Copper Isotope Constraints on the Genesis of the Keweenaw Peninsula Native Copper District, Michigan, USA: A Comment

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1. Introduction

Well-grouped δ⁶⁵Cu values (−0.3 to +0.8‰) from 120 samples of native copper from the Keweenaw native copper district have been attributed, by Bornhorst and Mathur [1], to isotopic fractionations toward heavy δ⁶⁵Cu values during oxidative leaching of copper (Cu⁰ → Cu⁺) from deeply buried Portage Lake Volcanics (PLV) basalts, followed by isotopic fractionations toward lighter δ⁶⁵Cu values during reductive deposition of the leached copper in up-dip aquifers of the same basalt-dominant Keweenaw strata. The sum of these two independent and largely uncontrolled fractionations is unlikely to have produced such a well-grouped array of δ⁶⁵Cu values. An alternative copper isotopic fractionation history may be offered, as explained below.

It is also doubtful that the copper isotopic fractionations can be explained solely within the context of classic metamorphogenic models (e.g., [2,3]), as implied by the authors. Topography-driven evolved meteoric water could provide other complementary explanations [4,5].

2. Copper Isotopic Fractionations

The dehydration of deeply buried basalts and the consequent generation of hot cupriferous metamorphogenic solutions have long been called upon to explain the genesis of Keweenaw native copper deposits [2,3,6–8]. This concept continues to play a role in more recent explanations for these remarkable native copper deposits [1,4,5,9].

In the explanations of Bornhorst and Mathur, the key copper isotopic guidelines for the genesis of Keweenaw native copper deposits are based on the observation that important copper isotopic fractionations occur during valence changes [1,10]. For example, copper isotopic fractionations should have trended toward heavy δ⁶⁵Cu values during oxidative leachings of copper (Cu⁰ → Cu⁺) accompanying deep burial metamorphism (see red arrows of Figure 1), and fractionations toward lighter values should have taken place during subsequent up-dip reductive depositions of native copper (Cu⁺ → Cu⁰) (see orange arrows of Figure 1). According to the authors, oxidative fractionations must have also produced δ⁶⁵Cu values of +0.8‰ or greater in order to account for the heaviest δ⁶⁵Cu values measured. In the writer’s opinion, the qualifications “partial leaching” and “partial depositional” should also apply in their explanations, given that 100% leaching efficiencies would have resulted in leach solutions with δ⁶⁵Cu values equal to those of the basalt sources, and 100% efficiencies at up-dip depositional sites would have produced native copper deposits with δ⁶⁵Cu values equal to those of the ore solutions.
Partial leaching and depositional processes are problematic. First, partial ore-forming processes suggest undesirably inefficient means of forming orebodies. Second, the extents (i.e., efficiencies) of both partial leaching and partial deposition would have been essentially undefined in the authors’ interpretations. As such, the two independent fractionations, first toward heavy $\delta^{65}$Cu values during partial leaching and then toward lighter $\delta^{65}$Cu values during partial copper deposition, are very unlikely to have resulted in the remarkably well-grouped array of $\delta^{65}$Cu values ($-0.3$ to $+0.8\%$) found among 120 analyses of Keweenaw native copper deposits (see Figure 1).

3. An Alternative Oxidative Leaching-Reductive Deposition Model

A simpler, more geologically and geochemically satisfying interpretation of the observed analyses is possible. First, allow the deep-burial metamorphogenic leaching of copper to have proceeded to a near-complete level (Figure 2A). Leachings of copper from the source basalts into co-existing metamorphogenic leach solutions should have initially been relatively rapid, and with time, the rate of leaching would have become slow and the residual copper available for leaching from the solid
source basalt would have become minimal. Leachings cannot be expected to have ever attained 100% efficiency. A finite amount of copper would have remained in the source basalt (see range r in Figure 2A). At this advanced, near-complete level of leaching, all δ⁶⁵Cu values of the leach solutions would have converged toward to a narrow range slightly heavier than the δ⁶⁵Cu values of the source basalts (see range r in Figure 2B; see also the lower half of Figure 3).

**Figure 2.** A reinterpretation of progressive copper isotopic fractionation during the oxidative leaching of copper from deeply buried Portage Lake Volcanics (PLV) basalts, based on common geologic expectations. (A) Metamorphogenic leaching of trace-level copper from source basalts can be expected to have initially been rapid, and then to have progressed in ever slower increments, until, at near-complete leaching, negligible amounts of copper remained in the source basalts (see range r for four samples illustrated in this schematic diagram). (B) Similar to (A), but with the vertical axis representing δ⁶⁵Cu values. Initially, leached copper would have been heavy (greater than 0.8‰ according to Bornhorst and Mathur), but would have evolved toward a narrow range of lighter values (see r; e.g., −0.3 to +0.8‰, as observed in 120 analyses of Keweenaw native copper) at near-complete leachings, as a result of continued leaching of ever lighter residual copper in the source basalts.
Then, those cupriferous ore solutions ascended along PLV aquifers to deposit native copper lodes and veins. Copper deposition typically extended over vertical intervals measuring 1 km and more. Regardless of the possible causes of copper deposition, the process would have consisted basically of chemical precipitations (e.g., CuCl₂ → Cu₀ + 2Cl⁻) and may be expected to have been essentially 100% efficient within the kilometer-scale up-dip dimension of individual deposits. As such, copper isotopic fractionations would have been negligible and the native copper deposits should have retained the δ⁶⁵Cu values of their ore solutions (upper half of Figure 3). Their δ⁶⁵Cu values should have remained well-grouped and slightly heavier than the isotopic compositions of their source basalts (−0.3 to +0.8‰), as explained above.

![Diagram](image)

**Figure 3.** An alternate explanation for copper isotopic fractionation, based (a) on near-complete oxidative leaching at the basaltic sources and δ⁶⁵Cu values of deep-seated ore solutions that attained the range −0.3 to +0.8‰ during deep burial metamorphism (lower half of figure, portion a), and (b) on having retained that range during up-dip deposition of native copper due to the essentially 100% efficiency of copper deposition (upper half of Figure 3, portion b). Note that during the leaching of copper from deeply buried source basalts (five examples shown), the δ⁶⁵Cu values of developing ore solutions would initially have been isotopically heavy (e.g., δ⁶⁵Cu value S, for one example), and that solutions would have regained lighter values (e.g., δ⁶⁵Cu value F) during near-complete oxidative leaching of copper (see head of solid red arrow A, representative of the isotopic fractionation toward lighter δ⁶⁵Cu values during oxidative leaching). Having attained well-grouped, slightly heavy δ⁶⁵Cu values (−0.3 to +0.8‰, for all 120 samples of analyzed Keweenaw native copper), these ore solutions would then have ascended and deposited native copper with essentially unchanged δ⁶⁵Cu values because of 100% efficient reductive copper deposition (see orange dots, all falling within the observed well-grouped δ⁶⁵Cu values obtained from 120 analyzed native copper samples).

The progressive isotopic fractionation of copper during leaching from solid basalts into the co-existing in-situ metamorphogenic solutions could also be presented using well-defined Rayleigh fractionation curves (see Figure 4) [11–13]. Red curve A shows the cumulative δ⁶⁵Cu values of the metamorphic ore solutions, assuming that initial leached copper had an isotopic composition
of +1.0‰. According to this Rayleigh curve, the $\delta^{65}\text{Cu}$ values of the ore solution would have approached the $\delta^{65}\text{Cu}$ values of the basalt sources at near-complete leaching, much as portrayed by the progressive leaching curve of Figure 2A. Again, because all source basalts experienced advanced leaching, the isotopic compositions of the leach solutions would have converged toward a narrow range (see range $r$ in Figure 4), which is represented by the well-grouped array of $\delta^{65}\text{Cu}$ values found in Keweenaw native copper deposits (~0.3 to +0.8‰). Curve B shows the copper isotopic composition of the source basalt during progressive leaching, assuming an initial isotopic composition of 0.0 ± 0.3‰. Similar Rayleigh fractionation curves and similar interpretations would apply to up-dip precipitations of copper by reductive deposition. The tight grouping of $\delta^{65}\text{Cu}$ values would have been retained during copper deposition as a result of the essentially 100% efficiency of that process, as explained above.

Figure 4. Representation of copper isotopic compositions during oxidative leaching, based on Rayleigh fractionations. Red arrow A shows the expected progression in $\delta^{65}\text{Cu}$ values within the leach solutions, which initially would have been isotopically heavy (>0.8‰, according to Bornhorst and Mathur), and would then have trended toward lighter $\delta^{65}\text{Cu}$ values because of the progressive oxidative leaching of lighter residual copper from the source basalts [1,11–13]. At near-complete leaching, the $\delta^{65}\text{Cu}$ values of the leach (ore) solutions would have been slightly heavier isotopically (~0.3 to +0.8‰) than the original $\delta^{65}\text{Cu}$ value of the source basalts (presumed here to have been 0.0 ± 0.3‰). Black arrow B shows the expected progression of $\delta^{65}\text{Cu}$ values for the source basalts, assumed to have begun at 0.0 ± 0.3‰, and to have evolved progressively toward isotopically much-lighter values (see head of black arrow), as a result of the continuing greater loss of the heavier copper isotope to the leach solution. Precise $\delta^{65}\text{Cu}$ values for the ore solution and residual copper in the basalt (vertical axis) cannot be given because, for example, actual initial fractionation values of the leach solutions (see S) are unknown. See the text for further explanations.

In general, Rayleigh curves could provide more precise explanations for the evolution of $\delta^{65}\text{Cu}$ values during copper leaching and deposition. However, these geochemically rigorous fractionation curves are not pursued further here because, for example, quantitative input parameters are lacking.
(e.g., knowledge of the initial heavy $\delta^{65}$Cu values for the first increments of leached copper; see S in Figure 4), and because the open versus closed nature of environments at deep metamorphogenic leaching has not yet been thoroughly discussed or established.

4. Other Considerations

The classic metamorphogenic solution model has been found over the years to be deficient in two or more aspects. For example, rock/water equilibrations with the abundant ferrous minerals of the source basalts should have resulted in buffering to the ferrous–ferric redox stability boundary, at which the solubility of copper would have been negligible [3,4,14]. Second, metamorphogenic solutions are widely recognized as having low salinities (unless co-existing with evaporites) [15,16], whereas high copper solubilities depend on high salinities in order to form high concentrations of stable copper chloride complexes in aqueous ore solutions [4,17]. The upward circulation (and timing) of metamorphogenic solutions from their deep-burial sources may also require evaluation, given that the source basalts would have been cold soon after deposition, that local magmatic heat would have been absent at the time of native copper deposition [1,7], and that the influx of mantle heat would have been very sluggish [1,18]. In addition, the authors’ metamorphogenic model calls upon unidentified reductant(s) to produce reductive native copper deposition.

The merger of the classic metamorphogenic solution with evolved meteoric water provides answers to most of these problems by providing topography-driven, deep-circulating meteoric water having moderately oxidized redox levels and high-salinities favorable for high copper solubilities [4]. At the up-dip level of native copper deposition, the continued oxidation of abundant ferrous iron in aquifers should eventually have taken the redox level of the ore solution out of the moderately oxidizing conditions suitable for the high solubilities of copper in saline solutions and into more reduced, sulfide-free conditions, at which native copper would have deposited [4].

Nevertheless, the authors mention numerous arguments suggesting that evolved meteoric water did not likely play a role in forming the Keweenaw native copper deposits. For example, they dispute the possibility that evolved meteoric waters were driven by highland recharge, and they suggest, oddly, that evaporitic salts responsible for high salinities in the evolved meteoric waters would have generated sulfides, and would thus have deposited copper sulfides not generally characteristic of the Keweenaw native copper deposits. Readers may assess such objections as they see fit.

5. Conclusions

An alternative interpretation of copper isotopic data from native copper deposits in the Keweenaw district is offered in place of the interpretation of Bornhorst and Mathur [1]. Whereas the degrees of copper leaching from deeply buried source basalts are largely undefined in the authors’ isotopic fractionation model, it is proposed here that copper leaching from the basalts ($\text{Cu}^0 \rightarrow \text{Cu}^+$) would have continued to a geologically reasonable near-complete level. As a consequence, the cupriferous solutions would have attained well-defined, well-grouped $\delta^{65}$Cu values (approx. $-0.3$ to $+0.8\%$) that were only slightly heavier than the assumed $\delta^{65}$Cu values of the source basalts ($0.0 \pm 0.3\%$). Subsequent up-dip deposition of copper in PLV aquifers would have been a highly efficient chemical process ($\text{Cu}^+ \rightarrow \text{Cu}^0$), such that the $\delta^{65}$Cu signature of the native copper should have essentially equaled that of the copper in the ore solution ($-0.3$ to $+0.8\%$).

The generation of cupriferous brines by traditional deep-burial metamorphism alone is faced with numerous other challenges, such as explanations for the oxidation accompanying oxidative leaching of copper from source basalts, for the reduction involved in reductive deposition of native copper, and for the high salinities and moderate redox levels necessary for copper transport in saline brines. Many of these questions may be resolved by merging the traditional metamorphogenic model with a topography-driven evolved meteoric water model. The alternative interpretation of the copper isotopic fractionation data discussed above would also be consistent with this hybrid evolved meteoric water/metamorphogenic water model [4,5].
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References
1. Bornhorst, T.J.; Mathur, R. Copper isotope constraints on the genesis of the Keweenaw Peninsula native copper district, Michigan, USA. Minerals 2017, 7, 185. [CrossRef]
2. Stoiber, R.E.; Davidson, E.S. Amygdale mineral zoning in the Portage Lake Lava Series, Michigan copper district; Part I, Part II. Econ. Geol. 1959, 54, 1250–1277, 1444–1460. [CrossRef]
3. Jolly, W.T. Behavior of Cu, Zn, and Ni during prehnite-pumpellyite rank metamorphism of the Keweenawan basalts, northern Michigan. Econ. Geol. 1974, 69, 1118–1125. [CrossRef]
4. Brown, A.C. Genesis of native copper lodes in the Keweenaw district, northern Michigan: A hybrid evolved meteoric and metamorphogenic model. Econ. Geol. 2006, 101, 1437–1444. [CrossRef]
5. Brown, A.C. District-scale concentration of native copper lodes from a tectonically induced thermal plume of ore fluids on the Keweenaw Peninsula, northern Michigan. Econ. Geol. 2008, 103, 1691–1694. [CrossRef]
6. Cornwall, H.R. A summary of ideas on the origin of native copper deposits. Econ. Geol. 1956, 51, 615–631. [CrossRef]
7. White, W.S. The native-copper deposits of northern Michigan. In Ore Deposits of the United States, 1933–1967. (Graton Sales Volume); Ridge, J.D., Ed.; American Institute of Mining, Metallurgical, and Petroleum Engineers: New York, NY, USA, 1968; pp. 303–325.
8. Livnat, A. Metamorphism and Copper Mineralization of the Portage Lake Lava Series, Northern Michigan. Ph.D. Thesis, University of Michigan, Ann Arbor, MI, USA, 1983; pp. 1–292.
9. Bornhorst, T.J. Tectonic context of native copper deposits of the North American Midcontinent Rift system. Geol. Soc. Am. Spec. Pap. 1997, 312, 127–136.
10. Markl, G.; Lahaye, Y.; Schwinn, G. Copper isotopes as monitors of redox processes in hydrothermal mineralization. Geochim. Cosmochim. Acta 2006, 70, 4215–4228. [CrossRef]
11. Ohmoto, H.; Goldhaber, M.B. Sulfur and carbon isotopes. In Geochemistry of Hydrothermal Ore Deposits, 3rd ed.; Barnes, H.L., Ed.; John Wiley & Sons: Hoboken, NJ, USA, 1997; pp. 517–611.
12. Zhu, X.K.; Guo, Y.; Williams, R.J.P.; O’Nions, R.K.; Matthews, A.; Belshawa, N.S.; Canters, G.W.; de Waal, E.C.; Weser, U.; Burgess, B.K.; et al. Mass fractionation processes of transition metal isotopes. Earth Planet. Sci. Lett. 2002, 200, 47–62. [CrossRef]
13. Allègre, C.J. Isotope Geology; Cambridge University Press: Cambridge, UK, 2008; 512p.
14. Brown, A.C. A process-based approach to estimating the copper derived from red beds in the sediment-hosted stratiform copper model. Econ. Geol. 2009, 104, 857–868. [CrossRef]
15. Yardley, B.W.D.; Graham, J.T. The origins of salinity in metamorphic fluids. Geofluids 2002, 2, 249–256. [CrossRef]
16. Yardley, B.W.D.; Cleverley, J.S. The role of metamorphic fluids in the formation of ore deposits. In Ore Deposits in an Evolving Earth; Jenkin, G.R.T., Lusty, P.A.J., McDonald, I., Smith, M.P., Boyce, A.J., Wilkinson, J.J., Eds.; Geological Society, Special Publications: London, UK, 2015; pp. 117–134.
17. Asael, D.; Matthews, A.; Oszczepalski, S.; Bar-Matthews, M.; Halicz, L. Fluid speciation controls of low temperature copper isotope fractionation applied to the Kupferschiefer and Timna ore deposits. Chem. Geol. 2009, 262, 147–158. [CrossRef]
18. Cannon, W.F.; Woodruff, L.W.; Daines, M.J. A thermal lag model for native copper mineralization in the Midcontinent rift system of Lake Superior. Geol. Soc. Am. Abstr. Progr. 1992, 24, A61.