Copper Isotopic Perspectives on Supergene Processes: Implications for the Global Cu Cycle

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A compilation of copper isotopic compositions (δ^{65}**Cu) from supergene systems suggests distinct differences in the mean δ^{65}Cu of Cu in leach cap (δ^{65}Cu = −1.2 ± 3.5‰), enrichment zone (mean δ^{65}Cu = +1.2 ± 4.2‰), and fluids (mean δ^{65}Cu = +0.9 ± 1.3‰) relative to the high-temperature sulfides that comprise the primary ore (δ^{65}Cu = +0.1 ± 0.6‰). These isotopic differences can be explained by the oxidative dissolution of primary ore minerals, such as chalcopyrite, and the subsequent precipitation of oxides in the near-surface system and of sulfides at depth. A dynamic mass balance model predicts the observed Cu isotopic compositions of the Cu reservoirs in nature and constrains the temporal isotopic evolution of supergene systems. From the model, these systems isotopically evolve to substantial extents over 500 ka to 5 Ma time scales. In relatively closed systems, percent-level loss of Cu from the solid (with δ^{65}Cu values >>0‰) is possible, suggesting that supergene systems are important components of the global Cu cycle.**

KEYWORDS: supergene system, copper isotopes, reactive transport model, exploration geology, global Cu cycle

INTRODUCTION

Copper (Cu) is an element essential to life, cycled during the chemical weathering of rocks, intimately involved in reduction and oxidation (redox) processes, and a valuable economic metal. Supergene systems are important Cu resources because Cu is the principal metal that is redistributed and (re)concentrated (i.e. cycled) during supergene enrichment. Sillitoe (2005) notes that >50% of the copper currently mined on Earth is derived from supergene deposits. It is, therefore, important to understand how and why Cu ore deposits form, where they might be found, and which geochemical tools are best for finding them. More broadly, supergene systems cycle a substantial mass of Cu over millions of years, leading to the possibility that supergene systems play an important role in the global Cu cycle.

While Cu is a substantially heavier element than those elements whose isotopes have been traditionally targeted as tracers in natural systems (δ^{13}C, δ^{18}O, δ^{15}N, and δD), it fractionates isotopically in a mass-dependent manner in nature (Note: Cu isotopic composition is expressed in delta notation as δ^{65}Cu (in permil, ‰, units), which expresses the ^{65}Cu/^{63}Cu ratio of a sample relative to the NIST 976 standard). Redox processes are known to fractionate Cu isotopes to significant extents compared to other transition metals (FIG. 1). Supergene systems cycle Cu via redox processes and, therefore, exhibit a wide range of δ^{65}Cu values in both fluids and rocks that is characteristic of the main Cu reservoirs in the system (e.g. the leach cap, enrichment zone, and primary ore; FIGS. 1 AND 2). Accordingly, Cu isotopes may prove a useful tool for mineral exploration purposes.

Supergene systems have the potential to reveal isotopic variability in the global Cu cycle over time given the amount of copper that is cycled and the large variability in δ^{65}Cu in the supergene system. Understanding Cu isotopic variability in nature is critical to characterizing Cu fluxes in the modern global Cu cycle, identifying the processes that isotopically fractionate Cu, and developing Cu isotopes as a tool for constraining Cu cycling in the past (i.e. the Cu isotope "proxy"). Therefore, from the perspectives of both mineral exploration and geochemical cycling, Cu isotopes might prove effective tools for elucidating supergene-system processes and constraining how these systems evolve on regional and global scales.

COPPER CYCLING IN SUPERGENE SYSTEMS

The supergene system is a regional-scale weathering system in which Cu is mobilized in the near surface and transported to depth. The key processes that occur during supergene weathering are the oxidation of primary Cu-rich sulfide minerals, the downward migration of Cu-rich fluids, and the precipitation of secondary Cu-rich minerals at a redox boundary (i.e. the water table). Both oxidative dissolution and precipitation have been shown to fractionate Cu isotopes at low temperatures (see FIGS. 1 AND 2).

Previous studies have focused on understanding how Cu is mobilized and enriched in low-temperature aqueous supergene systems. The specific objectives of such work have been to identify the main mineral dissolution reactions that generate economically relevant Cu deposits, to constrain the temporal and spatial evolution of mineral assemblages and fluid compositions, and to address the extent to which supergene systems are open to the loss of metals and sulfur (Ague and Brimhall 1989; Lichtner and Biino 1992; Chavez 2000). Such work has demonstrated that supergene systems behave as closed systems (with respect to Cu) and that uplift and erosion are important processes for enriching Cu concentrations.

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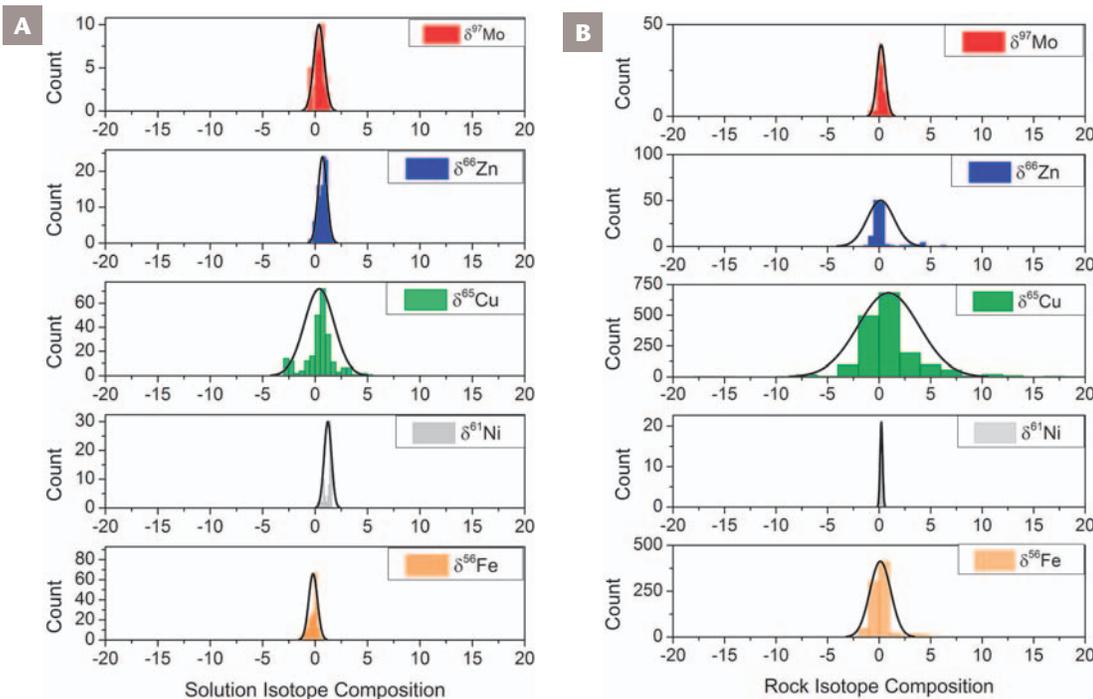
FIGURE 1 Histograms of literature-derived transition metal isotopic compositions of natural (**A**) rocks and (**B**) fluids, with number of papers utilized noted: Fe ($n = 35$), Ni ($n = 5$), Cu ($n = 37$), Zn ($n = 14$), Mo ($n = 16$). The reference standards are: IRMM 14 (Fe), NIST 986 (Ni), NIST 976 (Cu), and JMC Lyon (Zn). No consistent reference standard has been used across laboratories for Mo, though none of the ICP–MS standards that are currently used appear to vary significantly (<0.6‰) from NIST SRM 3134.

Local supergene activity can also persist over long timescales on the order of <10 Ma (Sillitoe and McKee 1996; Braxton et al. 2012). Supergene systems have sufficient time to be influenced by evolving surface geochemical and/or by geological conditions (e.g. surface Earth oxidation state, pCO_2, temperature, uplift rate). As conditions evolve, they can drive multiple cycles of metal mobilization, immobilization, and erosion that are difficult to decipher. Given such long timescales of evolution, supergene systems become potentially important components of the global Cu geochemical cycle and, perhaps, indicators of how surface geochemical conditions have evolved over time.

COPPER ISOTOPES IN THE SUPERGENE SYSTEM

Within supergene systems, there are distinct differences in $\delta^{65}Cu$ between the three reservoirs (i.e. the leach cap, enrichment zone, and primary ore; FIG. 2). Leach caps usually have the lowest $\delta^{65}Cu$ values, while the enrichment zone has the highest $\delta^{65}Cu$. From a mass balance perspective, a cyclic (leaching, erosion, recycling) open system dynamic is clearly expressed in supergene enrichment zones, for which Cu enrichments can reach as high as 700%. Such enrichments correspond to $\delta^{65}Cu$ values in secondary Cu sulfides that are isotopically heavy (mean: +1.2‰) relative to the primary ore but span a tremendous range ($\delta^{65}Cu$ of −6 to +8‰; FIGS. 1 AND 2). Supergene mobilization, transport, and precipitation also results in the generation of soils and leach cap Fe-oxides in which the secondary Cu minerals have modestly low $\delta^{65}Cu$ values, yet also cover quite a large range (−9‰ to +2‰; Mathur et al. 2009; Braxton and Mathur 2011).

Both oxidative dissolution and precipitation of sulfides can isotopically fractionate Cu. Experimental studies have demonstrated that the oxidation of Cu sulfides (Mathur et al. 2005; Fernandez and Borrok 2009; Kimball et al. 2009), chalcocite, bornite (Wall et al. 2011), and enargite (Kimball et al. 2009) generates solutions that are +1‰ to +3‰ relative to the initial reactant. Such values are corroborated by measurements of natural systems in which oxidative dissolution is occurring. (Fernandez and Borrok 2009; Kimball et al. 2009; Mathur et al. 2013a,b).

Experimental studies suggest that considerable isotopic fractionation is associated with sulfide precipitation on preexisting sulfides surfaces (approximately −2.6‰; Pekala et al. 2011), while the precipitation of Cu chlorides results in a much smaller isotopic effect (Ehrlich et al. 2004). Such empirical constraints on isotopic fractionation is generally consistent with theoretically predicted estimates of equilibrium isotope fractionation (Sherman 2013). Interestingly, experimental work demonstrates that the final sulfide precipitates appear to be in isotopic equilibrium with their solutions. This suggests that the bulk solid is capable of isotopic equilibration with its ambient fluid over experimental timescales. Given the slow pace at which equilibrium is achieved in natural geologic systems, this may obviate the need to call upon kinetic isotope effects when interpreting natural sulfide isotopic compositions.

Biological processes can also affect the $\delta^{65}Cu$ of solutions and solids in supergene systems, though such effects are going to be best seen close to the surface in the critical zone. Microbes and plants can both fractionate Cu isotopes (Kimball et al. 2009; Navarrete et al. 2011a,b). In most cases, biological material (i.e. cells) sequesters Cu with lower $\delta^{65}Cu$ values, though the magnitude of the expressed isotopic fractionation can vary greatly.

SUPERGENE WEATHERING AND THE GLOBAL COPPER CYCLE

The riverine input flux of dissolved Cu to the global ocean is ~7.7×10^8 mol y^{-1} and has a $\delta^{65}Cu$ of 0.63‰ (Little et al. 2014). The $\delta^{65}Cu$ of rivers is quite heavy, which could be partly explained by the leaching and/or erosion of Cu from supergene systems. Though supergene systems are typically regarded as closed, it is likely that enough Cu leaves them to be relevant to the global Cu cycle. A back-of-the-envelope calculation suggests that the flux of Cu from actively evolving supergene systems is ~10^8 mol y^{-1}. This figure assumes a subaerial landmass surface area of ~1.5×10^8 km² (Turcotte and Schubert 1982), supergene activity in the uppermost 100 meters of ~1% of this crustal area, an average primary ore Cu concentration of 0.024 mol Cu/kg rock (0.15 wt% Cu), an average rock density of 3 g/cm³, and the loss of 1% of this mass of Cu over a million-year
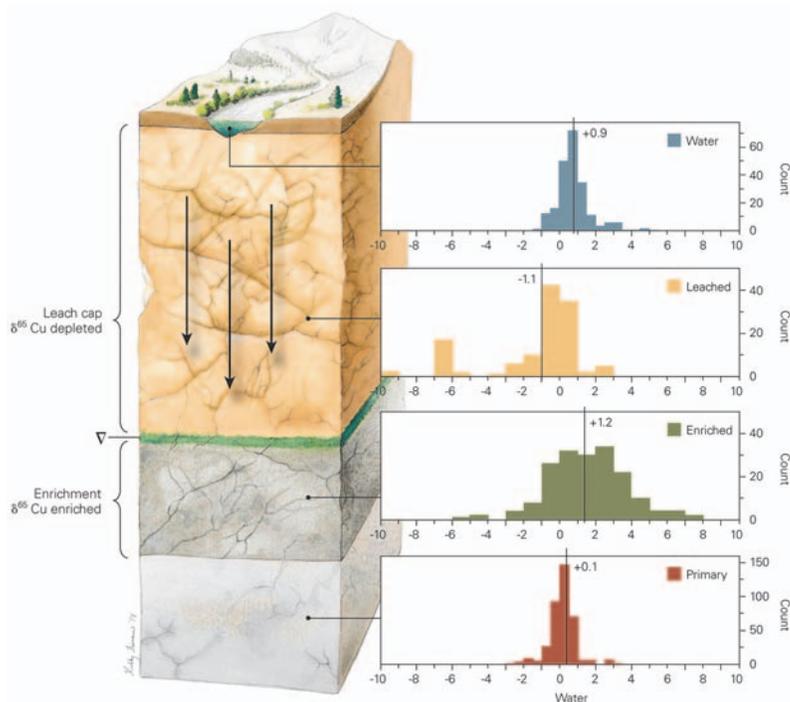
FIGURE 2 (**LEFT**) Schematic illustrating the spatial relationship between Cu reservoirs in a typical supergene system (leach cap, enrichment zone, and primary ore). ILLUSTRATION BY KELLY FINAN. (**RIGHT**) Histograms of literature-derived (n = 37) Cu isotopic compositions (δ^{65}Cu) of each reservoir and surface water.

time scale. This estimate is comparable to the total input flux to the modern ocean, which implies that a supergene-related flux is relevant to, and could even dominate, the global Cu cycle. A supergene flux is also relevant to the global Cu cycle from an isotopic perspective, given the significant in δ^{65}Cu variability in supergene systems. Such an estimate does not even consider the weathering flux of Cu from supergene systems after enrichment has ceased, which could generate a comparable mass flux with equally considerable isotopic leverage within the global Cu cycle.

To understand all this better, geochemists need to constrain quantitatively the temporal and spatial evolution of δ^{65}Cu in the output flux from active supergene systems (as a whole) and from distinct portions of the supergene system, because all may influence the global Cu cycle. The motivating questions are: Can supergene systems affect the global Cu cycle? If so, what is the likely δ^{65}Cu of the supergene input flux and how might the δ^{65}Cu of this flux evolve over time?

REACTIVE TRANSPORT MODEL FOR SUPERGENE PROCESSES

A simple reactive transport model (Fantle and DePaolo, 2006, 2007) can be used to approximate the dominant processes operating in supergene systems. The model simulates a single solid dissolving and reprecipitating such that there is no net change in the solid mass with time; in this case, the evolution of the pore fluid (f) is described by:

$$\frac{C_f}{t} = D\frac{^2 C_f}{z^2} - v\frac{C_f}{z} + RM(C_s - KC_f) \qquad (1)$$

while the evolution of the bulk, homogeneously reacting solid (s) is described by:

$$\frac{C_s}{t} = -R(C_s - KC_f) \qquad (2)$$

where D is the diffusion coefficient of the aqueous species under consideration in a porous medium (i.e. corrected for tortuosity, such that D = 0.0114 m^2 y^{-1} for Cu^{2+} at 25 °C and a porosity of 0.6), v is the advection velocity of the pore fluid (m y^{-1}), C_s is the concentration of Cu in the solid (mol kg^{-1}), C_f is the concentration of Cu in the fluid (mol kg^{-1}), R is the rate at which the solid reacts with pore fluid (y$_{-1}$), M is the local solid/fluid mass ratio, and K is the equilibrium distribution coefficient of the element between the solid and the fluid. The one-dimensional spatial reference frame (i.e. the model "column") is defined with z = 0 at the atmosphere–soil interface, with z being positive in the downwards direction. The evolution of isotopic composition is simulated by tracking each of the individual stable nuclides of Cu (^{63}Cu and ^{65}Cu) separately. Fractionation factors, which describe the preference for one nuclide over another during a specific process (α = 1, for example, indicates no preference), are applied to both the dissolution and precipitation fluxes, as described in the "What do the models of supergene processes tell us?" section below.

The model is designed to run iteratively for up to 10 sequential run cycles, with the results from the previous cycle used as the initial conditions for the subsequent cycle. A length-scale parameter (~150 m) is applied that resamples the solid concentration and isotopic composition from the bottom up, simulating rapid surface erosion of the model column between cycles. In the simulations, the depth variability in K is constrained by a logistic function, which varies from low values at shallow depths ($\rightarrow$0) to higher values at deeper depths ($\rightarrow$1000). The transition from low to high K is placed randomly around a mean depth from cycle to cycle to simulate the change in depth to groundwater.

The equations above are solved with a modified centered finite difference approach (e.g. Fantle and DePaolo 2006), with a modified leapfrog approximation utilized for the advection term to enhance stability (Bourchtein and Bourchtein 2012). The spatial resolution of the model (dz) is 10 meters, the time step (dt) is 0.1 years, the total column height is 300 m, the total time is 500 ka (per cycle), the reaction rate (R) is constant with depth and time (on the order of 5×10^{-6} y^{-1}, which is a reasonable rate given the observations made of reaction rates in nature (e.g. Maher et al. 2004, 2006; Fantle and DePaolo 2006), and the porosity is constant (= 0.6) in all simulations. Advection is assumed to occur only in the downwards (+) direction, and the advection velocity is constrained to be less than 0.1 m y^{-1} in all simulations (Ague and Brimhall 1989).

With regard to the fluid at the upper boundary is constrained to be closed to diffusion but open to advection in the positive direction, and the concentration (0.01 mM) and isotopic composition (0‰) of the advecting fluid held constant in time. The lower boundary, however, is technically open, though is more leaky than fully open. The reason for this is the numerical instability that arises in the presence of large concentration gradients in the fluid, even at exceedingly low dt (<0.005 y) and using the modified leapfrog approach. To minimize such gradients, the K value is varied smoothly over the model space and the reaction rate held constant as a function of depth. Similarly, the lower boundary is constrained to be no more than a few percent lower in concentration than, and identical in isotopic composition as, the lowermost grid point (i.e. lowermost point in the model domain at which the reactive transport equations are solved).

WHAT DO THE MODELS OF SUPERGENE PROCESSES TELL US?

Mass and Isotopic Evolution of Supergene Solids

Reactive transport models simulate supergene processes, replicating the gross features of a supergene deposit, including the generation of a leach cap and an enrichment zone over ten successive 500 ka cycles (5 Ma) of leaching, reprecipitation, and erosion (a single representative simulation cycle is shown in Fig. 3). The model results below are discussed relative to the degree to which the system is open or closed, which is expressed herein by the advective length scale, L_a (= v/RMK) (Fantle et al. 2010). This length scale reflects the relative dominance of the rate of advection compared to the rate of reaction in the model system, and it generally describes the distance ($\sim3{\cdot}L_a$) over which solid and fluid reach local equilibrium (e.g. Maher et al. 2004). For a relatively closed system ($L_a \approx$ 20 m), and assuming a primary ore Cu concentration of $\sim$0.024 mol Cu kg^{-1} (0.15% Cu), a reaction rate of $5{\times}10^{-6}$ y^{-1}, and a depth-variable K value, then a single 500 ka cycle can produce a maximum enrichment of up to three times the primary ore Cu concentration at $\sim$200 meters depth.
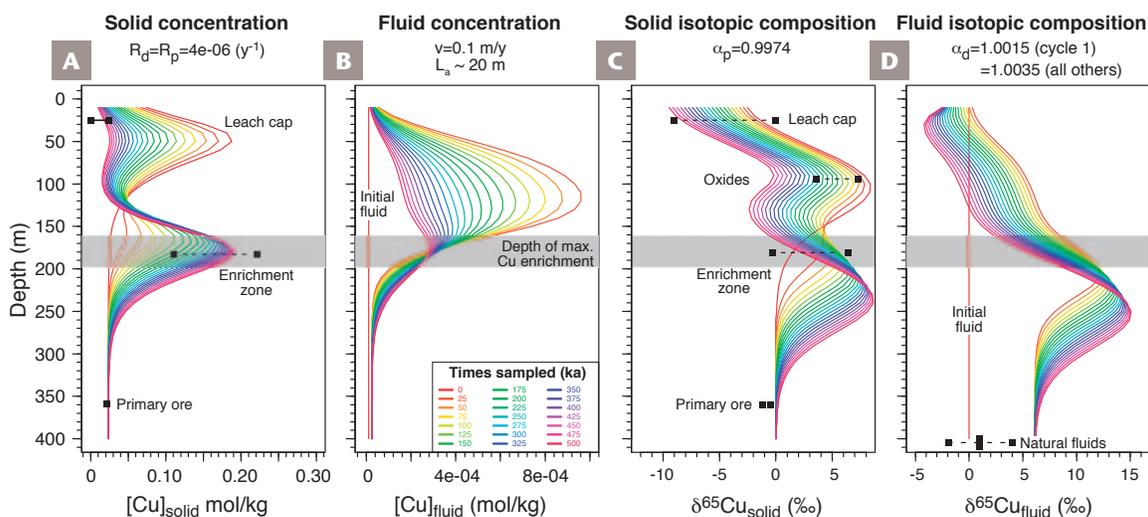
The extent of enrichment increases with each supergene Cu cycle, though not necessarily in a linear manner (Fig. 4A). However, the critical observation, based purely on mass balance constraints, is that a single 500 ka cycle cannot generate the type of enrichments typically observed in supergene systems (>0.10 mol/kg; Titley 1982). In the simulations conducted to date, at least four cycles (2 Ma) are needed to reach the lower range of enrichment values observed in nature. Further, in the relatively closed system scenario presented in Figure 3, on the order of 1% to 3% of the Cu is lost from the total solid per cycle (Fig. 4B).

In a more open system ($L_a = v/RMK \approx$ 60 m), the enrichment process is significantly retarded. When the rate is decreased by a factor of three, the cycle 1 (i.e. the first 500 ka) enrichment in the solid is only $\sim$50%, compared to $\sim$150% in the relatively closed system scenario (Fig. 4A). If the model system is even more open ($L_a \approx$ 200 m; not shown), the

enrichment is even smaller ($\sim$10%). Consequently, over the course of any given cycle in the relatively open system, a significantly larger proportion of Cu is removed from the solid (a fairly constant 3%) compared to that in a closed system (Fig. 4B).

The general Cu isotope systematics of the supergene system are also well characterized by the reactive transport model. The fractionation factor associated with dissolution (α_d) is assumed to be consistent with oxidative dissolution of either chalcopyrite (α_d = 1.0015 in cycle 1) or chalcocite (α_d = 1.0035 in cycles > 1). The fractionation factor associated with precipitation (α_p) is varied between 1.003 and 0.9974, thereby encompassing the maximum range of values one would expect for the precipitation of oxides such as tenorite and cuprite at low temperatures and the precipitation of sulfides on preexisting sulfide surfaces (e.g. Pękala et al. 2011; Sherman 2013). Generally, a single cycle of supergene enrichment has the potential to produce a leach cap that is isotopically light and portions of the enrichment zone that have δ^{65}Cu values that are higher than the primary ore ($\delta_{enrichment}$ − $\delta_{primary\ ore} \approx$ +1.5‰). In both the closed and relatively open system scenarios, the isotopically heavy enrichment zone is initially isotopically mass balanced by isotopically light Cu just below the main enrichment zone. The overall pattern from a single cycle of enrichment, therefore, is consistent with what is observed in nature, where the mean δ^{65}Cu of the leach cap is −1.1‰ and the mean δ^{65}Cu of the enrichment zone is +1.2‰.

Subsequent cycles of erosion and supergene weathering further fractionate the enrichment layer (Figs. 3 and 4). Relatively low δ^{65}Cu values in the lower part of the system are gradually overwritten and the maximum δ^{65}Cu of the enrichment zone increases. In the closed system case, the maximum δ^{65}Cu observed in the enrichment zone after 10 cycles (5 Ma) reaches $\sim$+4.5‰ (α_p = 1.003) to +8.5‰ (α_p = 0.9974). Critically, these relatively high δ^{65}Cu values are displaced relative to the depths of maximum Cu concentrations (Fig. 3), which is a consequence of isotopic distillation (expressed in the depth realm) in the presence of downwards advection. In a relatively open system, the

Solid concentration
$R_d = R_p = 4e{-}06$ (y^{-1})

A

Fluid concentration
v=0.1 m/y
$L_a \sim$ 20 m

B

Solid isotopic composition
α_p=0.9974

C

Fluid isotopic composition
α_d=1.0015 (cycle 1)
=1.0035 (all others)

D

Leach cap

Initial fluid

Depth of max. Cu enrichment

Enrichment zone

Primary ore

Oxides

Enrichment zone

Primary ore

Initial fluid

Natural fluids

Depth (m)

Times sampled (ka)

0	175	350
25	200	375
50	225	400
75	250	425
100	275	450
125	300	475
150	325	500

[Cu]$_{solid}$ mol/kg

[Cu]$_{fluid}$ (mol/kg)

δ^{65}Cu$_{solid}$ (‰)

δ^{65}Cu$_{fluid}$ (‰)

Figure 3 Representative dynamic mass balance simulation of supergene Cu enrichment for the case in which the system is relatively closed (L_a − 20 m), where L_a = v/RMK (v = advection velocity, R = reaction rate, M = mass ratio of solid/fluid, and K = equilibrium partition coefficient, C_s/C_f). The (**A**) solid and (**B**) fluid Cu concentrations and (**C–D**) δ^{65}Cu values are sampled as a function of time (sampling interval = 25 ka; total simulation time per cycle = 500 ka). The results shown represent the intracycle evolution of the supergene system during the last of ten cycles of mobilization, transport, and precipitation (i.e. the final 500 ka of 5 Ma of evolution). Between each cycle (i.e. every 500 ka), the column is resampled to simulate relatively rapid erosion at the top of the section and the resampled data used as the starting solid in the next cycle. Isotopic fractionation factors are denoted by α_i, where i refers to either precipitation (p) or dissolution (d).

solid evolves more slowly and does not develop enrichment zones with the high $\delta^{65}Cu$ values observed in the closed system scenario.

Mass and Isotopic Evolution of Supergene Fluids

The models of supergene processes suggest that supergene processes can generate fluids with a wide range of Cu concentrations and $\delta^{65}Cu$ values. Fluid concentrations are generally low in the model simulations, but this depends on the advective length scale (L_a): as the advective length scale increases, fluid concentrations decrease. At relatively small L_a (~20 m), fluid Cu concentrations are on the order of hundreds of µM in the early stages but can increase to mM levels as the enrichment zone evolves. By comparison, at L_a of ~60 m, fluid Cu concentrations are consistently less than 100 µM through the early stages, a consequence of the relative dominance of advection over reaction in such systems.

Similarly, the patterns of fluid $\delta^{65}Cu$ in the model column vary between open and closed systems. The simulated values are generally consistent with the data from natural systems, in which fluid $\delta^{65}Cu$ values are between –2 and +4‰ (mean = 0.9‰; FIG. 2). The model suggests that the $\delta^{65}Cu$ values of shallow fluids are distinct at any given point in time and can evolve over time to significant extents. For instance, in a given cycle, shallow fluids tend to have $\delta^{65}Cu$ values that are a few permil higher than the parent. With time, shallow fluid $\delta^{65}Cu$ values decrease, reflecting the isotopic evolution of the solid due to fractionation during oxidative dissolution (α_d = 1.0015 to 1.0035). Consequently, shallow fluids can attain relatively low deep fluid $\delta^{65}Cu$ values. Such an evolution is somewhat buffered in more open systems, resulting in relatively invariant fluid $\delta^{65}Cu$ in the early stages of supergene enrichment and, ultimately, $\delta^{65}Cu$ values that are ~3‰ higher than to primary ore.

By contrast, in a relatively closed supergene system, deep fluid $\delta^{65}Cu$ values generally vary over a more restricted range than do shallow fluids. Even so, there is potentially a ~4‰ to 5‰ range in deep fluids, both in space and time. If the fractionation factor associated with precipitation (α_p) is made to be consistent with experimental data (α_p = 0.9974), then deep fluids can be driven to extremely high $\delta^{65}Cu$ values (~+15‰; FIG. 3D). For the case where α_p = 1.003, relatively low deep fluid $\delta^{65}Cu$ values reflect distillation of the fluids caused by enrichment early in the cycle, whereas the increase in $\delta^{65}Cu$ values later in the cycle reflect the increasing contribution of the dissolution flux from the enrichment zone (high $\delta^{65}Cu$ values). In the latter case, the mass of Cu being supplied from above is extremely low so that the fluid is much more affected by continued reaction with the solid at depth than by either distillation or the supply of isotopically light Cu from the leach cap above. It is this late-stage fluid that is generally consistent with measured fluid $\delta^{65}Cu$ values (~+0.9‰; FIG. 2), though there are indications of low $\delta^{65}Cu$ fluids (0 to –1‰) that may reflect either the early stages of supergene evolution or simply fluids influenced by dissolution of the leach cap.

RELATING THE MODEL SUPERGENE SYSTEM TO REAL SYSTEMS

Assuming reasonable fractionation factors associated with dissolution (α_d = 1.0015 and 1.0035) and precipitation (α_p = 0.9974 and 1.003) in supergene systems, the dynamic mass balance model generates isotopically fractionated leach caps and enrichment zones that are comparable in magnitude to the $\delta^{65}Cu$ values measured in natural systems. The fractionation factors of 0.9974 and 1.003 are broadly consistent with both experimental and theoretical constraints on the fractionation factors associated with sulfide and oxide precipitation, respectively, while recognizing the considerable uncertainty in these values (e.g. Pękala et al. 2011; Sherman 2013). The simple approach to modeling supergene systematics described above is only an initial attempt; however, the relative mass balance between Cu immobilization in the shallow (small mass flux) and deep (large mass flux) supergene environment suggests that more complex simulations may not yield substantially different conclusions. Such a hypothesis is supported by simulations (not shown), in which distinct α_p are assigned to oxide precipitation in the shallow system (α_p = 1.0014) and sulfide precipitation at depth (α_p = 0.9974), whose results do not vary markedly from the depth-invariant α_p = 0.9974 scenario (FIG. 4).

The simulations highlight a few important points regarding the spatial and temporal development of supergene systems. As has been suggested previously (Cook 1988), multiple cycles of Cu mobilization and immobilization, punctuated by erosive episodes, are required to generate the magnitude of Cu concentrations observed in supergene enrichment
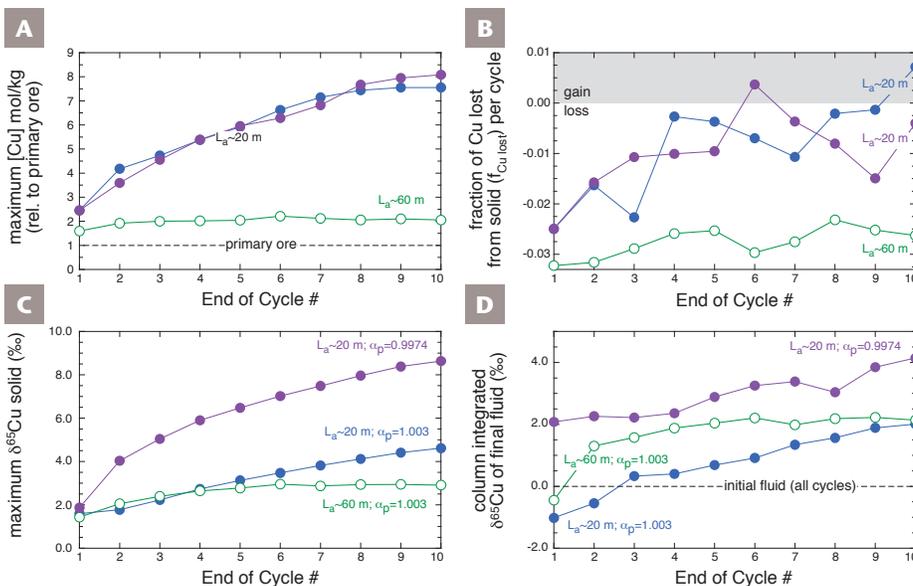
FIGURE 4 Summary of dynamic mass balance simulations: (**A**) maximum Cu concentration, (**B**) fraction of initial Cu lost from solid within each cycle, (**C**) maximum solid $\delta^{65}Cu$, and (**D**) column integrated $\delta^{65}Cu$ of the final fluid over the course of ten cycles, $\delta^{total}_{fluid} = \sum_n C^n_{fluid}\delta^n_{fluid} / \sum C^n_{fluid}$, for n grid points where C is the Cu concentration at each grid point, and the porosity is assumed constant over all n. Each point represents the value culled, or calculated, from the simulation result at the end of any given cycle. Stochastic behavior illustrated in panel (C) is attributable to the randomly selected depth to groundwater (~150–250 meters depth). Erosion is simulated between cycles by resampling the model section from the bottom up (~upper 150 m removed); this process is the source of considerable intercycle Cu loss from the supergene system.

zones (Fig. 4A). The only ways around this requirement are to increase the mass of initial primary ore leached and/or allow lateral transport of Cu into the system.

Additionally, assuming that the fractionation factors used are valid, a single cycle of enrichment can quite easily satisfy the Cu isotopic requirements of a mean leach cap $\delta^{65}Cu$ of –1‰ and a mean enrichment zone $\delta^{65}Cu$ of 1‰. However, if further processing is required from a mass balance point-of-view, then the isotopic evolution of the supergene system will continue, resulting in substantially fractionated leach caps and enrichment zones (Fig. 4C). Such a possibility highlights (1) the importance of thoroughly characterizing what is probably an isotopically heterogeneous system, and (2) the utility of modeling to provide clear expectations that place field data in context. Further, the requirement for subsequent cycling from a mass perspective suggests that Cu isotopes may then be useful for constraining the advective reaction length scales appropriate for a given supergene system, given reasonable constraints on process-specific fractionation factors. In other words, the Cu isotopic compositions of aqueous Cu in solution, leach cap minerals, and/or enrichment minerals can be used in conjunction with simple models to constrain the degree to which Cu has been recycled in the system. As discussed below, constraining advective length scales is fundamental to evaluating the role of supergene systems in the global Cu cycle.

The reactive transport modeling also points out that high spatial resolution mass and isotopic patterns with depth in supergene systems convey useful information regarding supergene isotope systematics. In particular, it is possible to constrain the fractionation factor associated with precipitation by considering where the maximum $\delta^{65}Cu$ value falls in the enrichment zone relative to the maximum Cu concentration (e.g. Fig. 3). The diagnostic patterns, which simply reflect distillation in a vertically mobile system, imply that preferential precipitation of the heavy Cu nuclide should generate a profile in which the maximum $\delta^{65}Cu$ and Cu concentrations generally co-occur (depth offset ~0 ± 2 meters). Such a pattern has been observed in the Ray and Silver Bell porphyry Cu deposits in southern Arizona, where chalcocites with higher $\delta^{65}Cu$ values covary with total Cu content (Mathur et al. 2010). By contrast, fractionation factors less than 1 suggests a sizeable vertical displacement between the maximum $\delta^{65}Cu$ and maximum Cu concentration in the enrichment zone (where the maximum $\delta^{65}Cu$ is ~50 meters deeper than the maximum Cu concentration; L_a ~20 m).

The simulations also indicate a noticeable difference in the temporal evolution of supergene $\delta^{65}Cu$ values over a rather restricted range of advective reaction length scales (L_a = 20 and 60 m). More open systems (L_a ~60 m) evolve much more slowly from both mass and isotopic perspectives (Fig. 4), and generally feature less in-cycle variability than the more closed system case (L_a ~20 m). As expected, considerably more Cu is lost from the more open system, and the difference generally scales with the advective length scale.

Finally, it should be noted that the model simulates a homogeneous solid reservoir, which does not necessarily explain or account for small-scale mineralogical heterogeneities. Such an approach does appear quite useful, however, for constraining the evolution of fluid $\delta^{65}Cu$ values within the supergene system, which may serve as a valuable reference for interpreting small-scale isotopic heterogeneities.

IMPLICATIONS FOR EXPLORATION GEOLOGY

Although the Cu isotopic compositions of chalcocite and the overall concentration of Cu in supergene systems are important to explain, the exploration geologist has slightly different priorities, and (s)he does not have the luxury of seeing enrichment zones in outcrop. Nearly all significant enrichment zones occur at depth, so developing a means of detecting enrichment requires a way of utilizing exposed, or easily accessible, geological materials, such as Fe-oxides and surface waters.

The use of Fe-oxides is complicated by the inability to isolate the weathering products of sulfide oxidation (Blanchard 1968) and, potentially, by the interactions between Cu and Fe-oxide surfaces. Desorption of Cu can isotopically fractionate Cu, making it unclear if the $\delta^{65}Cu$ of the Fe-oxides directly reflects weathered primary ore. Theoretically, the pH in supergene systems is low enough to inhibit adsorption of Cu onto Fe-oxide surfaces. From the standpoint of avoiding the effects of sorption, therefore, hematite (i.e. the residual of chalcocite weathering) and martite (i.e. the residual of chalcopyrite and chalcocite weathering) are ideal minerals to target for exploration, whereas jarosite (i.e. the residual of pyrite weathering that contains low concentrations of copper) is less ideal.

Iron-oxides with higher $\delta^{65}Cu$ values tend to correlate with enrichment at depth (Braxton and Mathur 2011), suggesting that high $\delta^{65}Cu$ values in the leach cap Fe-oxides are evidence of chalcocite weathering, thereby making high $\delta^{65}Cu$ Fe-oxides an ideal exploration tool. Model simulations support the concept that Cu cycling at shallow depths can generate Fe-oxides with consistently high $\delta^{65}Cu$ values compared to the leach cap above. Early in a given cycle, oxide $\delta^{65}Cu$ is even comparable to the enrichment zone, because it represents the enrichment zone from the previous cycle that has been brought to the surface by erosion. If this hypothesis is valid, the $\delta^{65}Cu$ of Fe-oxides exposed at the Earth's surface may prove to be an excellent exploration tool.

Surface waters are one of the most accessible targets for exploration purposes. Fluids that have been impacted by oxidative dissolution of sulfide minerals should have relatively high $\delta^{65}Cu$ values (Kimball et al. 2009; Mathur et al. 2013). In addition, fluids can integrate both laterally and vertically in space, making them unique probes of supergene systems. However, no published studies have, to date, presented the sort of district-scale studies of Cu isotopic variability in fluids that are needed to develop this tool.

IMPLICATIONS FOR THE GLOBAL COPPER CYCLE

A key observation of the model simulations is that the relatively closed-system dynamics of the supergene system as a whole has the potential to generate isotopically fractionated fluids, as well as a substantial mass flux of Cu out of the system (Fig. 4B). Though the proportion of Cu that is lost is minimal from the standpoint of supergene enrichment (~1–3% for the scenarios investigated), such a loss corresponds to Cu mass fluxes out of a supergene deposit of ~10^{-9} mol Cu/kg/y. Assuming the mass of rock impacted by supergene processes is >10^{17} kg (i.e. >0.1% of the current subaerial continental area down to 200 m depth), then the total flux out of supergene systems is on par with the total input flux of dissolved Cu that has been estimated for the modern ocean (Little et al. 2013).

A supergene-related Cu output flux is likely to have a δ^{65}Cu value that is substantially greater than 0‰ (Fɪɢ. 4D). In fact, loss of Cu either from active supergene systems or from weathering supergene enrichment zones will have tremendous leverage (~2 to 8‰, depending on the source) by which to alter riverine input to the ocean. An isotopically heavy weathering flux has been hypothesized to exist in low-order streams impacted by acid mine drainage and/or the weathering of sulfides (Fernadez and Borrok 2009; Kimball et al. 2009; Mathur et al. 2013). Such a heavy flux is not necessarily balanced by the isotopically light material lost (as inferred in Fɪɢ. 4C), because this material is lost mainly by erosion at the top of the supergene system (at least in the model). If lost as relatively insoluble particles, isotopically light material may not reach the ocean in the dissolved phase. This minimizes the ability of this isotopically light flux to balance the isotopically heavy flux and increases the leverage of supergene-derived Cu to affect the temporal evolution of seawater δ^{65}Cu.

Ultimately, supergene systems have the potential to account for the relatively high δ^{65}Cu of the global riverine flux (0.63‰). Further, variations in supergene activity and the abundance of supergene deposits at the Earth's surface over time could account for temporal variations in seawater δ^{65}Cu.

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