

# Pleistocene recycling of copper at a porphyry system, Atacama Desert, Chile: Cu isotope evidence

Carlos Palacios · Olivier Rouxel · Martin Reich ·  
Eion M. Cameron · Matthew I. Leybourne

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**Abstract** We present Cu isotope data of hypogene and supergene minerals from the Late Paleocene Spence Cu-Mo porphyry in the Atacama Desert of northern Chile. Chalcopyrite displays a restricted range of  $\delta^{65}\text{Cu}$  values within the values reported for primary porphyry Cu sulfides (+0.28‰ to +0.34‰,  $n=6$ ). Supergene chalcocite samples show heavier and remarkably homogeneous  $\delta^{65}\text{Cu}$  values, between +3.91‰ and +3.95‰ ( $n=6$ ), consistent with previous models of Cu leaching and enrichment in porphyry systems. Secondary Cu minerals from the oxide zone show a wider range of composition, varying from +1.28‰ and +1.37‰ for chrysocolla ( $n=6$ ) to very light Cu isotope signatures reported for atacamite between

-5.72‰ to -6.77‰ ( $n=17$ ). These data suggest redox cycling of Cu during supergene enrichment of the Spence Cu deposit, characterized by a first stage of supergene chalcocite formation from acidic, isotopically-heavy leach fluids of meteoric origin down-flowing in a semi-arid climate (44 to ~ 15–9 Ma). Reworking of the initial supergene copper assemblage, during the Pleistocene, by rising neutral and chlorine-rich deep formation waters under well-established hyper-arid climate conditions lead to the formation of atacamite with extremely fractionated Cu compositions. Essentially coeval chrysocolla formed by dissolution of atacamite during short episodes of wetter climatic conditions occurring in the latest Pleistocene.

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C. Palacios (✉) · M. Reich  
Departamento de Geología, Universidad de Chile,  
Plaza Ercilla 803,  
Santiago, Chile  
e-mail: cpalacio@ing.uchile.cl

O. Rouxel  
Marine Chemistry and Geochemistry Department,  
Woods Hole Oceanographic Institution,  
Woods Hole, MA 02543, USA

O. Rouxel  
IUEM European Institute for Marine Studies,  
Université Européenne de Bretagne,  
Technopole Brest-Iroise, Place N Copernic,  
29280 Plouzane, France

E. M. Cameron  
Eion Cameron Geochemical Inc.,  
865 Spruce Ridge Road,  
Carp, ON K0A 1L0, Canada

M. I. Leybourne  
Ocean Exploration, GNS Science,  
P.O. Box 30-368, Lower Hutt, New Zealand

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## Introduction

In the Cu deposits of the Atacama Desert, northern Chile, the meteoric supergene enrichment stage covered a long period extending from 44 Ma and ending near 14–9 Ma with a step-wise onset towards the hyper-aridity in the region (Sillitoe and McKee 1996; Mote et al. 2001; Rowland and Clark 2001; Bouzari and Clark 2002; Hartley and Rice 2005; Arancibia et al. 2006; Evenstar et al. 2009; Reich et al. 2009a, b). This first stage of supergene oxidation peaked between 21 and 15 Ma as the result of percolating oxygenated meteoric waters in a semi-arid setting. This was followed by a second stage of supergene oxidation where the Cu-hydroxychloride atacamite ( $\text{Cu}_2\text{Cl}(\text{OH})_3$ ) was formed from uprising basinal brines and subsequently preserved under hyper-arid conditions for the last 2 Ma (Cameron et al. 2002, 2007; Reich et al. 2008, 2009a,b).

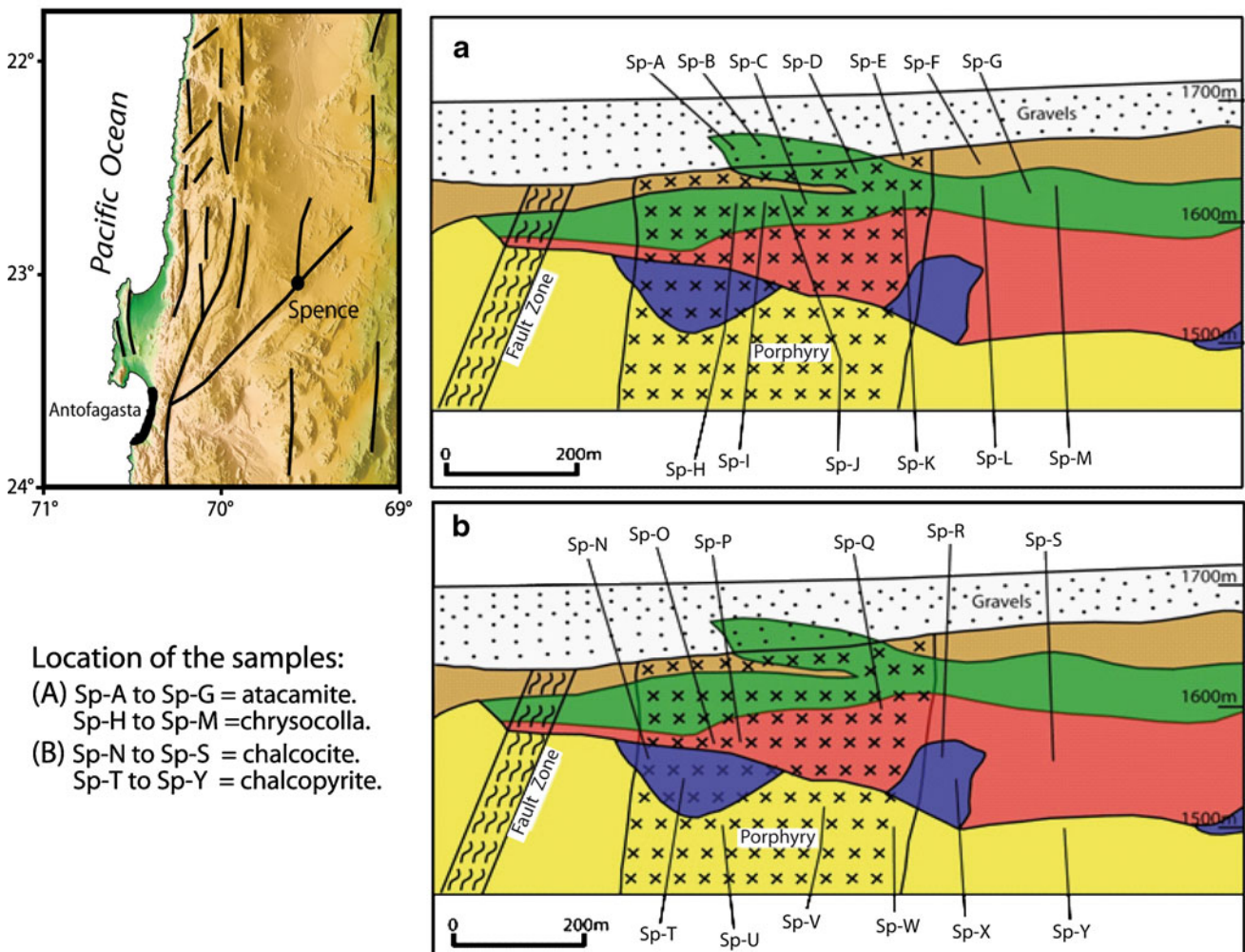
Aside from the characteristic occurrences of atacamite in the Atacama Desert, atacamite is rather rare because it requires high chloride activities to form and dissolves rapidly when exposed to meteoric water (Cameron et al. 2007).

Recent studies have shown that the two stable isotopes of Cu,  $^{65}\text{Cu}$  and  $^{63}\text{Cu}$ , can be fractionated during oxidative dissolution and reworking of primary Cu sulfides (Larson et al. 2003; Rouxel et al. 2004; Mathur et al. 2005, 2009; Borrok et al. 2008; Pokrovsky et al. 2008; Asael et al. 2009; Kimball et al. 2009). It has been suggested that Cu isotope systematics may be used to identify the nature and extent of supergene enrichment in porphyry Cu systems (Mathur et al. 2005, 2009). In particular, both experimental and field studies have revealed that during oxidative dissolution of primary Cu sulfides (e.g., chalcopyrite), the leach fluid becomes enriched in  $^{65}\text{Cu}$ , leaving the residue isotopically lighter as leaching continues (e.g., Mathur et al. 2005; Kimball et al. 2009). Likewise, the leach cap (e.g.,

Fe-hydroxides, hematite, and jarosite) of porphyry copper systems is commonly characterized by isotopically lighter signatures (negative  $\delta^{65}\text{Cu}$ ), whereas secondary sulfides (e.g., chalcocite) precipitated from the leach waters are characterized by more positive, heavier  $\delta^{65}\text{Cu}$  signatures (Mathur et al. 2009).

Cu isotope data has been made increasingly available in the last decade for hypogene and supergene Cu minerals, including sulfides, carbonates, sulfosalts, oxides, and hydrous silicates (e.g., Larson et al. 2003; Markl et al. 2006; Mathur et al. 2009). However, no data are yet available for atacamite, a major constituent of oxide zones in Cu deposits in the Atacama Desert, with the exception of one isolated, geographically unconstrained sample from the Atacama Desert reported by Gale et al. (1999) showing a very negative Cu isotopic signature ( $\delta^{65}\text{Cu}=-7.71\text{‰}$ ).

In this study, we report the first geologically constrained Cu isotope data set of atacamite from the Spence



**Fig. 1** Location of the Spence copper porphyry. In the right, an E–W cross section of the Spence orebody at 7,480,500 N is presented. Leach cap is shown in brown, oxide blanket in green, supergene-

enriched sulfides in red, hypogene-enriched zones in blue, and hypogene sulfides in yellow (based on Cameron et al. 2007)

porphyry copper deposit (Atacama Desert), along with Cu isotope data of chrysocolla, chalcocite, and chalcopyrite from the same deposit. When coupled with the existing age constraints for supergene enrichment and oxidation in the region, we show that the Cu isotope data is most consistent with multiple cycles of supergene leaching and oxidation of Cu that started at 44 Ma and continued at least until the late Pleistocene.

### Geologic setting and samples

The location of the Spence copper porphyry is shown in Fig. 1. The Spence porphyry copper deposit is related to three stocks of dacitic porphyries and tourmaline-bearing hydrothermal breccias, which were emplaced in andesitic volcanic rocks of the Upper Cretaceous–Lower Tertiary. Laser  $^{40}\text{Ar}/^{39}\text{Ar}$  plateau ages in magmatic biotites of pre- and post-mineralization dacitic stocks show evidence that hypogene mineralization (chalcopyrite, pyrite, molybdenite, and lesser amounts of bornite and tennantite) occurred between 56 and 57 Ma (Rowland and Clark 2001). Unconsolidated gravel deposits and a leach cap cover an oxidation blanket characterized by atacamite, chrysocolla, and minor brochantite, in which the Cu-hydroxychloride is by far the dominating mineral. Underlying the oxide zone is a well-developed chalcocite- and lesser covellite-bearing supergene enrichment blanket. Supergene alunite and natroalunite from the leached and enriched zones were dated between  $44.4\pm 0.5$  and  $27.7\pm 5.4$  Ma, based on 13 inverse isochron  $^{40}\text{Ar}/^{39}\text{Ar}$  ages (Rowland and Clark 2001). Following a long interval, there was substantial modification of the initial supergene assemblage, principally the formation of atacamite, during the Pleistocene by rising basinal brines. Reich et al. (2008) reported fissionogenic  $^{36}\text{Cl}$  analysis for atacamite indicating a maximum age of 1.5 Ma for its formation. Reich et al. (2009a) further refined this dating by measuring U-series disequilibrium ages of atacamite-gypsum intergrowths in atacamite-bearing assemblages, indicating precipitation at 127 ka.

Representative samples from pit walls and drill cores were selected in order to cover most of the hypogene and supergene zones, including chalcopyrite from the hypogene-enriched sulfides and hypogene zones, chalcocite from the supergene-enriched sulfides and hypogene-enriched blankets, chrysocolla from the oxide blankets, and atacamite from the oxide zone within the host rocks and gravels and leach cap (Fig. 1 a, b).

### Methods

Copper minerals were handpicked from crushed hand specimens and separated under a binocular microscope.

The analyzed specimens consist of individual minerals that were inspected with a petrographic microscope and X-ray diffraction. The isotopic compositions of the samples are expressed as a deviation relative to the standard following the equation:  $\delta^{65}\text{Cu} = 10^3 \times (R_{\text{spl}}/R_{\text{std}} - 1)$ , where  $R_{\text{spl}}$  is the measured  $^{65}\text{Cu}/^{63}\text{Cu}$  ratio for the sample and  $R_{\text{std}}$  is the  $^{65}\text{Cu}/^{63}\text{Cu}$  ratio of the NIST 976 Cu standard. Copper isotope ratios were determined using a multicollector ICPMS (Neptune, Thermo-Electron TM) operated by the Woods Hole Oceanographic Institution and the French Research Institute for Exploitation of the Sea.

Isotope analyses of chalcopyrite, atacamite, chrysocolla, and chalcocite followed previously published methods. In short, the samples were purified by an anion exchange chromatography column using a procedure modified from that of Merechal et al. (1999), Chapman et al. (2006), and Borrok et al. (2007). After a complete digestion step in concentrated  $\text{HNO}_3\text{-HCl}$ , the sample was dissolved in 2 ml 6 N distilled HCl in a closed beaker on a hot plate. A precise volume of this solution, corresponding to about 10  $\mu\text{g}$  Cu, was then purified using anion exchange AG1-X8 resin (Bio-Rad, 200–400 mesh). After elution of matrix elements, Cu was eluted (and separated from Fe) with 30 ml 6 N HCl, collected in a Teflon vial, and evaporated to dryness. The residue was re-dissolved in 2–3 ml of 2%  $\text{HNO}_3$  and then further diluted to form a 0.1 to 0.5 ppm Cu solution ready for isotope analysis. Analyses of  $^{65}\text{Cu}/^{63}\text{Cu}$  were carried out on a MC-ICPMS operating at low resolution mode. The samples were introduced into the plasma using a double spray quartz spray chamber system (cyclonic and double pass) and a micro-concentric PFA nebulizer operating at a flow rate of about 60  $\mu\text{l min}^{-1}$ . Instrumental mass bias was corrected for using Zn isotopes as an internal standard and involves simultaneously measurement of a Zn standard solution (SRM 3168a Standard Solution). In addition, a standard bracketing approach, which normalizes the Cu isotope ratio to the average measured composition of a standard (SRM 976) was carried out before and after each sample. The internal precision of the data has 95% confidence levels based on isotopic deviation of duplicated sample analysis. Two internal standards: Spex solution and chalcopyrite FL-DR-03 were processed through the entire chemical procedure and gave  $\delta^{65}\text{Cu}$  values of  $-0.17\pm 0.08\text{‰}$  ( $n=4$ ) and  $1.22\pm 0.04\text{‰}$  ( $2\sigma$ ,  $n=7$ ), respectively.

### Results

Chalcopyrite samples show  $\delta^{65}\text{Cu}$  values ranging between  $+0.28\text{‰}$  and  $+0.34\text{‰}$ , with an average of  $+0.31\text{‰}$  ( $n=6$ ; Table 1; Fig. 2a). These  $\delta^{65}\text{Cu}$  values are within the range of reported values for primary chalcopyrite from

**Table 1** Cu isotope composition of copper minerals from the Spence porphyry copper

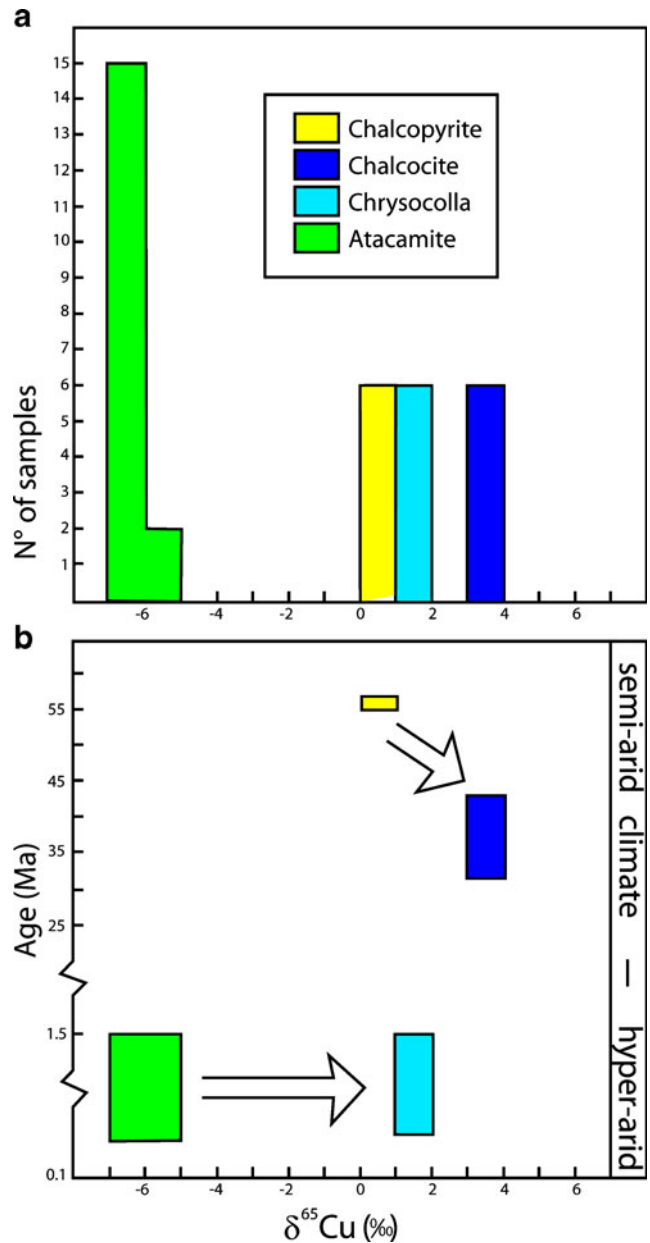
Sample	Mineral	Number of analysis	$\delta^{65}\text{Cu}$	$1\sigma$
SP-A	Atacamite	4	-6.31	0.02
SP-A	Atacamite	4	-6.27	0.02
SP-B	Atacamite	4	-5.77	0.01
SP-B	Atacamite	4	-5.72	0.03
SP-C	Atacamite	4	-6.77	0.03
SP-C	Atacamite	4	-6.70	0.03
SP-D	Atacamite	4	-6.45	0.02
SP-D	Atacamite	4	-6.45	0.01
SP-E	Atacamite	4	-6.69	0.02
SP-E	Atacamite	4	-6.66	0.02
SP-E	Atacamite	4	-6.68	0.01
SP-F	Atacamite	4	-6.12	0.02
SP-F	Atacamite	4	-6.16	0.01
SP-F	Atacamite	4	-6.15	0.01
SP-F	Atacamite	4	-6.14	0.01
SP-G	Atacamite	4	-6.14	0.02
SP-G	Atacamite	4	-6.13	0.00
SP-H	Chrysocolla	4	1.33	0.01
SP-I	Chrysocolla	4	1.37	0.02
SP-J	Chrysocolla	4	1.34	0.06
SP-K	Chrysocolla	4	1.32	0.01
SP-L	Chrysocolla	4	1.28	0.03
SP-M	Chrysocolla	4	1.37	0.03
SP-N	Chalcocite	4	3.92	0.02
SP-O	Chalcocite	4	3.94	0.04
SP-P	Chalcocite	4	3.95	0.02
SP-Q	Chalcocite	4	3.94	0.01
SP-R	Chalcocite	4	3.92	0.03
SP-S	Chalcocite	4	3.91	0.04
SP-T	Chalcocopyrite	4	0.32	0.02
SP-U	Chalcocopyrite	4	0.33	0.01
SP-V	Chalcocopyrite	6	0.28	0.03
SP-W	Chalcocopyrite	6	0.28	0.03
SP-X	Chalcocopyrite	6	0.31	0.04
SP-Y	Chalcocopyrite	4	0.34	0.02

Location of the samples is shown in Fig. 1

Chilean Cu-Mo porphyries ( $-1\text{‰} < \delta^{65}\text{Cu} < +1\text{‰}$ ; Mathur et al. 2005, 2009). In contrast, chalcocite samples from Spence show fractionated, but homogeneous  $\delta^{65}\text{Cu}$  ratios between  $+3.91$  and  $+3.95\text{‰}$  (average  $+3.95\text{‰}$ ;  $n=6$ ; Table 1; Fig. 2a), which are slightly higher than the previously reported values for this supergene Cu sulfide in the Chilean porphyry copper deposits ( $+2.07\text{‰} < \delta^{65}\text{Cu} < +3.61\text{‰}$ ; Mathur et al. 2009). Chrysocolla samples from Spence show intermediate  $\delta^{65}\text{Cu}$  values between  $+1.28\text{‰}$  and  $+1.37\text{‰}$ , with an average of  $+1.34\text{‰}$  ( $n=6$ ; Fig. 2a; Table 1). At

Spence, chrysocolla samples show a heavier isotopic signature, in comparison to those reported at the Collahuasi copper porphyry ( $-4.54\text{‰} < \delta^{65}\text{Cu} < +0.79\text{‰}$ ; Mathur et al. 2009).

Atacamites from Spence show the lightest isotopic signatures reported to date for any copper minerals:  $\delta^{65}\text{Cu} = -5.72\text{‰}$  to  $-6.68\text{‰}$ , with an average of  $-6.31\text{‰}$  ( $n=17$ ; Fig. 2a; Table 1). These strongly depleted Cu isotope values contrast with atacamite (paratacamite s.s.) samples from sea-floor hydrothermal fields, derived from direct oxidation of copper sulfides (Hannington 1993), which show enrichment in  $^{65}\text{Cu}$  ( $\delta^{65}\text{Cu} = +0.37\text{‰}$  to  $+4.70\text{‰}$ ; e.g., Rouxel et al. 2004).



**Fig. 2** Distribution of **a**  $\delta^{65}\text{Cu}$  values in chalcocopyrite, chalcocite, chrysocolla, and atacamite from the Spence copper porphyry and **b** Cu fractionation of the analyzed minerals versus age at which these minerals formed

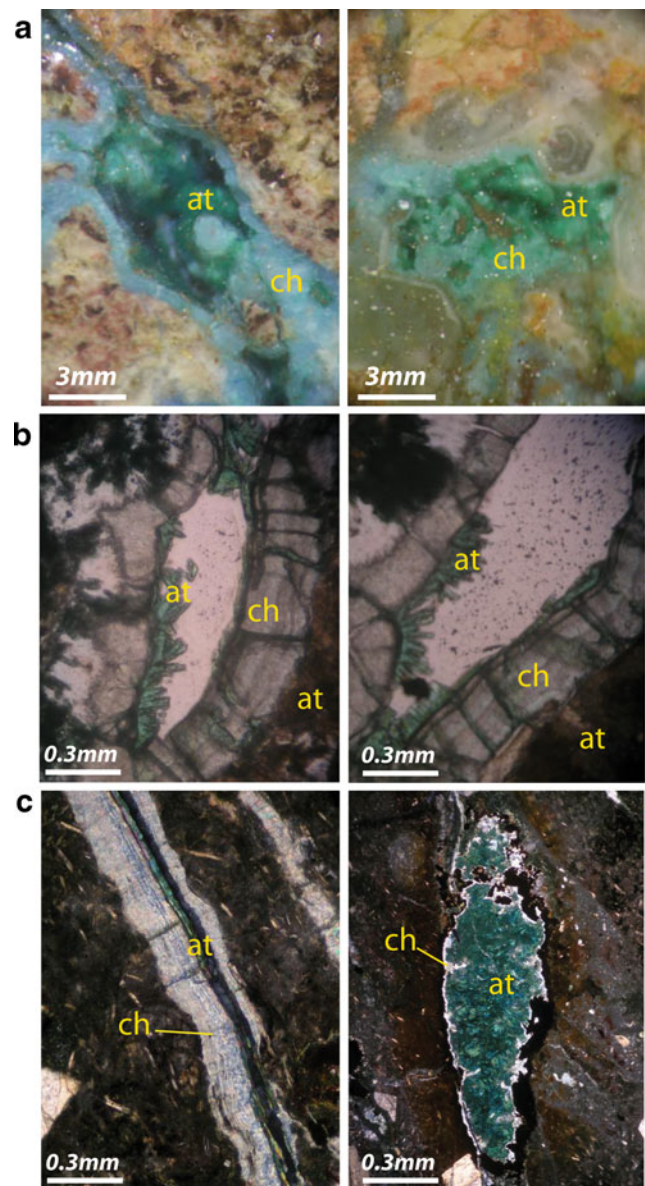
## Discussion

There are two points revealed by the data presented in this study: (a) Cu isotope values exhibit a very large range of  $\delta^{65}\text{Cu}$  values, exceeding 10‰, between mineral types and (b) each mineral type has isotopically homogeneous  $\delta^{65}\text{Cu}$  values. This pattern is most likely related to large-scale redox changes due to successive alteration, remobilization, and enrichment histories.

The mineral assemblage that we studied can be placed into a paragenetic sequence with respect to the age of supergene alteration stages at the Spence ore deposit and the variation of  $\delta^{65}\text{Cu}$  of the Cu minerals (Fig. 2b). Hypogene mineralization (i.e., chalcopyrite, pyrite, molybdenite, bornite, and tennantite) at the Spence deposit occurred between 56 and 57 Ma (Rowland and Clark 2001). The hypogene chalcopyrite has Cu isotope values ( $\delta^{65}\text{Cu}=+0.28\text{‰}$  and  $+0.34\text{‰}$ ) within the range of hypogene Cu mineralization in Chile and elsewhere (e.g., Larson et al. 2003; Graham et al. 2004; Asael et al. 2009; Maher and Larson 2007), and is within the range for modern hydrothermal systems and estimates of the mantle (Zhu et al. 2000; Rouxel et al. 2004).

During the initial stage of supergene alteration (44–28 Ma; Rowland and Clark 2001) hypogene Cu sulfides underwent oxidation and leaching by infiltrating meteoric water in a semi-arid climate, leading to the precipitation of secondary chalcocite at the redox front. Chalcocite at the Spence deposit ranges from  $+3.91\text{‰}$  to  $+3.95\text{‰}$   $\delta^{65}\text{Cu}$  (Fig. 2), which represents fractionation of  $\sim+3.6\text{‰}$  from the hypogene sulfides. The observed pattern towards higher  $\delta^{65}\text{Cu}$  values at Spence is supported by experimental studies by Mathur et al. (2005) showing that aqueous Cu in leach fluids released during oxidative dissolution (and from which secondary chalcocite precipitates) is isotopically heavier than the initial starting material (chalcopyrite). This pattern is also similar, albeit to larger extent, to Cu isotope fractionation in acid mine drainage where stream waters yield heavier  $\delta^{65}\text{Cu}$  values by up to 1.6‰ relative to chalcopyrite. In addition, Ehrlich et al. (2004) showed an average fractionation of  $\Delta^{65}\text{Cu}=+3.06\pm 0.14\text{‰}$  between aqueous Cu(II) and Cu(I) sulfides, similar to our results for the Spence deposit.

During the latest stages of supergene oxidation in the Atacama Desert, dominated by hyper-arid climate conditions, the largest differences in  $\delta^{65}\text{Cu}$  signatures at the Spence deposit are found between atacamite and chrysocolla ( $\Delta^{65}\text{Cu}_{\text{chrysocolla} - \text{atacamite}}$  of  $\sim 8\text{‰}$ ). This large fractionation between chrysocolla and atacamite may reflect differences in the source of the leaching fluids, but interpretations can be obscured by (a) complex mineralogical relationships between atacamite and chrysocolla, (b) lack of geochronological data for chrysocolla, and (c) lack



**Fig. 3** Photographs of chrysocolla (*ch*), atacamite (*at*), and chalcocite (*Cs*) in the Spence copper porphyry. **a** Zoom photos showing chrysocolla replacing atacamite. **b** Transmitted light photos showing chrysocolla veinlet (gray botryoidal bands) cross-cutting massive atacamite (black), and in turn, late atacamite as suture within the vein. **c** Transmitted light photos showing chrysocolla veinlet with atacamite in suture and chrysocolla replacing atacamite in cumulus aggregate

of an identifiably isotopically heavy Cu reservoir. Our previous studies have shown, however, that supergene weathering and formation of atacamite is much younger than previously thought, with atacamite dated as young as 127 ka at the Spence deposit (Reich et al. 2009a), most likely from movement of saline basinal fluids up through the deposit (Cameron et al. 2007; Reich et al. 2008; 2009a). Any explanation for the isotopic fractionation between

these younger secondary copper chlorides and silicates compared to the older supergene Cu sulfides must take into account the following constraints: (a) mineral paragenetic relationships, (b) the small standard deviation in  $\delta^{65}\text{Cu}$  for each mineral type, and (d) the likely Eh, pH, and  $[\text{Cl}^-]$  conditions during mineral formation.

It is well-known that chrysocolla commonly occurs as a direct replacement for atacamite in the Chilean porphyries (Sillitoe 2005). At the Spence deposit, our observations indicate that chrysocolla replaces atacamite in veins and disseminated masses, but atacamite also forms cross-cutting veins after chrysocolla (Fig. 3). Unlike atacamite, which is relatively soluble in meteoric waters, chrysocolla is highly insoluble in meteoric and saline water (Helle and Kelm 2005). Along with the fact that atacamite formation and preservation at Spence is recent (1.5 Ma to 127 ka; Reich et al. 2008, 2009a), the mineralogical relations shown in Fig. 3 indicate that at least part of the chrysocolla was formed during the Pleistocene, when hyper-arid climatic conditions were dominant. The tight clustering of  $\delta^{65}\text{Cu}$  values for both chrysocolla and atacamite would suggest, however, that at least for the samples we analyzed, these minerals were essentially coeval.

During the early stage of supergene mineralization, weathering conditions above the water table were most likely oxidizing and acidic, consistent with the classic supergene profile at the Spence deposit, and presence of secondary Cu sulfates. These Eh and pH conditions are typical in supergene oxidation blankets of sulfide deposits (Boyle 1994, 2003; Alpers and Brimhall 1989; Mote et al. 2001). By contrast, during the later supergene stage, dominated by modern hyper-arid conditions (<2 Ma), near-neutral, saline, old basinal waters were pumped upward triggered by earthquakes, passing through the deposit and leaching Cu (Cameron et al. 2002, 2007; Leybourne and Cameron 2006, 2008; Reich et al. 2008, 2009a). Evidence exists that modern hyper-aridity in the Atacama region has been characterized by episodes of increased precipitation and wetter conditions during the latest Pleistocene (Grosjean et al. 2001, 2003; Nester et al. 2007). Due to its relatively high solubility in meteoric water, atacamite formed from saline brines may have partially dissolved and reprecipitated as chrysocolla in different stages. Therefore, the strongly negative  $\delta^{65}\text{Cu}$  values of atacamite (−5.72‰ to −6.77‰) and the rather positive signatures of chrysocolla (+1.28‰ and +1.37‰) may reflect an intense recycling of Cu in a redox cycling system within the deposit in the last 1.5 Ma. This mechanism would suggest a relatively constant  $\Delta^{65}\text{Cu}_{\text{chrysocolla} - \text{atacamite}}$  of ~8‰ to explain the tight  $\delta^{65}\text{Cu}$  values of both minerals. This in turn would require that chrysocolla only forms from atacamite dissolution.

Indeed, studies of formation of secondary Cu minerals from hypogene sulfide oxidation have shown that the

secondary Cu(II) minerals are typically isotopically enriched in  $^{65}\text{Cu}$  by up to 3‰ compared to the primary sulfides (Mathur et al. 2009; Ehrlich et al. 2004). A recent study of turquoise, which is formed under acidic meteoric water conditions, found  $\delta^{65}\text{Cu}$  values as high as +17.5‰ (Hull et al. 2008). By contrast, under neutral pH conditions, copper isotope fractionation can occur via adsorption such that oxide surface preferentially retain  $^{65}\text{Cu}$  by up to ~3‰ (Pokrovsky et al. 2008). Thus, it is possible that during replacement of brochantite, saline fluids preferentially leached  $^{63}\text{Cu}$  to form atacamite.

An alternative mechanism to the adsorption might be redox cycling due to salinity changes in the groundwater (fluid sources dominated by periodic rainfall alternated with saline deep water feeder events). Precipitation of isotopically light atacamite would leave a  $^{63}\text{Cu}$ -depleted residual fluid as a source for heavier chrysocolla formation. In either case, probably additional Rayleigh fractionation processes may be operating in order to generate the very large Cu isotopic fractionation reported.

Finally, results show that Cu isotope studies and dating of supergene Cu minerals may be used as a paleoclimate proxy for determining rainfall events in the Atacama Desert, and thus trace desertification processes in hyper-arid regions.

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