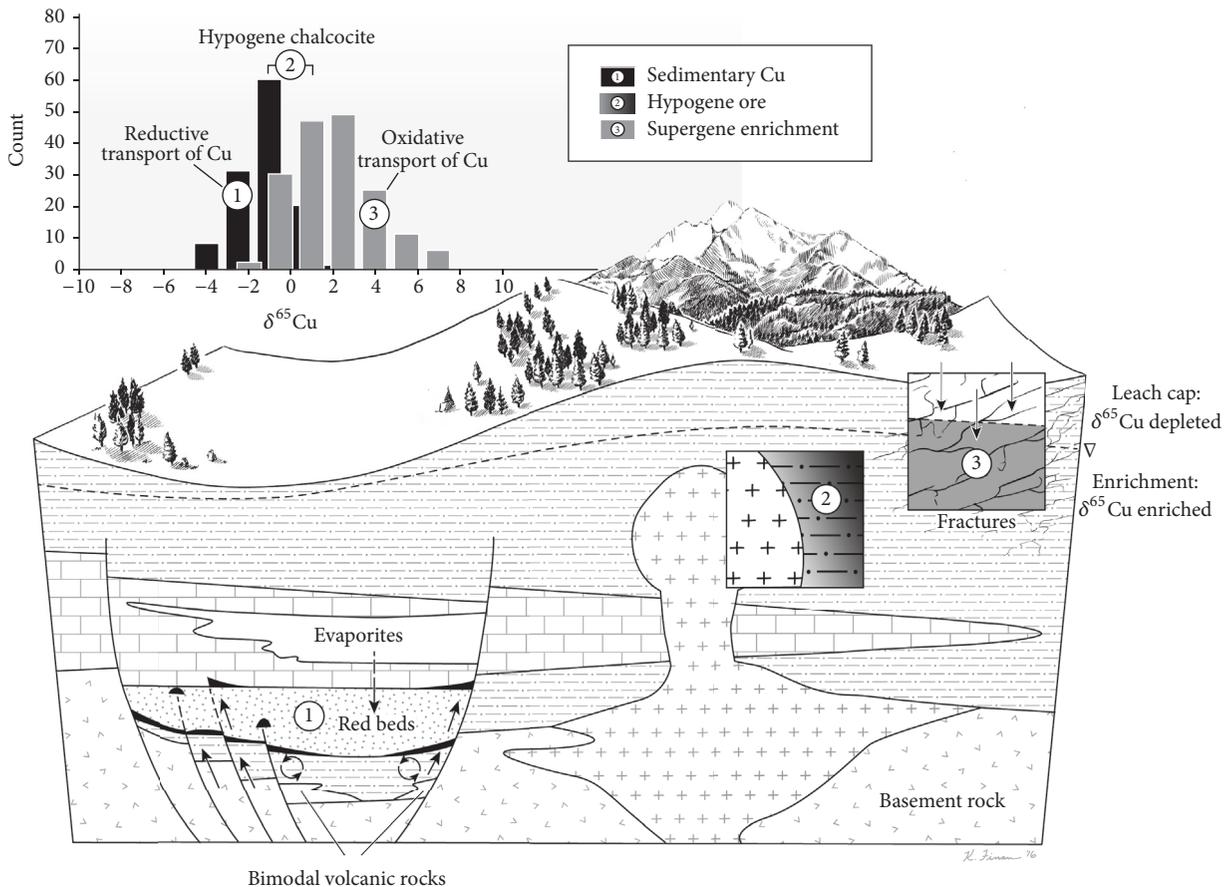


FIGURE 1: Histogram plot combined with a cartoon model of copper isotope values of chalcocite formed in three different environments. Data from the supergene group show the largest range and overlap the ranges of the other two deposit types.

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 $\delta^{65}\text{Cu} = 0.02 \pm 0.1$ (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 $\pm 0.1\%$ 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 $\delta^{65}\text{Cu} = +1.9 \pm 1.8\%$ ($n = 182$), for sedimentary copper chalcocite are $\delta^{65}\text{Cu} = -0.9 \pm 1.0\%$ ($n = 161$), and for hypogene chalcocite is $\delta^{65}\text{Cu} = -0.001 \pm 0.6\%$ ($n = 18$). Although the three populations show considerable overlap in the weakly fractionated range, 64% of the sedimentary copper measurements are less than -0.8% , and

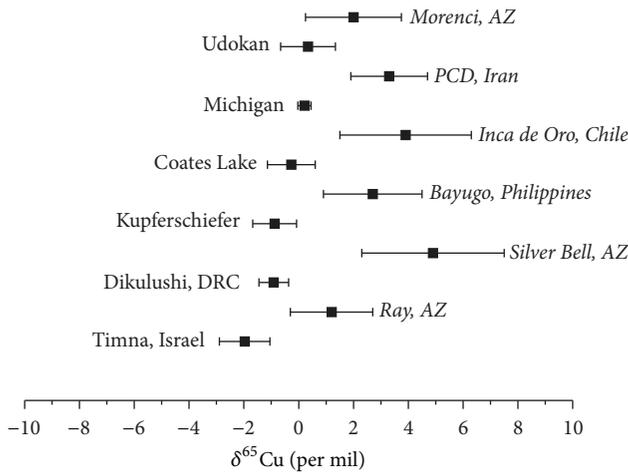


FIGURE 2: Mean and 1σ error plot of specific deposit types comparing the supergene and sedimentary chalcocite from the presented data.

65% of the chalcocite from supergene enrichment has $\delta^{65}\text{Cu}$ values greater than +1‰. The data portrayed in this manner indicates that the copper isotopic composition of chalcocite can be related to deposit types, with values less than -1‰ most likely related to sedimentary copper deposits, whereas values greater than +1‰ are most likely formed under supergene processes. To further detail variations in copper isotope compositions between the two genetically distinct, lower temperature deposits, a deposit specific comparison is presented in Figure 2, with 1σ variations calculated by the standard deviations of all presented data. It is significant that the deposit types have little overlap and lie completely within the ranges suggested above. Despite the fact that range boundaries are approximate and that none of the limiting values define sharp divide, this approach provides a statistically valid means for differentiating chalcocite from sedimentary and supergene processes based on copper isotope composition.

Note that the variation associated with the supergene enrichment deposits is significantly larger than that for the other environments of mineralization and almost twice that of sedimentary copper deposits. This most likely reflects the fact that these supergene systems are still active, with continued mobilization and migration of copper with associated evolution of copper isotopic compositions; that is, the active supergene enrichment blanket is continuing to weather and lose ^{65}Cu during oxidation as is evident at Morenci where the top of the enrichment blanket contains chalcocite with lower copper isotope values than that found at deeper levels [30].

It is interesting to note that the $\delta^{65}\text{Cu}$ range of high-temperature hypogene chalcocite directly overlaps the $0 \pm 1\%$ range in $\delta^{65}\text{Cu}$ that has been documented in other copper-rich sulfide minerals (bornite, chalcopyrite) from high-temperature hypogene mineralization, as compiled by Wall et al. (2011) and Saunders et al. (2015). The overlap in isotopic composition of high-temperature hypogene chalcocite with that of high-temperature hypogene chalcopyrite and bornite

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

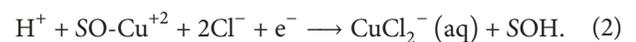
The hydrothermal systems being considered involve metal migration at $<150^\circ\text{C}$ in mixtures of brine, diagenetic, and meteoric fluids associated with typical sedimentary copper and supergene enrichment processes [15, 25]. Geochemical modeling of reaction kinetics and equilibrium of the observed 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_2S) 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+} . As all of the deposits examined are still in the process of developing, the reaction has not been completed and some Cu is left behind in the leached zone. Thus, the source of the copper is well understood.

In contrast, copper sources in sedimentary copper deposits are much debated [13, 15]. However, it is agreed that a likely source of the metal is Cu^{2+} adsorbed onto Fe oxides within sandstones. The following two reactions (Davies, 1978) describe how copper adheres to the adsorption of sites of Fe-oxide surfaces (see (1)) and how it is transported (see (2)) from adsorption sites:



where S is the surface of the Fe oxide or other minerals



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^0 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^{2-}) 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) $\delta^{65}\text{Cu}$ values less than -1.0 are most likely associated with sedimentary copper deposits; (2) $\delta^{65}\text{Cu}$ values greater than -1.0 are most likely associated with supergene enrichment; and (3) a tightly clustered population of $\delta^{65}\text{Cu}$ at 0.0 is most consistent with hypogene ores. These distinct variations in $\delta^{65}\text{Cu}$ 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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References

- [1] D. A. Crerar and H. L. Barnes, "Ore solution chemistry v solubilities of chalcopyrite and chalcocite assemblages in hydrothermal solution at 200°C to 350°C ," *Economic Geology*, vol. 71, no. 4, pp. 772–794, 1976.
- [2] H. T. Evans, "Crystal Structure of Low Chalcocite," *Nature Physical Science*, vol. 232, no. 29, pp. 69–70, 1971.
- [3] D. J. Vaughan, "Sulfide mineralogy and geochemistry: Introduction and overview," *Reviews in Mineralogy and Geochemistry*, vol. 61, pp. 1–5, 2006.
- [4] W. Li, S. E. Jackson, N. J. Pearson, O. Alard, and B. W. Chappell, "The Cu isotopic signature of granites from the Lachlan Fold Belt, SE Australia," *Chemical Geology*, vol. 258, no. 1–2, pp. 38–49, 2009.
- [5] S. A. Liu, J. Huang, J. Liu et al., "Copper isotopic composition of the silicate Earth," *Earth and Planetary Science Letters*, vol. 427, pp. 95–103, 2015.
- [6] E. M. Ripley, S. Dong, C. Li, and L. E. Wasylenki, "Cu isotope variations between conduit and sheet-style Ni-Cu-PGE sulfide mineralization in the Midcontinent Rift System, North America," *Chemical Geology*, vol. 414, pp. 59–68, 2015.
- [7] S. Graham, N. Pearson, S. Jackson, W. Griffin, and S. Y. O'Reilly, "Tracing Cu and Fe from source to porphyry: In situ determination of Cu and Fe isotope ratios in sulfides from the Grasberg Cu-Au deposit," *Chemical Geology*, vol. 207, no. 3–4, pp. 147–169, 2004.
- [8] K. Ikehata and T. Hirata, "Copper isotope characteristics of copper-rich minerals from the horoman peridotite complex, Hokkaido, Northern Japan," *Economic Geology*, vol. 107, no. 7, pp. 1489–1497, 2012.
- [9] P. B. Larson, K. Maher, F. C. Ramos, Z. Chang, M. Gaspar, and L. D. Meinert, "Copper isotope ratios in magmatic and hydrothermal ore-forming environments," *Chemical Geology*, vol. 201, no. 3–4, pp. 337–350, 2003.
- [10] W. Li, S. E. Jackson, N. J. Pearson, and S. Graham, "Copper isotopic zonation in the Northparkes porphyry Cu-Au deposit, SE Australia," *Geochimica et Cosmochimica Acta*, vol. 74, no. 14, pp. 4078–4096, 2010.
- [11] G. Markl, Y. Lahaye, and G. Schwinn, "Copper isotopes as monitors of redox processes in hydrothermal mineralization," *Geochimica et Cosmochimica Acta*, vol. 70, no. 16, pp. 4215–4228, 2006.
- [12] C. Meyer et al., "Ore deposits at Butte, Montana," in *Ore deposits of the United States, 1967*, pp. 1373–1416, 1968.
- [13] A. W. Rose, "The effect of cuprous chloride complexes in the origin of red-bed copper and related deposits," *Economic Geology*, vol. 71, no. 6, pp. 1036–1048, 1976.
- [14] A. C. Brown, "Close linkage of copper (and uranium) transport to diagenetic reddening of "upstream" basin sediments for sediment-hosted stratiform copper (and roll-type uranium) mineralization," *Journal of Geochemical Exploration*, vol. 89, no. 1–3, pp. 23–26, 2006a.
- [15] M. W. Hitzman, D. Selley, and S. Bull, "Formation of sedimentary rock-hosted stratiform copper deposits through earth history," *Economic Geology*, vol. 105, no. 3, pp. 627–639, 2010.
- [16] D. Asael, A. Matthews, M. Bar-Matthews, and L. Halicz, "Copper isotope fractionation in sedimentary copper mineralization

- (Timna Valley, Israel),” *Chemical Geology*, vol. 243, no. 3-4, pp. 238–254, 2007.
- [17] D. Asael, A. Matthews, M. Bar-Matthews, Y. Harlavan, and I. Segal, “Tracking redox controls and sources of sedimentary mineralization using copper and lead isotopes,” *Chemical Geology*, vol. 310-311, pp. 23–35, 2012.
- [18] D. Asael, A. Matthews, S. Oszczepalski, M. Bar-Matthews, and L. Halicz, “Fluid speciation controls of low temperature copper isotope fractionation applied to the Kupferschiefer and Timna ore deposits,” *Chemical Geology*, vol. 262, no. 3-4, pp. 147–158, 2009.
- [19] M. Haest, P. Muchez, J. C. J. Petit, and F. Vanhaecke, “Cu isotope ratio variations in the Dikulushi Cu-Ag deposit, DRC: of primary origin or induced by supergene reworking?” *Economic Geology*, vol. 104, no. 7, pp. 1055–1064, 2009.
- [20] E. C. Jowett, “Genesis of kupferschiefer cu-ag deposits by convective flow of rotliegende brines during triassic rifting,” *Economic geology Lancaster, Pa*, vol. 81, no. 8, pp. 1823–1837, 1986.
- [21] A. C. Brown, “Genesis of native copper lodes in the Keweenaw District, Northern Michigan: A hybrid evolved meteoric and metamorphic model,” *Economic Geology*, vol. 101, no. 7, pp. 1437–1444, 2006.
- [22] T. J. Bornhorst, J. B. Paces, N. K. Grant, J. D. Obradovich, and N. K. Huber, “Age of native copper mineralization, Keweenaw Peninsula, Michigan,” *Economic Geology*, vol. 83, no. 3, pp. 619–625, 1988.
- [23] F. M. Chartrand and A. C. Brown, “The diagenetic origin of stratiform copper mineralization, Coates Lake, Redstone copper belt, N. W. T., Canada,” *Economic Geology*, vol. 80, no. 2, pp. 325–343, 1985.
- [24] E. D. Kindle, “Classification and description of copper Deposits, Coppermine River area, District of Mackenzie,” Tech. Rep. 214, 1972.
- [25] S. R. Titley and D. C. Marozas, “Processes and products of supergene copper enrichment,” *Arizona Geological Society Digest*, vol. 20, pp. 156–168, 1995.
- [26] W. X. Chavez, “Supergene oxidation of copper deposits; zoning and distribution of copper oxide minerals,” *SEG Newsletter*, vol. 41: 1, pp. 10–21, 2000.
- [27] D. Braxton and R. Mathur, “Exploration applications of copper isotopes in the supergene environment: A case study of the bayugo porphyry copper-gold deposit, Southern Philippines,” *Economic Geology*, vol. 106, no. 8, pp. 1447–1463, 2011.
- [28] R. Mathur and M. S. Fantle, “Copper isotopic perspectives on supergene processes: Implications for the global Cu cycle,” *Elements*, vol. 11, no. 5, pp. 323–329, 2015.
- [29] S. Asadi, R. Mathur, F. Moore, and A. Zarasvandi, “Copper isotope fractionation in the Meiduk porphyry copper deposit, Northwest of Kerman Cenozoic magmatic arc, Iran,” *Terra Nova*, vol. 27, no. 1, pp. 36–41, 2015.
- [30] R. Mathur, M. Dendas, S. Titley, and A. Phillips, “Patterns in the copper isotope composition of minerals in porphyry copper deposits in Southwestern United States,” *Economic Geology*, vol. 105, no. 8, pp. 1457–1467, 2010.
- [31] R. Mathur, L. Munk, M. Nguyen, M. Gregory, H. Annell, and J. Lang, “Modern and paleofluid pathways revealed by Cu isotope compositions in surface waters and ores of the Pebble porphyry Cu-Au-Mo deposit, Alaska,” *Economic Geology*, vol. 108, no. 3, pp. 529–541, 2013.
- [32] R. Mathur, L. A. Munk, B. Townley et al., “Tracing low-temperature aqueous metal migration in mineralized watersheds with Cu isotope fractionation,” *Applied Geochemistry*, vol. 51, pp. 109–115, 2014.
- [33] R. Mathur, J. Ruiz, S. Titley, L. Liermann, H. Buss, and S. Brantley, “Cu isotopic fractionation in the supergene environment with and without bacteria,” *Geochimica et Cosmochimica Acta*, vol. 69, no. 22, pp. 5233–5246, 2005.
- [34] R. Mathur, S. Titley, F. Barra et al., “Exploration potential of Cu isotope fractionation in porphyry copper deposits,” *Journal of Geochemical Exploration*, vol. 102, no. 1, pp. 1–6, 2009.
- [35] H. Mirnejad, R. Mathur, M. Einali, M. Dendas, and S. Alirezaei, “A comparative copper isotope study of porphyry copper deposits in Iran,” *Geochemistry: Exploration, Environment, Analysis*, vol. 10, no. 4, pp. 413–418, 2010.
- [36] C. Palacios, O. Rouxel, M. Reich, E. M. Cameron, and M. I. Leybourne, “Pleistocene recycling of copper at a porphyry system, Atacama Desert, Chile: Cu isotope evidence,” *Mineralium Deposita*, vol. 46, no. 1, pp. 1–7, 2011.
- [37] D. M. Borrok, D. A. Nimick, R. B. Wanty, and W. I. Ridley, “Isotopic variations of dissolved copper and zinc in stream waters affected by historical mining,” *Geochimica et Cosmochimica Acta*, vol. 72, no. 2, pp. 329–344, 2008.
- [38] S. Ehrlich, I. Butler, L. Halicz, D. Rickard, A. Oldroyd, and A. Matthews, “Experimental study of the copper isotope fractionation between aqueous Cu(II) and covellite, CuS,” *Chemical Geology*, vol. 209, no. 3-4, pp. 259–269, 2004.
- [39] X. K. Zhu, Y. Guo, R. J. P. Williams et al., “Mass fractionation processes of transition metal isotopes,” *Earth and Planetary Science Letters*, vol. 200, no. 1-2, pp. 47–62, 2002.
- [40] J. Bermin, D. Vance, C. Archer, and P. J. Statham, “The determination of the isotopic composition of Cu and Zn in seawater,” *Chemical Geology*, vol. 226, no. 3-4, pp. 280–297, 2006.
- [41] S. M. Ilina, J. Viers, S. A. Lapitsky et al., “Stable (Cu, Mg) and radiogenic (Sr, Nd) isotope fractionation in colloids of boreal organic-rich waters,” *Chemical Geology*, vol. 342, pp. 63–75, 2013.
- [42] S. H. Little, D. Vance, C. Walker-Brown, and W. M. Landing, “The oceanic mass balance of copper and zinc isotopes, investigated by analysis of their inputs, and outputs to ferromanganese oxide sediments,” *Geochimica et Cosmochimica Acta*, vol. 125, pp. 673–693, 2014.
- [43] D. Vance, C. Archer, J. Bermin et al., “The copper isotope geochemistry of rivers and the oceans,” *Earth and Planetary Science Letters*, vol. 274, no. 1-2, pp. 204–213, 2008.
- [44] T. Fujii, F. Moynier, M. Abe, K. Nemoto, and F. Albarède, “Copper isotope fractionation between aqueous compounds relevant to low temperature geochemistry and biology,” *Geochimica et Cosmochimica Acta*, vol. 110, pp. 29–44, 2013.
- [45] M. Pękala, D. Asael, I. B. Butler, A. Matthews, D. Rickard, and M. Pękala, “Experimental study of Cu isotope fractionation during the reaction of aqueous Cu(II) with Fe(II) sulphides at temperatures between 40 and 200°C,” *Chemical Geology*, vol. 289, no. 1-2, pp. 31–38, 2011.
- [46] J. H. Seo, S. K. Lee, and I. Lee, “Quantum chemical calculations of equilibrium copper (I) isotope fractionations in ore-forming fluids,” *Chemical Geology*, vol. 243, no. 3-4, pp. 225–237, 2007.
- [47] M. S. Enders, C. Knickerbocker, S. R. Titley, and G. Southam, “The role of bacteria in the supergene environment of the Morenci porphyry copper deposit, Greenlee County, Arizona,” *Economic Geology*, vol. 101, no. 1, pp. 59–70, 2006.

- [48] A. J. Hartley and C. M. Rice, "Controls on supergene enrichment of porphyry copper deposits in the Central Andes: A review and discussion," *Mineralium Deposita*, vol. 40, no. 5, pp. 515–525, 2005.
- [49] R. H. Sillitoe, "Supergene oxidized and enriched porphyry copper and related deposits," in *Economic Geology*, 100 Anniversary Volume, pp. 723–768, 2005.
- [50] E. V. Belogub, K. A. Novoselov, V. A. Yakovleva, and B. Spiro, "Supergene sulphides and related minerals in the supergene profiles of VHMS deposits from the South Urals," *Ore Geology Reviews*, vol. 33, no. 3-4, pp. 239–254, 2008.



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