

Supergene enrichment of copper deposits since the onset of modern hyperaridity in the Atacama Desert, Chile

Martin Reich · Carlos Palacios · Gabriel Vargas ·
Shangde Luo · Eion M. Cameron ·
Matthew I. Leybourne · Miguel A. Parada ·
Alejandro Zúñiga · Cheng-Feng You

Received: 22 December 2008 / Accepted: 16 January 2009 / Published online: 10 February 2009
© Springer-Verlag 2009

Abstract Supergene enrichment of Cu deposits in the Atacama Desert has played a critical role in making this the prime Cu-producing province of the world. Previously, this has been believed to have occurred exclusively over a long period from the middle Eocene to the late Miocene, which ended when climatic conditions changed from arid to hyperarid. Here, we report U-series disequilibrium ages in atacamite-bearing supergene assemblages that provide a new conceptualization on both the supergene enrichment process and the onset of extreme hyperaridity in the Atacama Desert. ^{230}Th – ^{234}U ages of gypsum intergrown

with atacamite in supergene veins from Cu deposits cluster at ~240 ka (Chuquicamata), 130 ka (Mantos Blancos, Spence), and 80 ka (Mantos de la Luna, Michilla). When coupled with previous data, these results indicate that supergene enrichment of Cu deposits did not cease after the onset of hyperaridity. We propose that supergene enrichment in the Atacama region developed in two main stages. The main phase, caused by downward circulation of meteoric waters in a semi-arid setting, was active from 45 until ~9 Ma, with a last pulse ca. 5 Ma in the southern Atacama Desert. During this phase, atacamite-bearing supergene assemblages were not preserved because atacamite requires saline water for its formation and rapidly dissolves when contacted by meteoric water. This was followed by a second stage starting at ~2–1.5 Ma and continuing until at least the late Pleistocene, when deep formation waters derived from the basement passed up through and modified the pre-existing supergene Cu oxide minerals. Atacamite has then been preserved in the prevailing hyperarid climate.

Editorial handling: B. Lehmann

M. Reich (✉) · C. Palacios · G. Vargas · M. A. Parada
Departamento de Geología,
Facultad de Ciencias Físicas y Matemáticas,
Universidad de Chile,
Santiago, Chile
e-mail: mreich@ing.uchile.cl

S. Luo · C.-F. You
Earth Dynamic System Research Center & Department of Earth
Sciences, National Cheng-Kung University,
Tainan 701 Taiwan, Republic of China

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

M. I. Leybourne
Ocean Exploration, GNS Science,
Lower Hutt, New Zealand

A. Zúñiga
Departamento de Ingeniería Mecánica,
Facultad de Ciencias Físicas y Matemáticas,
Universidad de Chile,
Santiago, Chile

Keywords Copper porphyry deposits ·
Supergene enrichment · U-series disequilibrium ages ·
Atacamite · Chile

Introduction

Supergene enrichment of Cu deposits in the Atacama Desert of northern Chile has been a principal factor in this region becoming the greatest producer of Cu in the world. Supergene enrichment zones are believed to have formed by exposure of Cu sulfides to the effects of oxidative weathering during moderate precipitation. Thus, their development is strongly coupled to the climatic evolution

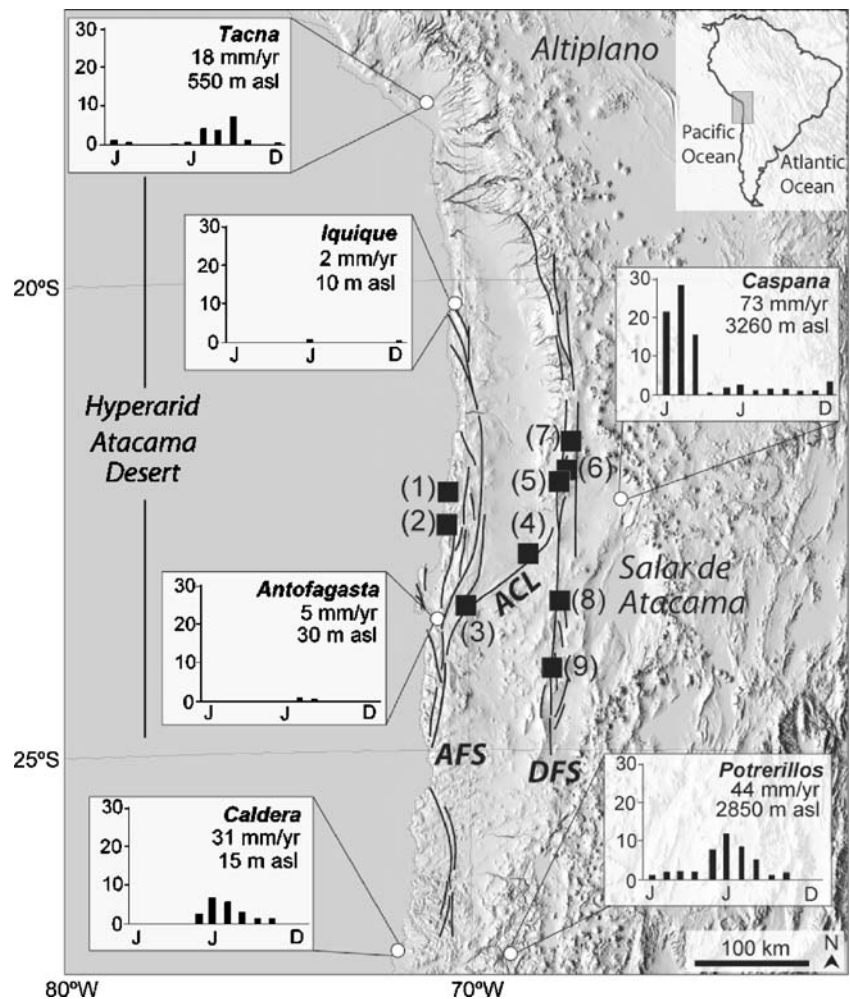
of the region since the early Oligocene (Alpers and Brimhall 1988; Sillitoe and McKee 1996; Mote et al. 2001; Hartley and Chong 2002; Hartley and Rice 2005; Arancibia et al. 2006; Clarke 2006). Isotopic dating of supergene minerals, principally alunite group minerals, has shown that supergene enrichment occurred over a long period from ~45 to 9–5 Ma, reaching a maximum at 14–21 (Alpers and Brimhall 1988; Sillitoe and McKee 1996; Mote et al. 2001; Arancibia et al. 2006). Supergene enrichment is traditionally believed to have ceased when arid conditions, with significant pluvial precipitation, changed to hyperarid. However, there is no consensus about the onset of hyperaridity, which may have commenced as early as 25 Ma (Dunai et al. 2005) or 19–13 Ma (Rech et al. 2006) or as late as 3–4 Ma (Hartley and Chong 2002; Hartley and Rice 2005). Also, it is debatable if supergene processes ceased completely as a result of hyper-aridification. Recent geochemical and isotopic studies reveal that atacamite, a major constituent of supergene Cu oxide zones in this region, formed within the last 1.5 Ma as a product of the upward flow of saline basement waters through the pre-

existing oxide zones and has been preserved in the hyperarid climate prevailing since that time (Cameron et al. 2007; Leybourne and Cameron 2008; Reich et al. 2008). Despite this new evidence, our knowledge of the timing and mechanism(s) of formation of the final supergene assemblages is limited. We present here U-series disequilibrium data in atacamite-bearing assemblages from Cu deposits in the Atacama Desert that provide new age constraints and extend supergene oxidation into the Pleistocene. We then explore how climate and active tectonics have influenced the development of supergene oxidation zones before and after the onset of hyperaridity.

Geologic background and samples

The Atacama Desert of northern Chile is the driest desert on Earth and hosts the world's largest known accumulation of Cu, the primary Cu sulfide hydrothermal mineralization having formed during Late Jurassic to Early Oligocene time as part of the geological evolution of the southern segment

Fig. 1 Digital elevation map (from SRTM 90 m dataset) of the studied area of the Atacama Desert in northern Chile showing the distribution of copper deposits containing atacamite in oxide zones (squares, (1) Mantos de la Luna, (2) Michilla, (3) Mantos Blancos, (4) Spence, (5) Chuquicamata, (6) Radomiro Tomic, (7) El Abra, (8) Gaby Sur, (9) Escondida). Insets show modern precipitation seasonality in the Atacama Desert, taken from Vargas et al. (2006) and Betancourt et al. (2000). Major structural features are shown, including the Atacama Fault System (AFS), the Antofagasta-Calama Lineament (ACL), and the Domeyko Fault System (DFS)



of the Central Andes (Maksaev et al. 2007). There are four main NS-trending metallogenic belts decreasing in age to the east: Late Jurassic stratabound-volcanic hosted “Manto-type” (e.g., Michilla, Mantos de la Luna), Early Cretaceous porphyry-type Cu (e.g., Mantos Blancos, Antucoya Buey-Muerto), Late Paleocene–Early Eocene porphyry Cu deposits (e.g., Spence, Lomas Bayas), and Late Eocene–Early Oligocene (e.g., Chuquicamata, Radomiro Tomic, El Abra; Maksaev et al. 2006; 2007; Ramírez et al. 2006). Weathering of the primary (hypogene) sulfide mineralization in these deposits produced several hundred meters of higher grade caps of secondary Cu sulfides, oxides, hydroxides, carbonates, sulfates, and chlorides. This supergene mineralization is a reflection of the history of groundwater flow, tectonics, landscape, and climate of the Atacama Desert (Alpers and Brimhall 1988; Sillitoe and McKee 1996; Chávez 2000; Clarke 2006). The green mineral atacamite (Cu₂Cl(OH)₃) is a major constituent of supergene zones in the Atacama Desert, and increasing evidence suggests that atacamite-bearing oxide assemblages are late products of supergene enrichment, likely to have formed by the replacement of pre-existing oxide assemblages during the passage of saline water (Cameron et al. 2007; Leybourne and Cameron 2008; Reich et al. 2008).

Atacamite-bearing assemblages were sampled in supergene oxide zones of five Cu deposits (Fig. 1, numbers 1–5). In these deposits, atacamite is a major constituent of supergene zones and occurs in veins, veinlets, and fine-

grained disseminations, commonly associated to gypsum. For details about sample location and their characteristics, see Table 1 (and caption). Careful examination of selected samples under the polarizing optical microscope and transmission electron microscope (TEM) revealed that atacamite is intimately associated to gypsum at all scales, supporting the recent notion that both minerals formed contemporaneously (Reich et al. 2008; Fig. 2). Since there is no geochronometer to directly date atacamite, the intimate association of gypsum and atacamite provides an alternative dating method by applying the U-series disequilibrium method to gypsum intergrown with atacamite.

U-series method and ²³⁰Th–²³⁴U ages

Isochron method

The U-series disequilibrium method is based on the natural fractionation of U and Th isotopes that lead to the preferential precipitation in authigenic minerals (e.g., gypsum) of parent nuclides over certain insoluble daughter products in the decay series (Ku 1976; Luo and Ku 1991; Ku et al. 1998). The method has been successfully applied to obtain absolute ages of formation of salt minerals that precipitate from aqueous solutions (e.g., gypsum, anhydrite, and halite), in a range that falls between <10 and 350 kyrs (Ku et al. 1998). The isolation of uranium into a sample at

Table 1 U-series data for gypsum intergrown with atacamite in supergene zones from copper deposits, Atacama Desert, Chile

Deposit	Sample Location	Sub-sample	²³⁸ U (ppb)	²³² Th (ppb)	²³⁰ Th/ ²³² Th	²³⁴ U/ ²³² Th	²³⁸ U/ ²³² Th	²³⁴ U / ²³⁸ U	²³⁰ Th / ²³⁴ U	Age (ka)
Chuquicamata	22°26'32''S/68°55'03''W h = 2,960 m a.s.l.	CH-1	64.61	0.862	201.7	227.7	229.0	0.990 ± 0.004	0.884 ± 0.008	236.6 ± 8.0
		CH-2	347.43	11.423	81.92	92.96	92.96			
		CH-3	56.39	2.761	55.90	64.45	62.42			
		CH-4	409.66	12.016	92.51	99.03	104.19			
Mantos Blancos	23°29'08''S/70°09'58''W h = 1,200 m a.s.l.	MB-1	21.152	21.481	2.444	3.092	3.009	1.056 ± 0.004	0.738 ± 0.074	143 ± 29
		MB-2	18.517	18.827	2.463	3.060	3.006			
		MB-3	231.32	259.31	2.231	2.779	2.726			
Mantos de la Luna	22°15'18''S/70°08'44''W h = 1,000 m a.s.l.	ML-1	32.08	32.94	2.035	3.190	2.976	1.110 ± 0.007	0.545 ± 0.046	84 ± 11
		ML-2	149.48	244.82	1.350	2.042	1.866			
		ML-3	42.04	45.31	1.934	3.097	2.836			
		ML-4	36.60	36.39	2.087	3.452	3.074			
Spence	23°53'18''S/69°18'51''W h = 1,370 m a.s.l.	SP-1	4.263	7.541	1.380	1.877	1.728	1.110 ± 0.017	0.701 ± 0.087	127 ± 29
		SP-2	22.260	44.40	1.139	1.596	1.532			
		SP-3	5.492	8.842	1.408	1.999	1.898			
Michilla	22°42'44''S/70°11'31''W h = 1,050 m a.s.l.	SS-1	443.4	173.46	3.747	7.738	7.812	0.998 ± 0.003	0.499 ± 0.002	75.3 ± 0.4
		SS-2	568.6	225.10	3.721	7.687	7.720			
		SS-3	498.0	243.68	2.984	6.209	6.246			

Note: Non-detrital activity ratios of ²³⁰Th/²³⁴U and ²³⁴U/²³⁸U are derived from the slopes of isochron plots (Fig. 3), and their uncertainties estimated following the methods of Luo and Ku (1991). Age is estimated according to: $U = \frac{1}{W} [1 - \exp(-\lambda_{230Th} t)] + \left(1 - \frac{1}{W}\right) \left(\frac{\lambda_{230Th}}{\lambda_{230Th} - \lambda_{234U}}\right) [1 - \exp(-(\lambda_{230Th} - \lambda_{234U}) t)]$, where $U = (^{230}\text{Th} / ^{234}\text{U})$ and $W = (^{234}\text{U} / ^{238}\text{U})$, and λ are the decay constants ($9.215 \times 10^{-6} \text{ y}^{-1}$ for ²³⁰Th and $2.794 \times 10^{-6} \text{ y}^{-1}$ for ²³⁴U). The uncertainties quoted are standard deviations (2σ) with a 95% confidence level.

Coordinates and altitude (in meters above the sea level) of the samples are shown in the second column. Sample from Chuquicamata was taken from the Banco Sur in the Chuqui pit and is a 5-cm-wide gypsum/atacamite veinlet, oriented N5°E. Sample from Mantos Blancos is an 18-cm-wide atacamite/gypsum vein, oriented N55°E, taken from the oxidation zone at the Banco Oriental, Mantos Blancos pit. Sample from Mantos de la Luna was taken at the entrance of the main pit (eastern wall) and corresponds to a N4E° trending atacamite/gypsum vein 10 cm wide occurring in the limit between the leach cap and the oxidation zone. Samples from Spence and Michilla are atacamite/gypsum veinlets 2 and 7 cm wide (N60°E and N3°W trending, respectively), taken at the Banco Sur, Spence pit, and at the entrance of the underground mine, respectively.

the time of precipitation leads to the growth of radioactive ^{230}Th from the decay of ^{238}U and ^{234}U radionuclides. Therefore, the extent of growth of ^{230}Th toward secular equilibrium with ^{234}U is a function of time (or age). The U-series method requires simultaneous measurements of the degree of radioactive disequilibrium between ^{230}Th and ^{234}U and between ^{234}U and ^{238}U in the salt minerals. However, age uncertainties can arise due to (a) the presence of inclusions or clays in the samples containing detrital ^{230}Th and ^{234}U that cannot be removed by physical and chemical means from the primary phases and (b) the required closed system condition for the isotopes of interest is not ensured due to recrystallization or dissolution of the minerals.

In order to overcome these potential difficulties, we have analyzed only primary gypsum associated with atacamite in veins and veinlets, with no evidence of recrystallization or

dissolution (Fig. 2). The methods used for U-series dating of gypsum intergrown with atacamite followed the isochron approach of Luo and Ku (1991) that corrects for initial ^{230}Th contamination. Samples were homogenized by grinding into powder and separated into three or four subsamples by dispersing the sample in an ethanol solution. The subsamples contain various amounts of U and Th isotopes such that isochron plots can be constructed to determine the non-detrital $^{230}\text{Th}/^{234}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$ activity ratios and thus a reliable age of the sample. About 0.2–1 g was weighed for each subsample and dissolved with HNO_3 and HF under the presence of ^{236}U and ^{229}Th tracers. Separation and purification of U and Th from the samples were done using anion exchange columns. The purified U and Th were measured for isotope concentrations of U (^{234}U and ^{238}U) and Th (^{230}Th and ^{232}Th) by using a

Fig. 2 Atacamite–gypsum assemblages from supergene zones in Atacama: *A* atacamite–gypsum vein from the Spence deposit; *B* atacamite–gypsum veinlet from the same deposit; *C, D* photomicrograph of fine-grained aggregates of atacamite–gypsum in the veinlet shown in *B* (reflected light polarizing microscopy); *E* TEM image of the atacamite aggregates showing a close relation with gypsum at the micrometer scale. Both minerals were identified by energy-dispersive X-ray spectrometer (EDS) analysis (*F, G*). *gyp* gypsum, *atac* atacamite. TEM observations were performed at the Department of Geology, University of Chile, using a FEI Tecnai F20 FEG TEM operated at 200 kV, with an EDAX ED (~0.5–1 wt.% detection limit)

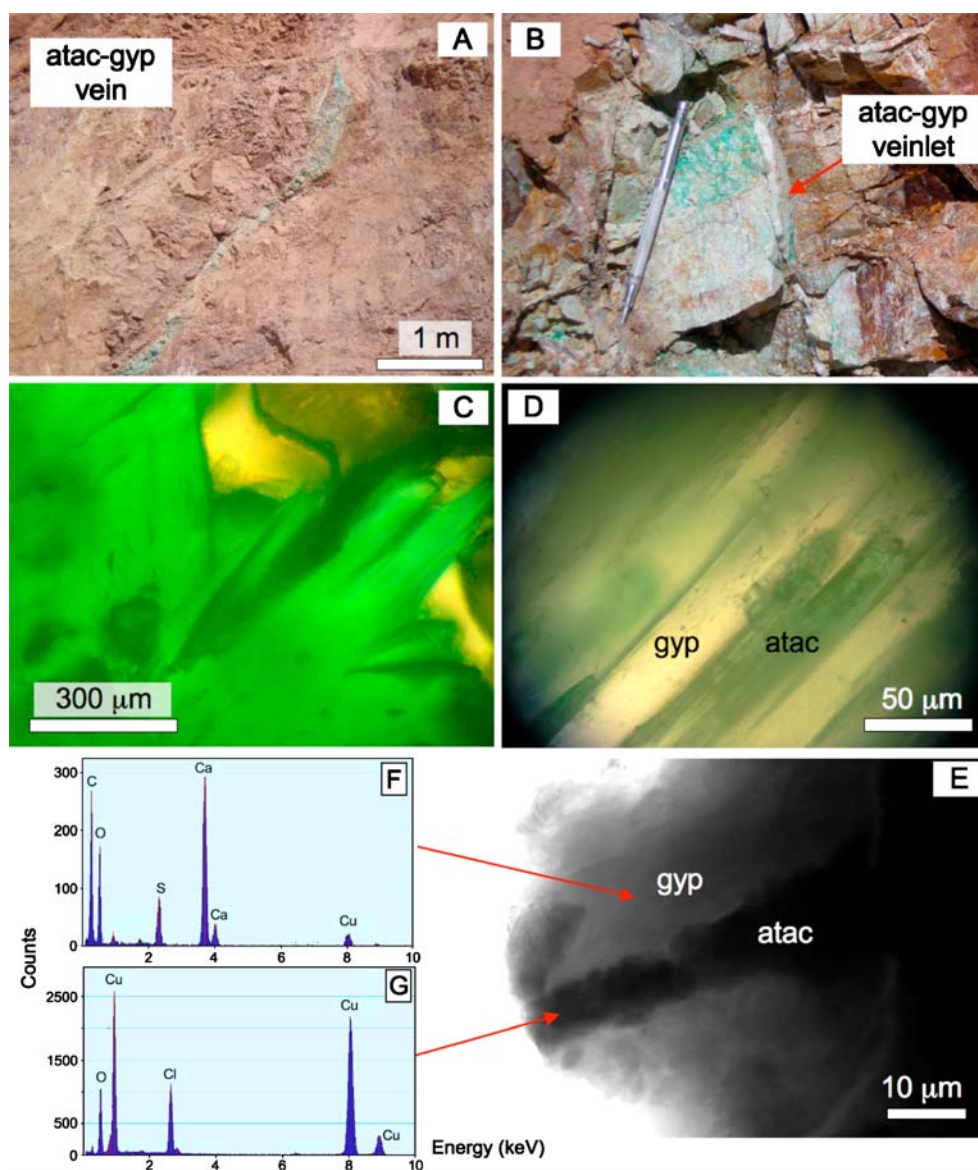
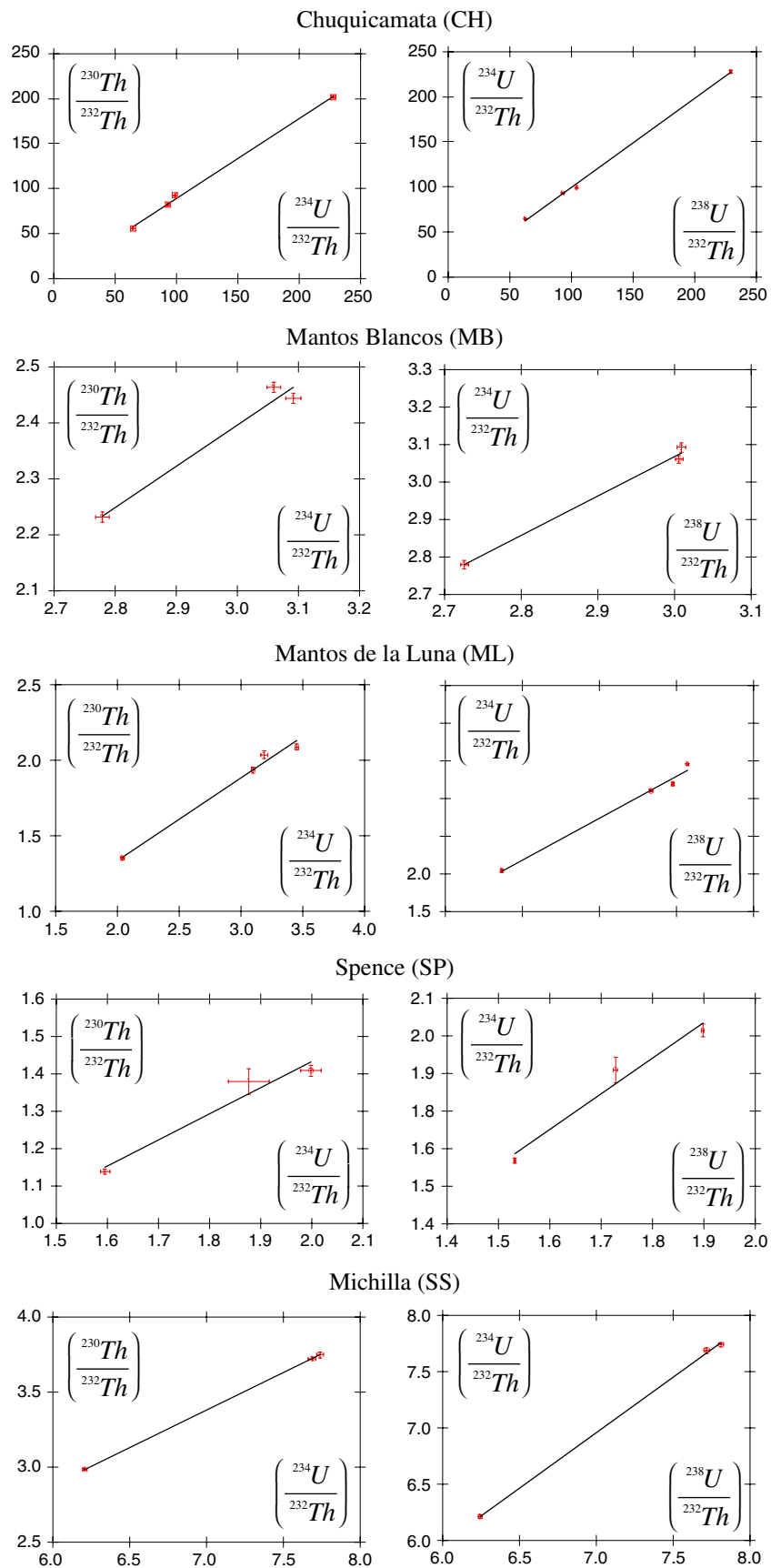


Fig. 3 Isochron plots of $^{230}\text{Th}/^{232}\text{Th}$ vs. $^{234}\text{U}/^{232}\text{Th}$ and $^{234}\text{U}/^{232}\text{Th}$ vs. $^{238}\text{U}/^{232}\text{Th}$ for samples from Chuquicamata, Mantos Blancos, Mantos de la Luna, Spence, and Michilla



double focusing magnetic sector field ICP-MS (Element II, Thermo Scientific) at the National Cheng-Kung University, Taiwan. The overall blanks of the procedures were measured to be about <0.2 ng for ^{238}U , <0.08 ng for ^{232}Th , and negligible for ^{234}U and ^{230}Th , respectively.

^{230}Th – ^{234}U ages

Measurements of U and Th isotopes in gypsum associated to atacamite in supergene zones of Cu deposits from the Atacama are shown in Table 1. Absolute ages were calculated based on the U–Th non-detrital activity ratios of $^{230}\text{Th}/^{234}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$ derived from the slopes of isochron plots (Fig. 3), following the methods of Luo and Ku (1991). All samples analyzed show Pleistocene ages, with Chuquicamata being the oldest at 237 ± 8 ka (Middle Pleistocene). Younger, Late Pleistocene ages are obtained for Mantos Blancos at 143 ± 29 ka, Spence at 127 ± 29 , Mantos de la Luna at 84 ± 11 ka, and Michilla at 75 ± 0.4 ka.

Discussion

Two-stage model for supergene enrichment in Atacama

U-series dating of gypsum–atacamite-bearing assemblages shows that supergene oxidation processes in Cu deposits were active during the Middle and Late Pleistocene when hyperarid climate conditions prevailed in the Atacama Desert of northern Chile.

When combined with previously published isotope ages, our data constrain the chronology of supergene enrichment and oxidation in copper deposits from the Atacama Desert, from the Middle Eocene (~45 Ma) to the Late Pleistocene (~100 ka; Fig. 4). K–Ar and Ar–Ar dating of supergene alunite-group minerals documents almost continuous supergene oxidation from 33 to 9 Ma, with a peak coeval with semiarid conditions between 21 and 14 Ma (Alpers and Brimhall 1988; Sillitoe and McKee 1996; Mote et al. 2001; Arancibia et al. 2006). Based on the alunite data, supergene oxidation of copper deposits has been previously interpreted to cease completely after a last pulse at ca. 5 Ma in the southern Atacama, as a result of the climate desiccation (Arancibia et al. 2006).

We propose that supergene oxidation did not cease after the onset of hyper-aridity, but continued until Middle-to-Late Pleistocene based on U-series ages and previously published ^{36}Cl data of atacamite-bearing assemblages (Reich et al. 2008). As atacamite requires saline water for its formation and dissolves rapidly when exposed to meteoric water (Hannington 1993; Cameron et al. 2007), hyperarid climate conditions are necessary for its preservation in supergene zones. Based on this argument, the age of formation of atacamite can be used as a climate marker of hyperaridity in the Atacama Desert. The presence of low but detectable ^{36}Cl of fissionogenic origin in atacamite from supergene zones indicates that the hyperarid conditions necessary for its preservation were already established at 1.5 Ma, ~five times the half-life of ^{36}Cl (Reich et al. 2008). Therefore, we propose a two-stage model for the development of supergene oxidation zones in copper deposits in the

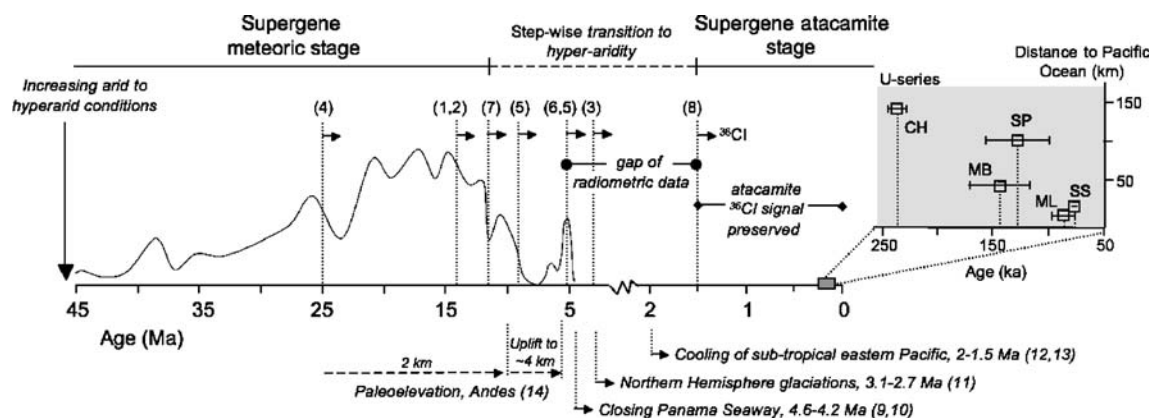


Fig. 4 Chronology of supergene oxidation of copper deposits in the Atacama Desert, Chile, and its relation with climate change in the region. Dotted vertical lines mark the onset of hyperaridity according to different authors (numbers), with hyperarid prevalence towards the right (arrow direction). Isotope data for supergene minerals (data curve taken from Arancibia et al. 2006 and references therein) define an extended period of supergene oxidation between ~45 to 9–5 Ma with a peak at ~21–14 Ma, dominated by downward circulation of meteoric water under semi-arid to arid climate conditions. A transitional period, characterized by a gap in isotope data (between ~5 and 2 Ma) precedes the late stage of supergene oxidation

dominated by the formation (and preservation) of atacamite under hyperarid conditions (<1.5 Ma, ^{36}Cl). Absolute ages of formation of atacamite in various copper deposits cluster between ~250 and 75 ka (Middle to Late Pleistocene), with decreasing ages westwards (see inset on the right). References: (1) Alpers and Brimhall (1988), (2) Sillitoe and McKee (1996), (3) Hartley and Chong (2002), (4) Dunai et al. (2005), (5) Arancibia et al. (2006), (6) Hartley and Rice (2005), (7) Rech et al. (2006), (8) Reich et al. (2008), (9) Haug and Tiedemann (1998), (10) Haug et al. (2001), (11) Haug et al. (1999), (12) Cannariato and Ravelo (1997), (13) Ravelo et al. (2004), (14) Garziona et al. (2008)

Atacama Desert: a supergene meteoric, “pre-atacamite” stage, developed under semiarid to arid conditions, followed by a supergene “atacamite” stage, coeval with modern hyperarid climate conditions (Fig. 4).

The long-lived supergene meteoric stage was comprised between ~45 and 9–5 Ma, where transient downward circulation of meteoric water weathered hypogene sulfide mineralization to form higher-grade caps of secondary Cu sulfides, oxides, and hydroxides. During this stage, characterized by a semiarid climate (>10 mm/year precipitation), oxide zones were exposed to percolating rainwater during the uplift of the Central Andes. A maximum in K–Ar and Ar–Ar ages between 21 and 14 Ma recorded by alunite-group minerals implies wetter conditions, followed by a first pulse of climate desiccation at 13 Ma in the eastern margin of the Atacama Desert (Rech et al. 2006). The paucity of supergene alunite ages after 9 Ma, with a final pulse at ca. 5 Ma in the southern margin of the Atacama Desert (Arancibia et al. 2006), is consistent with arid conditions at 3–4 Ma as suggested from sedimentological evidences in northern Chile (Hartley and Chong 2002; Hartley and Rice 2005). During this period, ~9 to 2 Ma for the central Atacama Desert, meteoric circulation waned due to reduced precipitation precluding the formation of supergene alunite-group minerals and therefore making the “meteoric” isotopic signal obscure. At the same time, formation and preservation of atacamite was inhibited by the reduced but still active meteoric infiltration, resulting in a gap of radiometric data between ~5 to 1.5 Ma (Fig. 4). Thus, the presence of ^{36}Cl in the atacamite–gypsum assemblages suggests that atacamite has been preserved only since ~1.5 Ma, marking the onset of modern extreme hyperarid conditions (< 1–4 mm/year) in the Atacama Desert.

Climatic implications

Our findings support a stepwise aridification of the Atacama Desert, rather than a single major climate shift, most probably driven by a combination of tectonic and global-to-regional ocean-climate reorganizations. Although a first significant pulse towards aridification occurred at 13 Ma, possibly related to the uplift of the Central Andes to elevations that were high enough to block moisture entrained in the South American Summer Monsoon from entering the Atacama region (Rech et al. 2006), greater aridification seems to have occurred coetaneously with a rapid pulse in the uplift of the Andes, e.g. towards elevations up to 4 km between 10 and 6 Ma as suggested by Garzzone et al. (2008). The occurrence of alunite ages of ca. 5 Ma suggests that the southern margin of the Atacama Desert received significant amounts of precipitation shortly after this date, probably reflecting the asynchronous installation of hyperaridity in the Atacama region.

The increase of aridity that characterizes the following period is coincident with the initial global reorganization of climate that followed the closing of the Panama seaway from 4.6 to 4.2 Ma (Haug and Tiedemann 1998; Haug et al. 1999, 2001). A close match is observed between the onset of the modern east–west sea surface temperature gradient in the tropical–subtropical Pacific at 2–1.5 Ma (Cannariato and Ravelo 1997; Ravelo et al. 2004) and the maximum ^{36}Cl atacamite “preservation” ages in the Atacama (Fig. 4). This match suggests that strong Walker circulation and cool subtropical temperatures in the eastern Pacific should have reinforced the atmospheric subsidence associated to the subtropical high pressure cell, blocking the humidity from the Pacific Ocean basin, turning the Atacama into the modern extreme hyperarid desert (< 1–4 mm/year), with the consequent preservation of atacamite in supergene Cu deposits. The close spatial correlation between atacamite-bearing Cu deposits and major structures in the region (Fig. 1), coupled with the high salinity and the isotopic composition of the waters from which it precipitated (Leybourne and Cameron 2006; 2008; Reich et al. 2008), suggests that supergene enrichment under hyperarid conditions has been driven by upwards circulation of deep saline waters during active faulting along major structures (Armijo and Thiele 1990; Cameron et al. 2002; 2007; Vargas et al. 2005; Gonzalez et al. 2006).

Acknowledgments The authors acknowledge the support of this study by the FONDECYT grant no. 1070736. We thank Anglo American, BHP-Billiton, Compañía Minera Mantos de la Luna, Minera Michilla S.A., and Codelco for logistical assistance and samples. We are grateful to Yi-Chen Wu for her contribution to ICP-MS analyses and isochron dating. The transmission electron microscope used in this work was acquired under the MECESUP grant UCH-0205. Gabriel Vargas thanks the additional funding by Milenio Project no. P06-064-F. We are grateful to Gerhard Wömer and Bernd Lehmann for their constructive reviews of the manuscript.

References

- Alpers CN, Brimhall GH (1988) Middle Miocene climatic change in the Atacama Desert, northern Chile: evidence from supergene mineralization at La Escondida. *Geol Soc Am Bull* 100:1640–1656
- Arancibia G, Matthews SJ, De Arce CP (2006) K–Ar and Ar-40/Ar-39 geochronology of supergene processes in the Atacama Desert, Northern Chile: tectonic and climatic relations. *J Geol Soc London* 163:107–118
- Armijo R, Thiele R (1990) Active Faulting in Northern Chile - Ramp Stacking and Lateral Decoupling Along a Subduction Plate Boundary. *Earth Planet Sc Lett* 98:40–61
- Betancourt JL, Latorre C, Rech JA, Quade J, Rylander KA (2000) A 22, 000-year record of monsoonal precipitation from Northern Chile's Atacama Desert. *Science* 289:1542–1546
- Cameron EM, Leybourne MI, Kelley DL (2002) Exploring for deeply covered mineral deposits: formation of geochemical anomalies in northern Chile by earthquake-induced surface flooding of mineralized groundwaters. *Geology* 30:1007–1010

- Cameron EM, Leybourne MI, Palacios C (2007) Atacamite in the oxide zone of copper deposits in northern Chile: involvement of deep formation waters? *Miner Deposita* 42:205–218
- Cannariato KG, Ravelo AC (1997) Pliocene-Pleistocene evolution of eastern tropical Pacific surface water circulation and thermocline depth. *Paleoceanography* 12:805–820
- Chávez WX (2000) Supergene oxidation of copper deposits: zoning and distribution of copper oxide minerals. *Society of Economic Geologists Newsletter* 41:1–21
- Clarke JDA (2006) Antiquity of aridity in the Chilean Atacama Desert. *Geomorphology* 73:101–114
- Dunai TJ, González-Lopez GA, Juez-Larre J (2005) Oligocene–Miocene age of aridity in the Atacama Desert revealed by exposure dating of erosion-sensitive landforms. *Geology* 33:321–324
- Garzzone CN, Hoke GD, Libarkin JC, Withers S, MacFadden B, Eiler J, Prosenjit G, Mulch A (2008) Rise of the Andes. *Science* 320:1304–1307
- Gonzalez G, Dunai T, Carrizo D, Allmendinger R (2006) Young displacements on the Atacama Fault System, northern Chile from field observations and cosmogenic Ne-21 concentrations. *Tectonics* 25(3):TC3006
- Hannington M (1993) The formation of atacamite during weathering of sulfides on the modern seafloor. *Can Mineral* 31:945–956
- Hartley AJ, Chong G (2002) Late Pliocene age for the Atacama Desert: Implications for the desertification of western South America. *Geology* 30:43–46
- Hartley AJ, Rice CM (2005) Controls on supergene enrichment of porphyry copper deposits in the Central Andes: A review and discussion. *Miner Deposita* 40:515–525
- Haug GH, Tiedemann R (1998) Effect of the formation of the Isthmus of Panama on Atlantic Ocean thermohaline circulation. *Nature* 393:673–676
- Haug GH, Sigman DM, Tiedemann R, Pedersen TF, Sarinthein M (1999) Onset of permanent stratification in the subarctic Pacific Ocean. *Nature* 441:779–782
- Haug GH, Tiedemann R, Zahn R, Ravelo AC (2001) Role of Panama uplift on oceanic freshwater balance. *Geology* 29:207–210
- Ku TL (1976) The uranium-series methods of age determination. *Annu Rev Earth Pl Sc* 4:347–379
- Ku TL, Luo S, Lowenstein TK, Li J, Spencer RJ (1998) U-series chronology of lacustrine deposits in Death Valley, California. *Quaternary Res* 50:261–275
- Leybourne MI, Cameron EM (2006) Composition of groundwaters associated with porphyry-Cu deposits, Atacama Desert, Chile: Elemental and isotopic constraints on water sources and water-rock reactions. *Geochim Cosmochim Acta* 70:1616–1635
- Leybourne MI, Cameron EM (2008) Source, transport, and fate of rhenium, selenium, molybdenum, arsenic, and copper in groundwater associated with porphyry-Cu deposits, Atacama Desert, Chile. *Chem Geol* 247:208–228
- Luo SD, Ku TL (1991) U-series isochron dating—a generalized-method employing total-sample dissolution. *Geochim Cosmochim Acta* 55:555–564
- Maksaev V, Munizaga F, Fanning M, Palacios C, Tapia J (2006) SHRIMP U-Pb dating of the Antucoya porphyry copper deposit: new evidence for an Early Cretaceous porphyry-related metallogenic epoch in the Coastal Cordillera of northern Chile. *Miner Deposita* 41:637–644
- Maksaev V, Townley B, Palacios C, Camus F (2007) Metallic ore deposits. In: Moreno T, Gibbons W (eds) *The geology of Chile*. The Geological Society, London, pp 179–199
- Mote TI, Brimhall GH, Tidy-Finch E, Muller G, Carrasco P (2001) Application of mass-balance modeling of sources, pathways, and sinks of supergene enrichment to exploration and discovery of the Quebrada Turquesa exotic copper orebody, El Salvador district, Chile. *Econ Geol* 96:367–386
- Ramirez LE, Palacios C, Townley B, Parada MA, Sial AN, Fernandez-Turiel JL, Gimeno D, Garcia-Valles M, Lehmann B (2006) The Mantos Blancos copper deposit: an Upper Jurassic breccia-style hydrothermal system in the coastal range of northern Chile. *Miner Deposita* 41:246–258
- Ravelo AC, Andreassen DH, Lyle M, Lyle AO, Wara MW (2004) Regional climate shifts caused by gradual global cooling in the Pliocene epoch. *Nature* 429:263–267
- Rech JA, Currie BS, Michalski G, Cowan AM (2006) Neogene climate change and uplift in the Atacama Desert, Chile. *Geology* 34:761–764
- Reich M, Palacios C, Parada MA, Fehn U, Cameron EM, Leybourne MI, Zúñiga A (2008) Atacamite formation by deep saline waters in copper deposits from the Atacama Desert, Chile: evidence from fluid inclusions, groundwater geochemistry, TEM, and ³⁶Cl data. *Miner Deposita* 43:663–675
- Sillitoe RH, McKee EH (1996) Age of supergene oxidation and enrichment in the Chilean porphyry copper province. *Econ Geol* 91:164–179
- Vargas G, Ortlieb L, Chapron E, Valdes J, Marquardt C (2005) Paleoseismic inferences from a high-resolution marine sedimentary record in northern Chile (23°S). *Tectonophysics* 399:381–398
- Vargas G, Rutllant J, Ortlieb L (2006) ENSO tropical-extratropical climate teleconnections and mechanisms for Holocene debris flows along the hyperarid coast of western South America (17 degrees–24 degrees S). *Earth Planet Sc Lett* 249:467–483