Copper Isotopes Used in Mineral Exploration

Ryan Mathur and Yun Zhao

Abstract

The use of copper isotopes related to ore deposit location and genesis has greatly expanded over the past twenty years. The isotope values in ores, rocks, soils, and water range greater than 10‰ and provide ample isotopic variation to identify and interpret complex geological process. From an exploration standpoint, the copper isotope values in waters, sulfides and weathered rocks vector to mineralization at depth. Ground and surface waters display the greatest potential for both green and brownfields exploration, whereas Fe-oxides and other related ore minerals isotope compositions for exploration are nascent. From an ore genesis perspective, the copper isotopes serve as a redox proxy to aid in unraveling magmatic and hydrothermal processes related to metal sulfide precipitation. In summary, the use of copper isotopic approaches by the mining industry are ideal as they point to processes directly related to the metal of economic interest and should be employed in all stages of the mine life from exploration to extraction, and to environmental monitoring post-mining activities.

1 Introduction

Copper isotope analysis of different types of earth materials is an expanding field in the transition metal isotope geochemistry. Copper isotopes are highly sensitive to redox reactions and the majority of the studies completed to this point have used the copper isotope ratios to trace and understand geochemical reactions involving electron transfer. Other mechanisms have been proposed as causes for isotopic shifts such as biogeochemical processes, liquid–vapour transitions, mixing of different geochemical reservoirs and other physiochemical characteristics related to fluid-rock interactions. From a mineral exploration perspective, the copper isotope signatures in ores, rocks, fluids, and soils have been used as a means to vector to ores and understand the fundamental aspects of ore genesis.

The first reported copper isotope values of earth materials was by Shields et al. (1965). The errors were too large to identify the isotope differences among these materials. It was not until the introduction of advanced mass spectrometry instrumentation in the mid 1990s that analytical techniques allowed for more precise and accurate isotope measurements. The Multi-Collector Inductively-Coupled-Plasma Mass-Spectrometer

R. Mathur (✉)
Department of Geology, Juniata College, Huntingdon, PA 16652, USA
e-mail: mathurr@juniata.edu

Y. Zhao
State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Beijing 100083, China

(MC-ICP-MS) permitted the simultaneous measurement of multiple metal isotopes with enhanced ionization of the metals to produce errors in the 4rd and 5th decimal place of isotope ratios (Halliday et al. 1995). This significant advancement led to the measurement of metal isotope variations that were initially predicted to be insignificant when isotopic fractionation principles were first developed in the 1940s (Urey 1947).

Copper ores received the majority of attention in the earliest studies of copper isotope because these materials contain large amounts of copper and were relatively simple to purify for isotopic analysis. It became apparent quickly within the literature that the degree of Cu isotope fractionation is significant and greater than the other isotope systems of similar mass (Fe, Ni and Zn). Thus, the mass spectrometry and purification of copper from different analytes received enhanced scrutiny to verify fractionation of greater than 10‰ (Fig. 1). The large range of isotopic compositions permits the ability to interpret and identify a variety of different geological processes.

Several different types of theoretical and experimental papers ranging from low to high temperature water–rock interactions have highlighted various mechanisms that lead to the fractionation of Cu isotopes (Zhu et al. 2002; Ehrlich et al. 2004; Weiss et al. 2004; Mathur et al. 2005; Markl et al. 2006; Seo et al. 2007; Pokrovsky et al. 2008; Balistrieri et al. 2008; Wall et al. 2011; Maher et al. 2011; Guo et al. 2020). Perhaps the most unique aspect of the studies of copper isotopes is the fact that redox reactions at low temperatures induce some of the largest fractionations measured in transition metals reported to date.

In this chapter we will provide an overview of the techniques used to measure copper isotopes, mechanisms that fractionate copper and most importantly, how these measurements can be used by exploration geologists in rocks, soils and solutions. Specifically, the organization of the chapter will focus on two themes: (1) the use of copper isotope signals in rocks, minerals and waters as a vector, and (2) the use of copper

isotope signals in rocks and ores as a means to define source of metals and trace metallogenic processes. The techniques proposed here can be applied to detect and define systems containing copper rich minerals or minerals with higher concentrations of copper. This chapter illuminates the power of using copper isotope analysis for a diversity of deposit types and materials that formed in high to low temperature geological settings through a comparative summary of the salient points from published literature.

2 Analytical Methods

To obtain meaningful copper isotope measurements on MC-ICP-MS, copper must be purified from all other analytes in solution. Several papers provide liquid ion chromatographic protocols to separate copper from complex chemical matrices (Marechal et al. 1999; Zhu et al. 2000; Marechal and Albarede 2002; Mason et al. 2005; Mathur et al. 2005, 2012a; Chapman et al. 2006; Borrok et al. 2007; Petit et al. 2008; Lobo et al. 2014; Sossi et al. 2015; Liu et al. 2014a, 2015). Each of the papers have used anion exchange resins in the chloride form and have eluted copper with different normalities of hydrochloric acids. The process removes unwanted ions that could cause a mass bias or interference during the measurement.

The most common resin used to separate copper is the BioRad MP-1 (maro porous HCl form of the resin beads) in 10 ml BioRad columns. Most of the columns used for the protocol have been 10 ml BioRad spin chromatography columns. The aspect ratio of the tapered end of the column can impact the separation of copper. Depending on the matrix of the solution, the column procedure was repeated if the copper was not adequately purified after one pass through the column. The process uses relatively larger volumes of ultrapure acids and has been scaled based on the amount of ions placed on the resin. More recently, Kidder et al. (2020) demonstrated that using a clean-up cation exchange column in an automated ion exchange chromatography is ideal for high Na rich matrices.
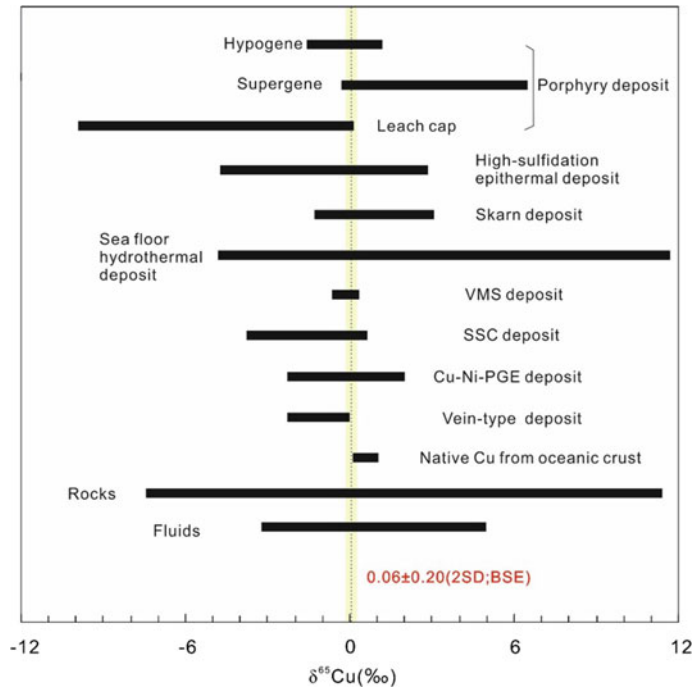
Fig. 1 Diagram showing variation in $\delta^{65}Cu$ values of different types of deposits, rocks and waters and soils, including porphyry deposits (Mathur et al. 2009; Wu et al. 2017), high-sulfidation epithermal deposits (Duan et al. 2015; Wu et al. 2017), skarn deposits (Maher and Larson 2007; Wang et al. 2017), sea floor hydrothermal deposits (Zhu et al. 2000; Rouxel et al. 2004), volcanic-associated massive sulfide (VMS) deposits (Mason et al. 2005; Housh and Çiftçi 2008; Ikehata et al. 2011), Cu–Ni deposits (Malitch et al. 2014; Ripley et al. 2015; Zhao et al. 2017, 2019, 2022; Tang et al. 2020), sediment-hosted stratiform copper (SSC) deposits (Asael et al. 2007, 2009, 2012), vein-type deposits (Haest et al. 2009), native Cu from oceanic crust (Dekov et al. 2013) as well as rocks and fluids (Mathur and Fantle 2015). The $\delta^{65}Cu$ value of bulk silicate Earth (BSE) is $0.06 \pm 0.20‰$ (2SD) (Liu et al. 2015)

Recovery of 90–100% of the copper during the chemical processing is critical to obtain meaningful results. Marechal et al. (1999) first pointed out that the resin can fractionate copper during the chromatographic separation on the order of 2–3‰ on synthetic solutions. They noted that ^{63}Cu is preferentially removed in the first 10 ml compared to the following 15 ml of copper eluted from the column. Different bonding strengths of the copper chlorides attached to the resin cause fractionation of copper during elution. Zhu et al. (2000) and Mathur et al. (2005) found the same relationships in natural rock and mineral matrices.

Copper minerals that possess 10's of % concentrations of copper do not require chemical purification by the ion exchange chromatography discussed above. Minerals such as chalcopyrite ($CuFeS_2$), chalcocite (Cu_2S), Cu-oxides (like copper carbonates such malachite and azurite), and native copper (Cu^o) have been dissolved and diluted for isotopic measurement both with and without chromatography and have generated the same copper isotope value. Therefore, measurement of these minerals does not require purification (Mathur et al. 2005; Zhang et al. 2020; Zhu et al. 2000).

The instrumentation setup and measurement of copper isotope on different MC-ICP-MS systems is relatively similar. The measurements were made in both wet and dry plasma in low-resolution mode. Solution concentrations range from 40 ppb in dry plasma mode up to 300 ppb in a wet plasma. The copper isotope voltages

range from 2 to 10 V in this setup. On peak background blank subtraction and matching of standards and samples within 30% produces reliable and repeatable measurements. Most studies do not use gases other than Ar during the measuring session.

There are two general approaches for mass bias correction during measurement. The simplest is through using the standard-sample-standard bracketing technique (SSB). The NIST 976 is the most common standard used in the literature, and copper isotope values are presented in the traditional per mil (‰) format relative to NIST 976 isotope standard. The second method involves doping the samples with either Ni or Zn standards and correcting mass bias through the exponential law as presented in Marechal et al. (1999). Since copper has only two isotopes, same element spikes cannot be added to solve for mass bias and there is no means to identify mass dependence in the natural samples nor during the measurements of copper isotopes. In order for this method to work, the added element standard must ionize in the plasma in nearly the identical means as copper. Smaller errors on the measurements have been reported using these techniques (± 0.12‰ for SSB in comparison to ± 0.06‰ for doping, 2σ). Liu et al. (2014a) established a method using a combination of SSB and Zn-doping, yielding external reproducibility better than ± 0.05‰ (2σ). The best accuracy and precision reported for doped samples was by the use of allium reported in Sullivan et al. (2020; Yang et al. (2019) with errors on the order of 0.03 ‰.

Error estimations for the analyses have been assessed in various ways. The error associated with background/blank copper is minimal in comparison to the samples analysed and is not considered a large source of error. Nor is the instrumentation measurement error, the counting statistics associated with measurement of copper isotope ratios are normally in the 4th to 5th decimal place of the measured value. The repeatability of the measurement has been assessed by comparing whole procedural replicates, measuring the solution multiple times in one session, and monitoring the variations of the NIST standard throughout the session (in this method the standard is bracketed to the other standard nearest in the session). Of the three techniques, the largest errors on samples reported are the variation of the standard throughout the session (Liu et al. 2014a).

2.1 Cu Isotope Fractionation Factors, Evidence from Experimental Work and Field Studies

The Cu isotope fractionation factors in different systems are of great importance for the application of Cu isotopes tracking complicated geological processes. High temperature experimental results show that the Cu-isotopic fractionation factors between aqueous fluids and silicates are controlled by Cu speciation in the fluids (e.g. $CuCl(H_2O)$, $CuCl_2^{2-}$ and $CuCl_3^{2-}$) and silicate melts ($CuO_{1/2}$), with $\Delta^{65}Cu_{fluid\text{-}melt}$ ranging from 0.08 ± 0.01‰ to 0.69 ± 0.02‰ (Guo et al. 2020). The fractionation factor between liquid and vapour ($\Delta^{65}Cu_{liquid–vapour}$) is estimated to be 0.10 ± 0.07‰ at 400–450 °C (Rempel et al. 2012). Experimentally determined Cu isotope fractionation factors between sulfide melt and silicate magma are controlled by Ni contents in sulfide, with high Ni (~ 25 wt%, $\Delta^{65}Cu_{sulfide\ melt\text{-}magma} = \sim -0.1$‰;) showing smaller fractionation than sulfides with low Ni [0.1 to 1.2 wt%, $\Delta^{65}Cu_{sulfide\ melt\text{-}magma} = 0.77 \times 10^6/T^2 - 4.46 \times 10^{12}/T^4$, where T is in °K (Xia et al. 2019)]. In the experiment work of Savage et al. (2015), sulfide phases also preferentially incorporate light Cu isotopes relative to bulk Cu ($\Delta^{65}Cu_{sulfide\ melt\text{-}bulk\ Cu} = \sim -0.1$‰). Numerical Rayleigh fractionation modeling based in massive sulphide ores in the Tulaergen magmatic Ni–Cu deposit indicates that $\Delta^{65}Cu_{residual\ sulfide\ melt–MSS}$ is approximately 1.0011 (Zhao et al. 2019). Finally, Ni et al. (2021) demonstrated through evaporation by the use of a laser, large copper fractionation factors result in 10's of ‰ fractionation during planetary processes because of volatile nature of copper in ultrahigh temperature processes.

For lower temperature applications copper isotope fractionation factors have been defined in great detail for redox, phase change, adsorption and other mechanisms. The oxidative dissolution of copper sulphide minerals results in the heavier isotope concentrating in the aqueous phase as pointed out in multiple contributions (Zhu et al. 2000, 2002; Marechal and Albarede 2002; Ehrlich et al. 2004; Mathur et al. 2005; Markl et al. 2006; Asael et al. 2007; Fernandez and Borrok 2009). Sherman (2013) provides a detailed theoretical argument that demonstrates how kinetics modelled with Rayleigh distillation models explain values measured in supergene sulfides. The lack electron transfer does not induce nearly the same magnitude of copper isotope fractionation as seen in the Cu oxide weathering experiments in Plumhoff et al. (2021). Both biological and adsorption mechanisms have been studied in great detail in association with soil and environmental geochemical where copper can be fractionated at relatively smaller degree in comparison to the sulphide redox reactions (Pokrovsky et al. 2008; Bigalke et al. 2009, 2010, 2011; Weinstein et al. 2011; Liu et al. 2014b; Fekiacova et al. 2015; Babcsányi et al. 2016; Li et al. 2016; Song et al. 2016; Guinoiseau et al. 2017; Kusonwiriyawong et al. 2017; Dótor-Almazán et al. 2017; Blotevogel et al. 2018; Mihaljevič et al. 2018). These studies have clearly shown how various mechanisms for copper isotope fractionation operate in conjunction in the low temperature interactions characteristic of the critical zone.

2.2 Copper Isotopes Used as a Vector and for Source Information

2.2.1 Copper Isotope Signatures in Minerals

Multiple studies have used the copper isotope compositions to assess the lateral and vertical variations as a means to use the copper isotope values as a vector to track concealed orebodies. The vector is developed through plotting isotope values on maps or within cross sections to deduce patterns through contouring of the data.

Most of these studies were performed on mineralization systems that operated at high temperatures. Here, we will summarize the findings and implications of the how and why copper isotope values change in these economically significant deposits.

The highest temperature systems concerning sulfide mineralization are mafic–ultramafic intrusions and associated deposits. In a large set of peridotites, basalts and subduction related andesites and dacites, Cu isotope fractionation is insignificant during mantle partial melting and magmatic differentiation, and the bulk silicate Earth (BSE) has an average $\delta^{65}Cu$ value of around 0.06‰ (Liu et al. 2015; Savage et al. 2015; Huang et al. 2016). However, mantle metasomatism with involvement of recycling crustal materials strongly fractionates Cu isotopes, spanning a wide range of $\delta^{65}Cu$ values from -0.64‰ to $+1.82$‰ (Liu et al. 2015). It seems that the addition of recycling crustal materials into the mantle source would result in obvious Cu isotope heterogeneity in the mantle source. The magmas derived from mantle partial melting are expected to inherit the Cu isotopic compositions of their sources.

Recent studies show that significant Cu isotope fractionation (~ 4‰ for $\delta^{65}Cu$ value) have been involved during the formation of the magmatic Ni–Cu deposits (Fig. 2; Malitch et al. 2014; Ripley et al. 2015; Zhao et al. 2017, 2019, 2022; Brzozowski et al. 2020; Tang et al. 2020). Many factors have been employed to explain the large variation of Cu isotopes (~ 4‰ for $\delta^{65}Cu$ value) in these deposits, including multiple mantle sources, variable degree of mantle melting, different magmatic processes, crustal contamination, R factor, and/or redox reactions (Malitch et al. 2014; Ripley et al. 2015; Zhao et al. 2017, 2019; Brzozowski et al. 2020; Tang et al. 2020). The generation of magmatic Ni–Cu deposits involves a series of stages: (1) mantle melting; (2) magma ascent; (3) segregation of sulfide melt from silicate melt and sulfide enrichment; and (4) silicate mineral crystallization and possible internal fractionation within segregated sulfide melt (Barnes and Lightfoot 2005; Naldrett 2010). Malitch et al. (2014) assert

that the Cu isotopic variation observed in the Noril'sk deposits region may result from multiple magmatic processes, different magma pulses, or assimilation of Cu from external sources. The distinct difference in δ^{65}Cu values between the sheet-style and conduit-style mineralization in the Lake Superior area is likely caused by mantle sources, variable degrees of melting, sulfide retention, and sulfide liquid fractionation (Ripley et al. 2015). It is difficult to precisely evaluate the contribution of the factors causing significant variations of Cu isotope compositions in the mafic–ultramafic intrusions of the Noril'sk region and Lake Superior area, since these intrusions are in different locations with diverse country rocks. Zhao et al. (2017 2019) reported a systematical Cu and Fe isotopes study of the Tulaergen Ni–Cu deposit, China. In this deposit, > 2‰ variation of δ^{65}Cu values has been observed, and the potential influence of crustal contamination, hydrothermal overprinting, diffusion, mantle sources or magmatic processes are excluded (Zhao et al. 2017, 2019). On the basis of negative correlation between δ^{65}Cu and δ^{56}Fe values of chalcopyrite and positive correlation between δ^{65}Cu values of chalcopyrite and δ^{56}Fe values of whole-rocks, redox reactions are expected to be the main factor governing the Cu isotope fractionation in magmatic Ni–Cu mineralization system (Zhao et al. 2017, 2019). However, Tang et al. (2020) proposed that Cu isotopic ratios show no correlation with intrusion/orebody shape, location of sample in the orebody, lithofacies or type of mineralization in the Kalatongke and Baishiquan deposits. The large variation of Cu isotopic compositions in these deposits is attributed to the degree of partial melting in the mantle source and associated magmas (Tang et al. 2020).

Even though debates addressing processes responsible for Cu isotope fractionation in mafic–ultramafic intrusions need to be addressed in further studies, Cu isotopes shed a new light on mineral explorations. Malitch et al. (2014) show a progression from lower copper isotope values in distal mineralization (Kharaelakh deposit) and the Talnakh occurrences to the higher values proximal to the Noril'sk-1

intrusion. The negative correlation of S and Cu isotope compositions for an individual intrusion in the Noril'sk region may be a useful indicator of the potential for hosting Ni-Cu-PGE sulfide deposits (Malitch et al. 2014). The distinct difference of Cu isotopic compositions between sulfides in disseminated sheet style and conduit style mineralization may be indicative of different types of mineralization, even though assimilation of Cu from external sources should be carefully evaluated (Ripley et al. 2015). Zhao et al. (2017) reported the Cu isotopic compositions in the Tulaergen deposit and point out that the proximal parts of the system tend to enrich light Cu isotopes than the distal samples. Zhao et al. (2019) further modelled the Cu isotope variation with the combination of PGE tenors, and conclude that sulfide segregation enriches light Cu isotopes, which is consistent high-temperature experimental work (Xia et al. 2019). Numerical calculations also indicate that significant Cu isotope fractionation occurs between monosulfide solid-solution (MSS) and evolved sulfide melt, with heavy Cu isotopes preferring evolved liquid to MSS (Fig. 3; Zhao et al. 2019). Considering that Ni and IPGE are preferentially incorporated in MSS, and Cu, Ni and PPGE tend to enriched in evolved sulfide melt (e.g., Li et al. 1996; Barnes and Lightfoot, 2005; Naldrett, 2010, 2011), Zhao et al. (2019) proposed that the mafic–ultramafic intrusions with light Cu isotopes may be favourable hosts for Ni and PGE mineralization, whereas elevated δ^{65}Cu values are potentially indicative of enrichment in Cu, Ni, Pt, Pd, and Au (Fig. 3). We notice that the Cu isotopes of the Baishiquan deposit are slightly heavier than the Kalatongke deposit (Tang et al. 2020), which is potentially related to different mineralization processes. Further work needs to be done to clarify how to use Cu isotopes as a vector for mineral exploration in different mafic–ultramafic intrusions.

Perhaps the most studied mineralized systems by Cu isotopes are porphyry copper and hydrothermally related mineralization such as skarns and epithermal gold deposits. Figure 4 shows the general patterns recorded in chalcopyrites from porphyry copper deposits.

Fig. 2 Histograms of copper isotopic compositions of various types of basalts (Liu et al. 2015), and magmatic Ni–Cu deposits in the Lake Superior area (Ripley et al. 2015), in the Noril'sk Province (Malitch et al. 2014), in the Eastern gabbro (Brzozowski et al. 2020), at the Tulaergen deposit (Zhao et al. 2017, 2019), and at the Kalatongke and Baishiquan deposits (Tang et al. 2020). The $\delta^{65}Cu$ value of bulk silicate Earth (BSE) is 0.06 ± 0.20 ‰ (2SD) (Liu et al. 2015)
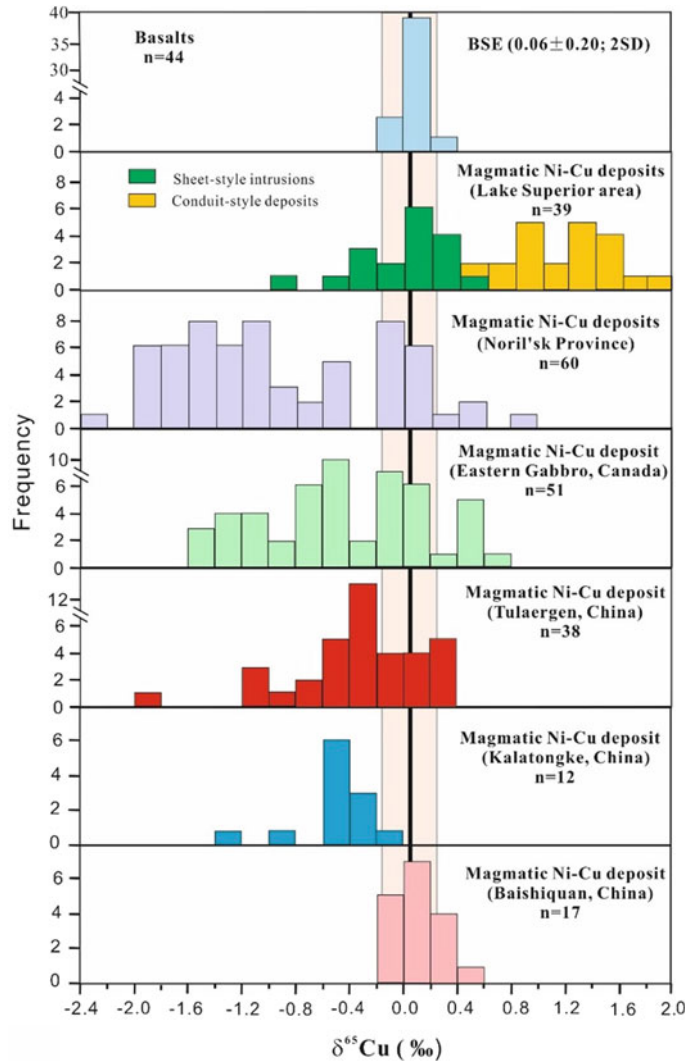
Chalcopyrite in veins from cores of the systems associated with higher temperature alteration silicate minerals like biotite and potassium feldspar have lower copper isotope values that cluster around 0‰ (Mathur et al. 2009, 2010, 2018; Mirnejad et al. 2010; Wall et al. 2010; Braxton and Mathur 2011; Asadi et al. 2015; Graham et al. 2004; Li et al. 2010; Duan et al. 2016; Gregory and Mathur 2017). In contrast, chalcopyrite in veins from distal part of the systems associated with lower temperature alteration silicate minerals like phyllite and kaolinite have higher copper isotope values. Other copper rich

minerals like bornite also show similar patterns to chalcopyrite (Dendas 2011).

Skarns display an inverse pattern where the higher copper isotope values are found in the cores of the systems and the lower values are found in the outer parts of the system (Maher et al. 2003; Larson et al. 2003; Yao et al. 2016). This inverse relationship is most likely related to the mechanisms that are fractionating copper during the formation of copper minerals from the hydrothermal solution. Experimental studies indicated that pH, fO_2 and salinity related to fluid-vapour separation controlled copper species
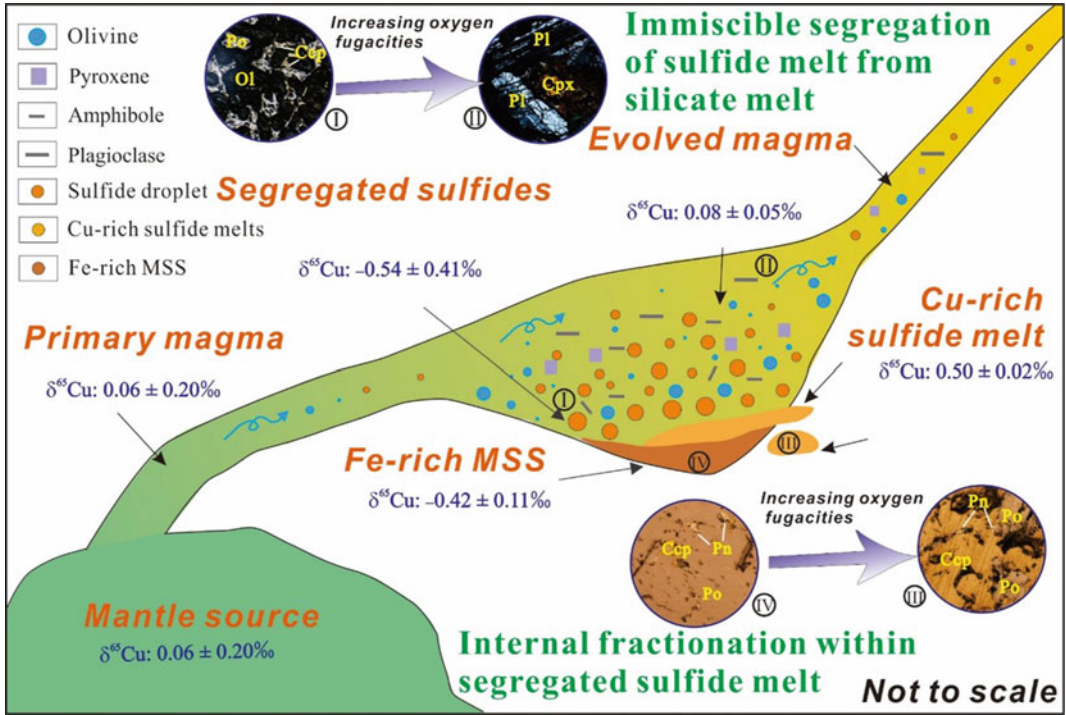
Fig. 3 A schematic model for the Cu isotope fractionation in the Tulaergen magmatic Ni–Cu deposit (modified from Zhao et al. 2019)

Fig. 4 Copper isotope values show pattern from proximal and distal locations in the stockwork and skarns associated with the intrusion of porphyritic rocks. Reproduced with permission from Mathur and Wang (2019); Copyright 2019 American Geophysical Union
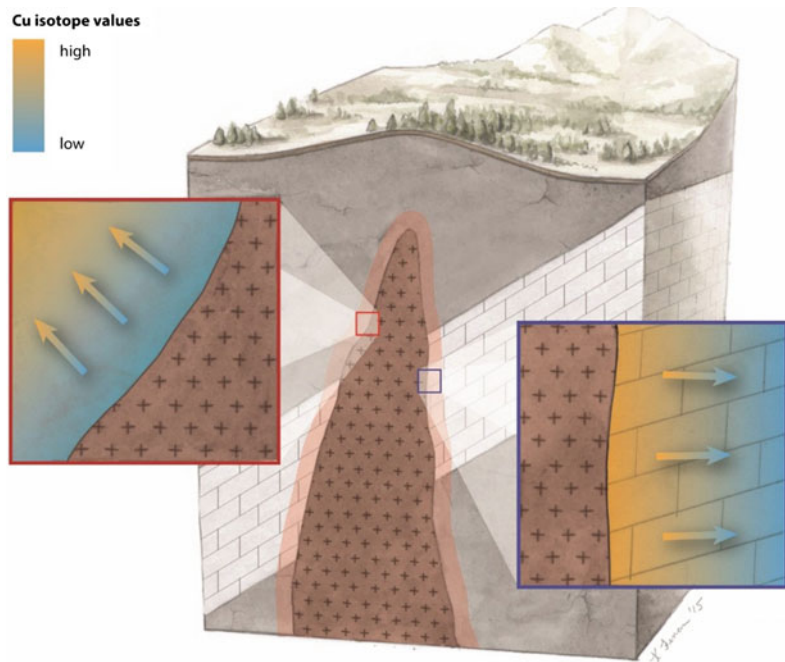
into the vapour phase (Maher et al. (2011). Thus, perhaps the difference in fractionation patterns between these two systems is related to metal transport with different ligands. For instance, CuCl species form in the acidic fluids associated with porphyry copper deposits in silicate rocks in contrast to CuCO species which form in buffered reactions associated with skarn mineralization. The different bonds strength associated with the metal–ligand could lead to the different fractionation factors during mineral precipitation. Seo et al. (2007) provided theoretical calculations relating different bond strength calculations that predicted the isotopic shifts that would be potentially happening in this system.

Epithermal Au deposits show a similar pattern to porphyry copper deposits (Duan et al. 2016) and the gold rich ores in these systems also have values that cluster around 0‰ (Saunders et al. 2015; Mathur et al. 2012b). Interestingly, the pattern of lower values in the core of the deposits and higher values on the borders is identical to porphyry copper deposits. If porphyry copper deposits are related to epithermal systems at depth, the isotopic values at the cores of the systems should be higher than that found in porphyries, instead they are identical. To date, the copper isotopes for a porphyry copper deposit beneath an epithermal system was only carried out at Yanacocha (Condon et al. 2012). At Yanacocha, the values of copper isotopes in chalcopyrite are lowest in the deepest parts of the porphyry and become higher to the base of the epithermal system. The two chalcopyrite and chalcocite values at the base of the epithermal system return 0‰ and then values become higher to the outer portions of the epithermal system. These preliminary data suggest that the two hydrothermal systems are unique and not linked to the same hydrothermal event.

Volcanogenic massive sulfide display the largest range of copper isotope variations within the higher temperature hydrothermal systems. Rouxel et al. (2004) presented values from an active VMS site in the Mid-Atlantic and reported ranges of copper isotope values of up to 3‰ which was attributed to reworking and later stage mobilization of copper. Berkenbosch et al. (2015) found smaller variations in a modern VMS in the Pacific and noted that the liquid vapour partitioning could explain the fractionation as vapours emitted from the chimneys are metal rich. Ancient VMS systems have not displayed as much copper isotope variations in the massive ores of the systems with values ranging around 1‰. These studies did not find simple, systematic spatial variations with copper isotopes in massive sulphides (Ikehata et al. 2011; Mason et al. 2005).

The lower temperature systems like sedimentary copper and supergene copper deposits display much larger copper isotopic variations than PCDs and LMIs. The interpretations for the copper isotope data involve understanding redox reactions associated with copper migration at lower temperatures. For sedimentary copper deposits, classic deposits of the Kuperschifer (Asael et al. 2007, 2009, 2012; Pękala et al. 2011) and the sedimentary copper deposits in the Democratic Republic of Congo (Haest et al. 2009) have copper isotope values in sulfide and oxide minerals that trace redox reactions and reflect fluid pathways in these systems (Fig. 5). Similar conclusions can be deduced from copper isotope values of native copper in large occurrence of native copper deposits in Michigan, USA (Bornhorst and Mathur 2017) and the native Cu deposits in Brazil (Baggio et al. 2018). Luczaj and Huang (2018) indicate little copper isotope fractionation in MVT ores of the central USA and point to the lack of redox reactions as the cause for this homogeneity.

Copper isotope fractionation is greatest at the lowest temperature deposits associated with supergene processes. Copper isotope values for sulfide minerals and residual Fe-oxides in leached zones range from − 10‰ to + 15‰. A general relationship of lower copper isotope values in leach cap minerals in comparison to the higher isotope values in the enrichment zones point to oxidation associated with the migration of the water table as the cause for the pattern. Multiple studies have demonstrated the use of copper isotope values in ores and leach cap minerals can be used to assess the degree of weathering (Mathur et al. 2005, 2009, 2010; Mirnejad et al. 2010; Asadi et al. 2015).
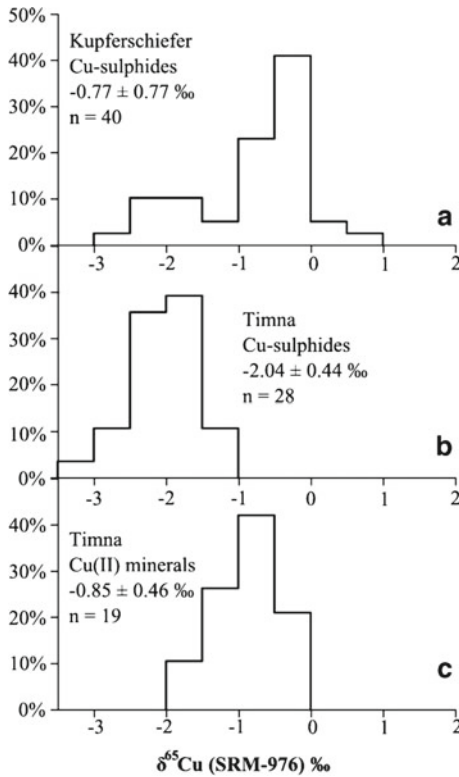
Fig. 5 Copper isotope variations in sedimentary copper deposits. Reproduced with permission from Asael et al. (2009); Copyright 2009 Elsevier

Specific examples of using the copper isotopes in exploration of supergene deposits are present in the following two contributions. Braxton and Mathur (2011) provide an excellent example of how the copper isotope values in the leach cap minerals can be used to identify the presence of multiple weathering steps of previous enrichment events. They demonstrated higher copper isotope values in the Fe-oxides of the leach cap correlate with larger concentrations of copper at depth. Equally important, they pointed to the fact that the copper isotope values of chalcocite change down hydrogeologic gradients and thus point to a flow path for the mineralization fluid. Braxton and Mathur (2014) show that in an area covered with Fe-oxide but no mineralization at surface, copper isotopes of Fe-oxide minerals vector to areas in the subsurface where supergene chalcocite has been weathered

and concentrated. Both studies point to the value in using copper isotope values in Fe-oxides on the surface, which are abundant and useful in identification of buried exploration targets.

Given that lower temperature process can cause greater degrees of fractionation coupled with the redox sensitivity of the Cu isotopes, Mathur et al. (2018) recognized that the copper isotope signature of chalcocite could be used to trace its origin. The influence or overprint of supergene processes in many mineral deposits makes identification of the process of chalcocite origins enigmatic. These authors suggested (as shown in Fig. 6) that lower copper isotope values in chalcocite originated from Cu-chloride complexes which formed sedimentary copper deposit chalcocite, whereas supergene chalcocite had higher copper isotope values because it formed in oxidative environments. Magmatic chalcocite has values hovering around 0‰ as smaller degrees of fractionation occur at higher temperatures (Fig. 6).

2.2.2 Copper Isotope Signatures in Rocks

The use of rocks in their relationship to ores has not been explored in any great detail. The main purpose of these studies would be a means to link the copper mineralization to the source materials in some fashion. There is not a large variation of copper isotopes compositions found in igneous, metamorphic and sedimentary rocks, and the range of copper isotope values is similar to that of chalcopyrite formed at high temperatures at $0 \pm 1‰$ (Chapman et al. 2004; Sossi et al. 2015; Fru et al. 2016; Wang et al. 2019; Liu et al. 2019, 2014a; Huang et al. 2016; Busigny et al. 2018). Zheng et al. (2019) offered the first argument that relates higher copper isotope values found in rocks associated with the PCDs in Tibet. Their argument focuses on a few values of intermediate igneous rocks that slightly heavier (by approximately $+ 0.3‰$) in which they argue the higher signatures are originated from weathered copper that is isotopically heavier copper transported by subducted materials. In another contribution, Wang et al. (2019) points to a similarity of the
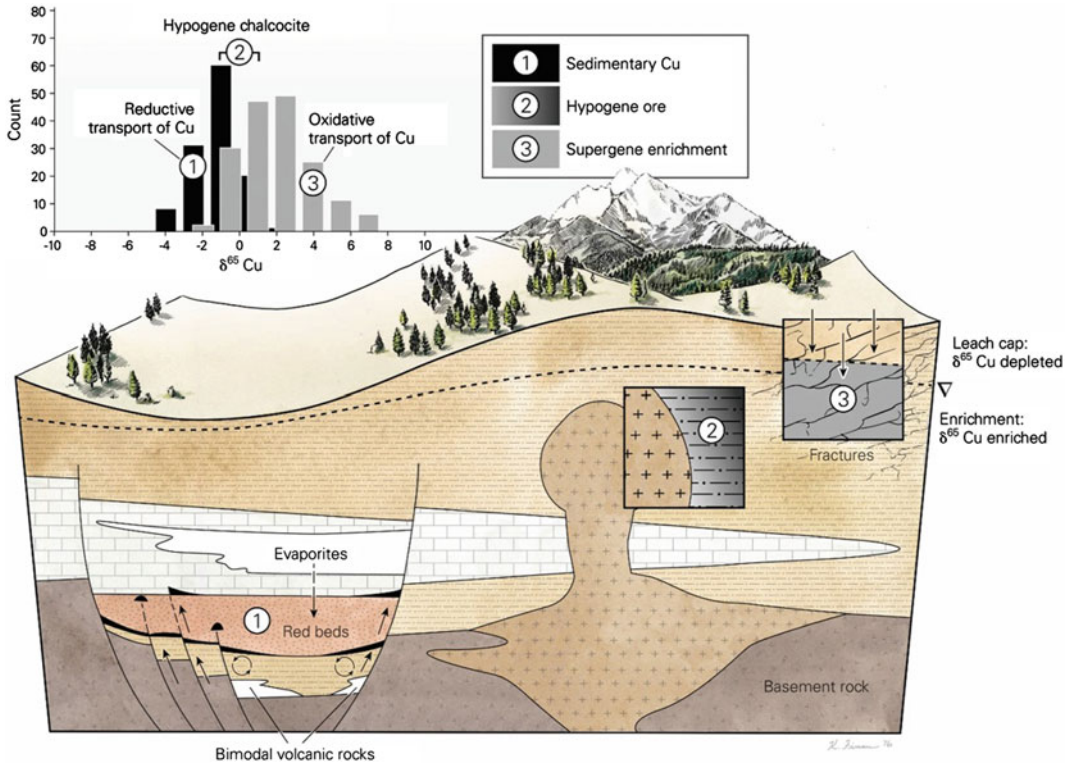
Fig. 6 The origins of chalcocite formation inferred through copper isotope analysis of chalcocite. The copper isotope compositions are linked to the different genetic processes associated with the formation of chalcocite. Reproduced from Mathur et al. (2018) (CC BY 4.0)

arc volcanic rock and sulfides in a non-economic type sulfide deposit. This suggests ores and rocks could have similar signatures and be used to trace metals.

There are no systematic studies that relate the mantle and metasomatized mantle to the genesis of magmas that are metal rich and are transported from the mantle through the lower crust into the upper crust. Several studies have shown that the metasomatized mantle (Liu et al. 2015; Zweifelhofer et al. 2018) could have highly variable copper isotope values, thus the starting point for the magmas is not homogeneous. Complicating the processes that could change the copper isotope values during petrogenesis is the fact that sulfide segregation at any point during ascent could greatly impact the copper isotope ratios found in the igneous rocks. At this point, what exactly the copper isotope values indicate in igneous rocks is not well constrained and more

study is needed to further interpret and understand the values measured in the rocks associated with ores at surface. One study by Höhn et al. (2017) provides copper isotope variations in pyrites from metamorphic deposits, yielding a narrow δ^{65}Cu range of -0.26 to $0.36‰$. Thus, how copper moves and what happens in the mantle and metamorphic rocks still deserves greater attention to resolve how the copper isotope values in these rocks can be interpreted.

Slightly larger isotope variations have been documented in sedimentary rocks. Again the variations are on the order of 1‰ with no studies to date that link the sedimentary rock copper isotope signatures to ores directly. Although Chi Fru et al. (2016) use the copper isotope signature as a redox signal that marks the start of the Great Oxidation Event in the Archean, to date not many other applications to sedimentary systems are available in the literature. Nonetheless, the

Fig. 7 Diagrams showing that Cu isotope compositions of waters can be used to infer the types of copper minerals weathering if the starting copper isotope composition of the minerals are constrained. Reproduced with permission from Mathur et al. (2014); Copyright 2014 Elsevier
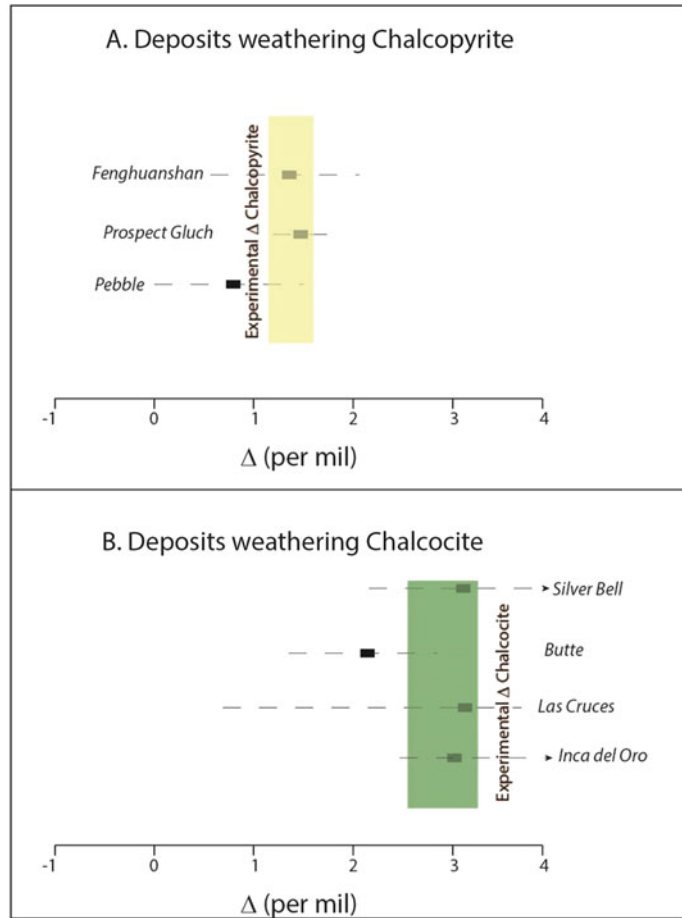
2.2.3 Cu Isotope Signatures in Waters and Soils

Copper isotope values in water has the greatest exploration potential because waters can sample the subsurface due to water rock interaction. Isotopic information from groundwater is far cheaper to obtain than data from drill core samples. Importantly, waters that have dissolved copper originating from sulfide-water interaction show unique copper isotope signatures. This is due to the fact that ^{65}Cu is favoured in the oxidation of copper due to bonding energies (Mathur et al. 2005; Pokrovsky et al. 2008;

Ehrlich et al. 2004; Wall et al. 2011). Thus, the oxidation product, in this case a solution, is relatively enriched in ^{65}Cu. For instance modern rivers and oceans have copper isotope values of $1.1 \pm 0.3‰$ (2σ) (Bermin et al. 2006; Vance et al. 2008, 2016; Little et al. 2014), and copper derived from leaching of copper sulfides has values of $1.2 \pm 0.3‰$ (2σ) (Mathur et al. 2005, 2012a, 2014; Kimball et al. 2009; Mathur and Fantle 2015). Kinetic processes clearly play an important role in the extent of reactions and the rates of sulfide dissolution, which controlled the Cu isotope fractionation in the critical zone.

An example of this in nature is the case study of the Pebble deposit in Alaska. This study demonstrated that waters collected from seeps within the 0.5% Cu grade contour (defined by extensive drilling) has distinctly higher copper

isotope values (2.6 ± 1.0‰, 2σ) than waters derived from seeps outside of this zone (Mathur et al. 2013). The range of the 0.5% copper is within 1.5 km distance from the mineralization center in this deposit, and the copper isotopic compositions are similar in these two mineralization zones. Kidder et al. (2021) show that the same patterns exists in groundwaters near PCDs and exotic Cu mineralization.

Importantly, the waters are approximately 1.5‰ heavier than the surrounding waters. It has been shown that the leaching of chalcopyrite results in waters that are 1.5‰ heavier than the leached chalcopyrite (Mathur et al. 2005; Kimball et al. 2009; Borrok et al. 2008). Leaching of other copper sulfide minerals also results in relatively different copper isotope compositions in waters. For instance, weathering of chalcocite which results in waters that 3‰ heavier than the leached chalcocite. Thus, using an estimation of the starting copper isotope composition of an ore, the copper isotope composition of the fluids not only indicates the weathering of copper sulfide, but also allows for the interpretation of the type of mineral providing copper to solution (Mathur et al. 2014).

The copper isotope composition of surface fluids can also be complicated by multiple types of other geochemical processes. For instance, waters interacting with soils and biological materials can impact the copper isotope composition of the fluids. Extensive studies on the biological and mineralogical impacts of clays on the copper isotope composition of fluids should also be considered during interpretation of the copper isotope values of waters (Pokrovsky et al. 2008; Bigalke et al. 2009, 2011; Weinstein et al. 2011; Liu et al. 2014b; Fekiacova et al. 2015; Babcsányi et al. 2016; Guinoiseau et al. 2017). Real time changes in copper isotope compositions of fluids and soils on a flood plain have demonstrated daily 0.5‰ shift in the copper isotope values as reported by Kusonwiriyawong et al. (2017). These studies illustrate that other processes may also impact the copper isotope signal in natural waters, however none of these processes fractionate copper in same direction and magnitude

as oxidation of copper sulfides. For instance, at low temperature, no biological, adsorption or temperature related process produces + 3‰ isotopic shifts.

Use of soils to target mineralization at depth has not received much attention. The variety of the studies of copper isotope and soils focus on how the copper isotope signals can be used to trace metal contamination (Sivry et al. 2008; Bigalke et al. 2010; Li et al. 2016; Song et al. 2016; Blotevogel et al. 2018; Mihaljevič et al. 2018). Some hope does exist for using copper isotope signatures in soils, as Mathur et al (2012a, b) pointed out that the weathering of soils with sulfides produces similar vertical profiles of copper isotope signatures as seen in leach cap environments. However, more study is needed to clearly identify the potential of copper isotope values in soils in mineral exploration.

3 Conclusions

Copper isotopic fractionation in ores and waters have potential as vectors to ore deposits. The greatest limitations of using the techniques is that the vector can point to the presence of copper sulfide mineralizaton, but cannot clearly be used to indicate the amount of copper present in the system. Used in tandem with other geophysical and geochemical evidence the copper isotopic data obtained clearly add valuable information for the exploration geologist. Further study of copper isotopic compositions of soils and rocks will lead to further our understanding of how these materials could be used in the search of ore systems.

Aside from exploration vectors, the copper isotopic evidence summarized above demonstrate that the analysis provides a means to quantify the degrees of weathering, different types of metal transport in high and low temperature systems, and electron transfer in all type of geochemical reactions. Data used in this light has clearly added value to ore genesis models and the ability to capture reaction dynamics and kinetics which was previously not quantified and/or identified.

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