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Reply

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

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Received: 15 October 2018; Accepted: 3 November 2018; Published: 6 November 2018

1. Introduction

We appreciate the opportunity to respond to Brown's [1] objections to our conceptual interpretation [2] of copper isotope data for native copper from the Keweenaw Peninsula native copper district and to provide a more complete view of our interpretation. Brown [1] proposes "A simpler, more geologically and geochemically satisfying interpretation" but, as we will describe below, his interpretation is not a reasonable option to explain our copper isotopic data [2]. Brown's [1] interpretation of our data relies on near-complete leaching followed by 100% efficient precipitation. Since 100% efficient precipitation would result in native copper having the same copper isotopic composition as the ore-forming fluids, Brown thereby attributes all of the variation in the copper isotopic composition of the native copper (−0.32‰ to +0.80‰ δ^{65}Cu, [2]) to variation in the ore-forming fluids.

Our interpretation of the copper isotope data [2] relies on the transport of copper as a $CuCl^-$ complex in which copper is +1 oxidation state [3,4]. Subsequent precipitation of native copper at less than 100% efficiency by reduction is expected to result in isotopic fractionation of copper with the δ^{65}Cu of the native copper being lower (lighter) than the δ^{65}Cu of the fluid. The degree of fractionation is largely dependent on the efficiency of precipitation and the temperature. Given this isotopic fractionation, we reasoned that the copper isotopic composition of the ore-forming hydrothermal fluids had a higher δ^{65}Cu (heavier) than we measured from native copper; the copper isotopic compositions of the native copper are normally distributed with an average of +0.28‰ δ^{65}Cu and range of −0.32‰ to +0.80‰. While uncertain, we believe the central tendency of the δ^{65}Cu of the ore-forming fluids was likely significantly elevated above the central tendency of measured δ^{65}Cu in the reductively precipitated native copper.

To derive the ore-forming hydrothermal fluids through the leaching of magmatic source rocks, with an expected starting isotopic composition of 0 ± 0.3‰ δ^{65}Cu, the leaching had to have been dominated by oxidation of copper from the source rock which favors higher δ^{65}Cu in the ore-forming fluids as compared to the source rocks since many native copper values are above the range of magmatic rocks. If copper in the ore-forming fluid is in a $CuCl^-$ complex (copper +1 oxidation state) we reasoned in order for copper to have been oxidized from the source rock then a significant fraction of the copper had to have been sited in native copper (Cu^0). We expect at least some of the copper in the source rock had a +1 oxidation state, since this state is generally favored in the magmatic environment, however leaching of this copper would not predict a shift in the copper isotope ratios as there is not a change in redox state. The proportion of copper leached in each oxidation state as

well as the degree of leaching and fractionation factor, largely dependent on temperature, will control the bulk copper isotope fractionation and hence, play a major role in the copper isotopic composition of the ore-forming fluids. Thus, we hypothesized [2] that incomplete/partial oxidative leaching of copper from the magmatic source rocks towards higher δ^{65}Cu followed by incomplete/partial reductive precipitation towards lower δ^{65}Cu can explain the copper isotopic composition measured from native copper.

In his Introduction, Brown [1] objects to this interpretation because "the sum of these two independent and largely uncontrolled fractionations is unlikely to have produced such a well-grouped array of δ^{65}Cu values." However, the two fractionations are not independent but are actually linked to each other as recognized by Brown later in his comment [1]. The copper isotopic composition measured in the native copper samples depends on both the composition of the ore-forming fluids and fractionation during reductive precipitation. Isotopic fractionation is not uncontrolled but is both controlled and constrained based on principles of stable isotope fractionation as also recognized by Brown [1]. The degree of fractionation is finite during both leaching and precipitation [2]. The existing copper isotopic experimental data are sufficient to define the vector of fractionation, which is controlled by the oxidation state of copper during leaching or precipitation. However, the current lack sufficient experimental data for copper isotopic fractionation forces us to only provide a conceptual model.

Brown states that "it is doubtful that copper isotopic fractionations can be explained solely within the context of classic metamorphogenic models as implied by" us. However, Brown's [1] own alternative interpretation of our data relies only on metamorphogenic processes as the source of ore-forming fluids.

Brown [1] concludes his Introduction with: "Topography-driven evolved meteoric water could provide other complementary explanations." However, Brown's comment [1] does not discuss the copper isotopic composition of copper in this evolved meteoric water or demonstrate how the copper in this evolved meteoric water can be incorporated to explain the measured copper isotopic composition of native copper. In Brown's model [4,5] the evolved meteoric fluids do acquire copper during descent toward the metamorphogenic source zone which would likely impact the copper isotopic composition of the ore-forming fluids. In other words, Brown [1] does not provide "other complementary explanations" of our [2] copper isotope data.

2. Evaluation of Brown's Model

2.1. Derivation the δ^{65}Cu in the Ore-Forming Fluids

As we propose [2], Brown [1] also proposes to derive copper in ore-forming fluids by oxidative leaching of magmatic rocks in the source zone with magmatic starting values of 0 to $\pm$0.3‰ δ^{65}Cu. However, by his interpretation the leaching of copper from the source rocks is near complete, or in other words nearly all of the copper in the source rock leaches into the fluid [1]. We agree that Brown's [1] "near-complete" oxidative leaching of magmatic rocks in the source zone with starting values of 0 to $\pm$0.3‰ δ^{65}Cu could result in ore-forming fluid with a tight range and slightly higher central tendency than that of the source rocks, 0.0 to +0.4‰ δ^{65}Cu (see Brown's [1] Figure 3 vertical dashed black arrowed lines). However, Brown [1] actually proposes that near-complete oxidative leaching generates ore-forming fluids with $-$0.32‰ to +0.80‰ δ^{65}Cu. To generate Brown's [1] values above +0.4‰ δ^{65}Cu, requires fractionation as a result of partial leaching up to the same level, +0.8‰ δ^{65}Cu, as we propose. Brown [1] states: "In the writer's opinion, the qualification "partial leaching" . . . . should apply to our explanation . . . ." Since Brown [1] proposes derivation of ore-forming fluids as high as our minimum of +0.80‰ δ^{65}Cu, his comment applies to his own model too. To derive those values between $-$0.32‰ to 0.0‰ δ^{65}Cu requires almost complete leaching of copper or more extreme than near-complete. Thus, Brown's [1] interpretation really includes almost-complete, near-complete, and incomplete/partial leaching of copper from the source zone and he invokes the same "independent and largely uncontrolled fractionation" as we do to interpret the data.

We [2] did not define the degree of uniformity of the copper isotopic composition of the ore-forming fluids nor did we define how much greater than +0.80‰ δ^{65}Cu was the central tendency of the copper isotopic composition of the ore-forming as implied by Brown's Figure 1 [1]. By our interpretation the copper isotopic composition of the ore-forming fluids is more uniform than implied by Brown [1]. We reasoned that the ore-forming fluids had a value of at least +0.80‰ δ^{65}Cu in order to explain the highest δ^{65}Cu measured for the native copper if, for this particular sample, it was possibly formed by 100% efficient precipitation. We expect that the central tendency of the copper isotopic composition of the ore-forming fluid was more likely to be greater than +0.80‰ δ^{65}Cu to accommodate fractionation upon precipitation, thus by our interpretation the measured isotopic composition of the native copper is a result of both fractionation during leaching and precipitation.

To generate values below 0.0‰ δ^{65}Cu to the low of the magmatic range, −0.3‰ δ^{65}Cu, requires almost-complete (approaching 100%) leaching of copper from the source rocks rather than near-complete leaching. Almost-complete (approaching 100%) leaching of the copper from the magmatic source rocks requires that the fluids must have remained within a finite volume of the magmatic source rocks, until all of the copper was leached from the entire volume of host rocks occupied by the fluids or the fractionation factor was zero. Significant amounts of an externally derived copper-bearing fluid moving into the finite volume and mixing with the metamorphogenic fluids will tend to shift the copper isotopic composition outside of this restricted range of −0.3‰ to 0.0‰ δ^{65}Cu unless, by chance, the copper isotopic composition of the incoming fluid has a δ^{65}Cu value within this range. The release of fluid from the finite volume before oxidative leaching of the copper is almost-complete will tend to result in the δ^{65}Cu of the released fluid that is fractionated towards higher δ^{65}Cu and the fluid remaining in the finite volume will also be shifted. The degree of the shift depends on the starting copper isotopic composition of source rocks (which may not be in the magmatic range if previously subjected to partial leaching), the % of leaching at the time of the release and the bulk fractionation factor (the bulk fractionation factor determined by the weighted sum of the fractionation factors of each oxidation state being leached). At the low end, ore-forming fluid between −0.3‰ to 0.0‰ δ^{65}Cu, needs to be generated by the unrealistic assumption of no incoming or outgoing copper-bearing fluid. Even ore-forming fluid between 0.0 to +0.4‰ δ^{65}Cu with the contained copper from near-complete leaching can only accommodate a very limited amount of incoming or outgoing copper-bearing fluid before the fluid will no longer have a copper isotopic composition within this range. The need of Brown's [1] model to have almost-complete leaching of copper to generate values at the lower end of the magmatic range requires practically a closed system as described above and is unrealistic in our view. Near-complete leaching is likewise questionable.

Brown [1] characterizes leaching of copper as being rapid at first, decreasingly important before less than $\frac{1}{2}$ of the copper has been leached, and very slow after roughly 90% of the copper is removed (Brown [1] Figure 2). Brown's Figure 2 [1] also illustrates that extraction of at least 90% of the copper from the source rock (near-complete) will result in a narrow near 0 to +0.4‰ range of δ^{65}Cu as shown in his Figure 3. By Brown's [1] own description of leaching, it would be very difficult for a slow-moving fluid to reside in a finite volume of rock for long enough to leach all of the copper or even nearly all of it. Enders et al. [6] has demonstrated the difficulty of almost- or near-complete leaching even in a highly acid, oxidizing environment (supergene) at Morenci where the maximum efficiency of leaching is 80%. By this additional reasoning almost-complete leaching is unrealistic and near-complete leaching is questionable.

Subaerial basaltic lava flows comprise most of the source and host rocks. These subaerial basaltic lava flows have a massive interior overlain by an amygdaloidal and/or brecciated flow top. The upper 5% to 20% of individual lava flows contains up to 50% vesicles although the abundance decreases gradationally downward into the massive interior [7]. About 20% of the flow tops are composed of brecciated amygdaloidal basalt. Within the exposed section in the Keweenaw Peninsula, the massive interiors are much less altered (relatively low porosity and impermeable) than the flow tops (relatively high porosity and permeable). Flows tops are important host rocks for the native copper deposits of

the Keweenaw Peninsula and were also likely the principal source rocks for the leaching of copper into the ore-forming fluid. Within the zone of precipitation, for flows with roughly average thickness or greater, the centers of massive flow interiors often lack overall demonstrable significant elemental mass transfer, except gradationally upward towards the flow top and downwards towards the base of the flow [8,9]. By analog in the source zone, it will be especially difficult for fluids to almost-completely or near-completely leach copper from these gradational parts of the massive flow interior. In surface exposures and drill core, some fractures within massive flow interiors have gradational alteration halos as they were pathways for the flow of ore-forming fluids. By analog in the source zone, similar fractures would be expected to only partially leach native copper. For thinner lava flows in surface exposures, the massive flow interiors are overall visibly more altered than in thicker flows although the degree of alteration is not uniform. By analog in the source zone, we expect that leaching of copper from the interior of thinner flows would have been incomplete/partial. This illustrates the difficulty of almost-complete or near-complete leaching of copper from the magmatic rocks in the source zone as required by Brown's model [1].

In Brown's model [1] a "batch" of fluid in a finite volume of copper source rock is likely static to nearly static in order to accomplish almost-complete to near-complete leaching of copper. The batch of fluids could be a small fraction of the entire source zone or the entire source zone. The ore-forming fluid ascends upwards through the overall same types of rocks as in the source zone. During ascent from the source zone, the fluids cannot acquire significant amounts of copper through reaction with these magmatic rocks except if all of the copper is leached or the fractionation factor was zero. Logically, we expect that ore-forming fluids acquire copper during ascent and because the fluids are moving almost-complete or near-complete leaching of copper is unlikely. Thus, copper added during ascent is likely partially leached or fractionated and will tend to shift the copper isotopic composition of the ore-forming fluids.

The difficulty of almost-complete or near-complete leaching of copper from the source rocks and during ascent is illustrated by hydrothermally altered basalt exposed in the Keweenaw Peninsula. Jolly [3] measured the copper contents of relatively unaltered basalt massive flow interiors and metadomains of the same flow in the oxidized hydrothermal environment. His data [3] document that the ore-forming fluids incompletely/partially leach copper rather than almost-completely or near-completely. This supports conclusions drawn above that the moving ore-forming fluids will partially leach copper.

We conclude that Brown's [1] proposed derivation of ore-forming fluids with the same range of values as those we measured [2] in the native copper samples by almost-complete, near-complete, and partial leaching is not "a simpler, more geologically and geochemically satisfying interpretation . . . " His proposed almost-complete or near-complete leaching is unrealistic and questionable.

2.2. Precipitation of Copper from the Ore-Forming Fluids

Brown [1] proposes that precipitation of copper is "essentially 100% efficient within the kilometer-scale up-dip dimension of the individual deposits" and as a result the precipitated native copper retains the copper isotopic composition of the ore-forming fluid. Brown [1] does not define what is meant by "within the kilometer-scale up-dip dimension of an individual deposit." Does he mean that the copper is progressively stripped from the ore-forming fluid resulting in the exiting fluid devoid of copper or does he mean that everywhere throughout the kilometer-scale up-dip dimension of the deposit that precipitation is 100% efficient at the very smallest scale? We will critique both of these possible interpretations.

Copper that is progressively stripped from an ore-forming fluid is in essence partially reductively precipitated. Native copper precipitated by reduction would be fractionated towards a lower δ^{65}Cu than in the ore-forming fluid. It would not retain the copper isotopic composition of the ore-forming fluid. The δ^{65}Cu of the residual ore-forming fluid would be higher than initially and as it moves upward the next precipitated copper would have a higher δ^{65}Cu than the first assuming the fractionation factor

was constant and that the residual fluid did not mix with other moving ore-forming fluid. In this way, copper would have been progressively stripped from the ore-forming fluid and if the initial "batch" of fluid did not mix with other ore-forming fluid (perhaps of a different composition) while progressively losing its copper, the cumulative precipitated masses of native copper would have a bounded range with the central tendency of δ^{65}Cu being the same as the initial value of the batch of fluid. Regardless of whether or not the fluid mixes with other fluids, partial reductive precipitation would result in native copper that does not retain the isotopic composition of the ore-forming fluid. If the δ^{65}Cu of the ore-forming fluids were the same range and central tendency as the measured isotopic composition of the native copper, as proposed by Brown [1], progressive stripping would result in an even larger range of δ^{65}Cu of the native copper than we measured.

At the very smallest scale, it is possible to imagine that the copper contained in a thin layer of ore-forming fluid could be 100% precipitated if the fluid is static. A moving fluid makes achieving 100% efficiency much more difficult. Considering the large volumes of ore-forming fluids that are moving through the deposits and precipitating microscopic to 100 s of ton sized masses of native copper, we think that 100% efficient precipitation is the exception and not always the case as required by Brown's model [1]. We have difficulty conceptualizing how ore-forming fluids become static time and time again to facilitate 100% precipitation of the copper contained in them. Models of other hydrothermal metallic ore deposits do not typically invoke 100% efficient precipitation. Any departure from 100% results in the native copper not retaining the copper isotopic composition of the ore-forming fluid. If the reductively precipitated native copper is usually fractionated towards a lower δ^{65}Cu then the δ^{65}Cu of the ore-forming fluid had to have been generally higher than the measured values from native copper. In turn to derive higher values in the ore-forming fluid generally requires partial oxidative leaching of copper from the source rocks as we proposed [2].

3. Evolved Meteoric Water

Brown [1] has criticized the classic metamorphogenic model as "deficient," and thereby his model [4,5] included descending evolving meteoric water that leaches copper in route to the metamorphogenic source zone at depth, a hybrid metamorphogenic-evolved meteoric water model. However, in his comment on our paper [1] he only relies on a metamorphogenic explanation for our copper isotope data and does not challenge our contention that the copper isotope data are difficult to explain when including a significant proportion of copper-bearing evolved meteoric waters.

A key argument by Brown [1] for involvement of evolved meteoric waters is that, as demonstrated by Jolly [3], high salinities are needed for high concentration of copper in ore-forming fluids. Brown points out that high salinity fluids are generally not generated by metamorphogenic processes unless they co-exist with evaporates or have sedimentary/seawater input. Brown's model [4] includes descending meteoric water dissolving speculative evaporites within the overlying sedimentary succession. While not observed in outcrop or geophysical data, evaporites in the overlying sedimentary succession are possible given the arid to semi-arid climate at the time of deposition [10,11]. The underlying thick succession of basalt lava flows that comprise the source zone were also deposited in a similar climate [11]. Thus, while there are no evaporite horizons interbedded within the basalt lava flows exposed on the flanks of the rift (the same as there are no significant evaporite horizons in exposed sedimentary horizons) it is equally possible that playa lakes existed in the topographically low center of the rift and thereby could have resulted in evaporite horizons interbedded between the lava flows (subsequently buried into the source zone). This speculative source of salinity is compatible with a metamorphogenic interpretation of the copper isotope data.

Other options for an input of salts into the ore-forming fluids include an incursion of seawater into the rift. On the basis of light stable isotopes, Livnat [12] proposed there was a seawater incursion into the rift. Thus, seawater could have penetrated into underlying basalt lava flows where it became trapped in or precipitated salts in the porous and permeable flow tops. Yet another option for an input of salts is magmatic fluids [7] since magmatic fluids are well known for elevated salinity [13].

While there is roughly a gap of 10 million years between the youngest exposed magmatism of the Midcontinent rift and the age of native copper mineralization [14,15], the very large magma bodies likely underplating the center of the rift may have been still crystallizing at the time of native copper mineralization although this is speculative. Thus, magmatic fluids could have contributed salts during the generation of ore-forming fluids or magmatic fluids generated earlier could have been trapped in the source rocks and subsequently modified by metamorphogenic processes. Light stable isotope data are compatible with fluids of metamorphogenic and evolved/modified magmatic origin [16]. A copper-bearing evolved magmatic fluid with magmatic copper isotopic values plus significant amount of additional copper from partial leaching during metamorphogensis is a plausible interpretation of the copper isotopic data. Alternatively, salinities may not have been as high as envisioned by Brown and instead the volume of ore-forming fluid was greater. While we have not provided an exhaustive evaluation of this topic, our short description should be sufficient to let the reader know that this part of the genetic model is still open to debate.

Brown [1] criticizes us for not describing the reductant to produce native copper precipitation in our metamorphogenic model. For either the "classic" metamorphogenic model or for his [4,5] hybrid metamorphogenic-evolved meteoric water model, Brown's [4] own proposed precipitation mechanism is applicable. He proposes [based on Jolly [3] and eH-pH diagrams drawn for 25 °C to model processes up to 350 °C [4]] that temperature decrease and the change from oxidized hydrothermal environment at depth to a reduced environment towards the surface resulted in copper supersaturation and precipitation of native copper from an ore-forming fluid without sulfur. We also proposed a similar explanation [2] as this explanation is compatible with the copper isotope data. In addition, mixing of reduced waters with ore-forming fluids in the sites of native copper deposits [17] is a viable precipitation mechanism so long as reduced waters are copper- and sulfur-poor.

We agree with Brown [1] that the source rocks would have been cold soon after deposition before burial, however, Woodruff et al. [18] have shown that there is more than sufficient time for temperatures to rebound prior to native copper deposition and that temperatures at depth during the time of native copper deposition were sufficiently high.

Our purpose here is to briefly reply to some of Brown's [1] other considerations in order to allow the reader to assess the two competing models for the genesis of the native copper deposits.

4. Dynamic Metamorphogenic/Hydrothermal Model

Our interpretation is that dynamic metamorphogenic/hydrothermal processes result in formation of native copper deposits of the Keweenaw Peninsula. Ore-forming fluids are dominantly derived by metamorphogenic processes during burial of a thick succession of mostly subaerial tholeiitic basalt lava flows although the source of salinity is debatable. The slow-moving fluids leach small amounts of copper from magmatic rocks in the source zone (mostly by incomplete/partial leaching) and as the fluids move along they continue to leach additional small amounts of copper from another "volume" of source rock (mostly by incomplete/partial leaching). The amount of copper leached by fluid in contact with a particular volume of rock at any instant or small interval of time is dependent on such factors as rate of fluid movement, the path of fluid movement, amount of copper previously extracted from the source rock, the proportion of oxidation states of copper, physiochemical conditions of the fluid (especially temperature and salinity), particulars of fluid-rock interaction and more. We envision that incomplete/partial leaching of copper into the ore-forming fluid continues during upward ascent through magmatic rocks similar to those in the source zone. This dynamic process produces a large volume of ore-forming fluid and operates over a significant period of time on the order of 100 s of thousands to a million years or more. Despite the number of factors, the averaging of continuous incomplete/partial leaching of copper from magmatic rocks in the source zone and during ascent, with restricted copper isotopic starting composition, results in an ore-forming fluid with a relatively uniform normal distribution of δ^{65}Cu values with a range less than that of the measured native copper values. Because of bulk fractionation as a result of incomplete/partial oxidative leaching of copper

of differing oxidation states from these magmatic rocks, the central tendency of the δ^{65}Cu of the ore-forming fluids was likely significantly elevated above the central tendency of measured δ^{65}Cu in precipitated native copper. White [7] has shown that there is more than sufficient copper in the proposed source zone to account for the native copper deposits.

Reductive precipitation of native copper occurs in the zone of precipitation and the δ^{65}Cu in the precipitated native copper depends on the δ^{65}Cu composition of the ore-forming fluids, the fractionation factor, and the efficiency of precipitation. Except for the special case of 100% efficiency, if this is in fact possible, the reductively precipitated native copper will have δ^{65}Cu values lower than the ore-forming fluid. Limited temperature variation during precipitation of native copper would have limited variation in the fractionation factor and thus, the degree of efficiency of precipitation would have been the principal cause of variation. We suggest that the degree of efficiency depended on the rate of fluid movement and mixing and was normally distributed. Process averaging resulted in bounded fractionation due to precipitation. Thus, by our view, the combination of fractionation during oxidative leaching of copper into metamorphogenic/hydrothermal ore-forming fluids followed by reductive precipitation can explain measured copper isotopic composition of native copper of the Keweenaw Peninsula.

5. Conclusions

We conclude that Brown's [1] proposed metamorphogenic model to produce ore-forming fluid with the same range and frequency as exhibited by our measured copper isotopic composition in native copper through almost-complete, near-complete, and partial oxidative leaching is unrealistic. Brown's [1] model that the native copper retains the copper isotopic composition of the ore-forming fluid because it is always 100% efficiently precipitated is also unrealistic. Brown [1] cites other considerations for inclusion of evolved meteoric water in the ore-forming fluid, however, the copper isotope data are not shown [1,2] to support significant amounts of copper-bearing evolved meteoric water. The simplest geological and geochemical interpretation is to derive copper isotopic compositions of native copper from the Keweenaw Peninsula of Michigan by metamorphogenic/hydrothermal processes ([2], and above).

Author Contributions: Both T.J.B. and R.M. wrote this Reply.

Conflicts of Interest: The authors declare no conflict of interest.

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