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Atacamite in the oxide zone of copper deposits in northern Chile: involvement of deep formation waters?

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Abstract Atacamite, a copper hydroxychloride, is an important constituent of supergene oxide zones of copper deposits in northern Chile, whereas in similar deposits elsewhere, it is rare. In Chile, it has generally been assumed to be a primary constituent of the supergene zones. There are two difficulties with this supposition. The first is that atacamite requires saline water for its formation, whereas supergene oxidation was caused by percolating, oxygenated meteoric water, mainly rainwater. The second is that atacamite dissolves rapidly or undergoes phase change when exposed to fresh water. Supergene enrichment of copper deposits in northern Chile extended over a long period, 44 to 9 Ma, being terminated by the onset of hyperaridity. During this period, there was at least intermittent rainfall, exposing previously formed atacamite to dissolution or phase change. Furthermore, atacamite-bearing oxide zones in several deposits are directly overlain by thick Miocene alluvial gravels; the stream waters that transported these gravels would have permeated the oxide zones. In some deposits, atacamite-bearing assemblages occur both in the oxide zones and in contiguous gravels. We suggest that atacamite-bearing oxide assemblages are more likely to have been a replacement of preexisting oxide phases after the onset of hyperaridity at about 9 Ma. A hyperarid climate made possible evaporation and concentration of chloride in meteoric waters. In this paper, we discuss another source of saline waters to modify oxide zones. Dewatering of the Domeyko Basin expelled brines along faults, some of which had earlier guided the location of porphyry deposits. At the Spence porphyry copper deposit, saline waters, which δD vs $\delta^{18}O$ isotope analyses identify as basinal brines, are presently rising through the deposit, then flowing away along the base of the covering gravels. Compositions of these waters lie within the stability fields of atacamite and brochantite, the two minerals that comprise the oxide zone. Evidence is presented for other porphyry deposits, Radomiro Tomic and Gaby Sur, that basinal brines may have been involved in the late formation of atacamite.

Keywords Atacamite · Copper deposits · Northern Chile

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Introduction

The most notable occurrences of the dark green mineral, atacamite $[Cu_2Cl(OH)_3]$, are in supergene zones of copper deposits in the Atacama Desert of northern Chile. Atacamite is present in variable proportions with other oxide minerals in several major porphyry deposits, including Cerro Colorado, Chuquicamata, El Abra, Escondida, Gaby Sur, Lomas Bayas, Radomiro Tomic, and Spence and in other types of copper deposit, including Michilla, Mantos Blancos, and Sierra Miranda (Fig. 1). In porphyry deposits elsewhere, atacamite is rare, an exception being the Florence deposit,
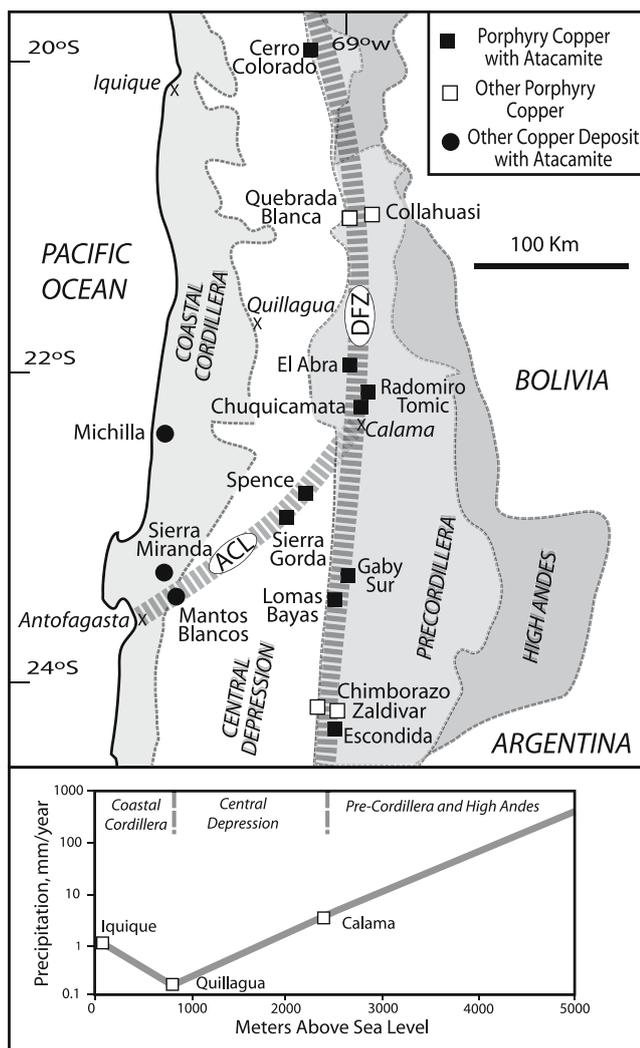
Fig. 1 Distribution of copper deposits in northern Chile containing atacamite in the oxide zone. DFZ is the Domeyko Fault Zone and ACL is Antofagasta–Calama Lineament. The land between the High Andes and the coast is the hyperarid central Atacama Desert, as shown by the precipitation trend from the coast to the High Andes. Precipitation data from Houston and Hartley (2003)

Casa Grande, Arizona (Nelson and Johnston 1994). In northern Chile, atacamite is widely believed to be a primary product of supergene oxidation, (e.g., in situ oxidative replacement: Chavez 2000). However, its presence in supergene zones is enigmatic because it requires high chloride activity, whereas supergene enrichment of porphyry deposits is believed to be by oxygenated meteoric water percolating through sulfides in the vadose zone. High chloride activity accounts for other important occurrences of atacamite, e.g., as a product of seafloor weathering of copper-bearing sulfides (Hannington 1993) and as a corrosion product of copper and its alloys in marine environments. The dimorph of atacamite, paratacamite $[Cu_4Cl_2(OH)_6]$, precipitates under acidic conditions; atacamite precipitates under more alkaline conditions (Woods and

Garrels 1986). Both forms occur in Chilean copper deposits, with atacamite apparently being more common. In this paper, we refer to both crystal forms as atacamite.

Atacamite is unstable in fresh waters, so that it is rarely preserved in near-surface environments. Assemblages of cupric hydroxy minerals, atacamite, brochantite, malachite, and tenorite, respond rapidly to changes of solution composition, within, at most, weeks (Woods and Garrels 1986). MacFarlane et al. (2005) describe continuous leach experiments on samples of soils, rocks, and ores. In these experiments, leach solutions, starting with water, then a series of nitric acid solutions of increasing concentration, were allowed to flow through 50 mg of powdered sample into an inductively-coupled plasma mass spectrometer (ICP-MS). The flow rate was kept low, 100 μl/min, to distinguish peaks in the dissolution of different elements. One of the samples tested was atacamite-bearing exotic ore from northern Chile (K. Kyser, personal communication). The resulting profile (Fig. 2) showed that all Cl and most of the Cu in the sample was removed in less than an hour during the passage of water.

In the hyperarid climate of the Atacama Desert (Fig. 1), there is negligible recharge of groundwater through the vadose zone by direct precipitation. Instead, groundwater is derived by inflow from the Andes to the east (Magaritz et al. 1990). Thus, atacamite is preserved. Supergene alteration of porphyry copper deposits in the central Atacama Desert occurred over a long period extending from 44 Ma, reaching a maximum at 14–21 Ma, and ending near 9 Ma with the onset of hyperaridity (Arancibia et al. 2006). Supergene enrichment required significant rainfall. Alpers and Brimhall (1988) estimated a groundwater recharge rate of about 8 cm/year, necessitating rainfall rates one to two orders of magnitude greater than at present; Clark et al. (1990) suggested rates >10 cm/year, compared to the present rainfall of <10 mm/year. In this paper, we review
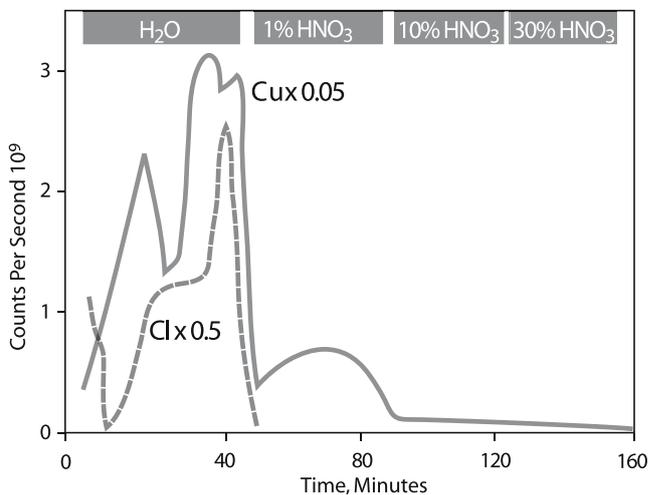

Fig. 2 Continuous leach extraction of a sample of atacamite-bearing ore from northern Chile. Modified from MacFarlane et al. (2005)

data that suggest atacamite is a secondary product resulting from the flushing of preexisting oxide zones with saline water after the onset of hyperaridity.

Spence deposit

Geological features

The Spence deposit, discovered by RioChilex in 1996, is located along the prominent Antofagasta–Calama Lineament (Fig. 1). Porphyry intrusion and hypogene mineralization took place during the Palaeocene. The long axis of porphyry intrusion and mineralization is orientated north–northeast, subparallel to the lineament. Copper minerals are atacamite and brochantite within the oxide zone, and chalcocite, covellite, and pyrite in the enriched zone. Primary sulfides comprise chalcopyrite, bornite, molybdenite, tennantite, and pyrite. Reserves recoverable by open-pit mining are 79 Mt of oxide ore at 1.18% Cu and 231 Mt of sulfide ore at 1.13% Cu. Based on laser ^{40}Ar–^{39}Ar measurements of supergene alunite, Rowland and Clark (2001) identified a long period of supergene activity from 44.44±0.54 to 27.74±5.42 Ma, which was extended by a K–Ar date of 20.9±2.2 Ma. The deposit is covered by piedmont gravels of Miocene age. The gravels are indurated, and for the most part, are poorly sorted with a fine-grained matrix that makes them impermeable, except where fractured, or in better sorted layers, as near their base. In a section through the southern part of the deposit (Fig. 3), andesitic country rock is intruded by porphyry, both as larger bodies and as thin dikes in the fracture zones.

The atacamite–brochantite assemblage is continuous through the leached cap into the basal gravels, indicating that oxide deposition continued after supergene oxidation and gravel deposition. Oxides occur in the gravels only south of 7,495,000 N (Fig. 4); elsewhere, the gravels rest on leached cap. As the gravel surface is even, sloping to the west at 30 m/km, the thickness of the gravels (Fig. 4a) is a proxy for basement topography. The water table lies in the gravels except in the south. Here, within the 50-m gravel contour, the deposit forms a ridge and the water table passes through the deposit. Water flow is to the west–southwest.

Groundwater geochemistry

We carried out sampling of groundwaters and soils within and around the deposit in 1999 and 2000 (Cameron et al. 2004; Cameron and Leybourne 2005). A detailed description of sampling and analytical methods for the groundwaters and the results are given by Leybourne and Cameron (2006). The groundwater samples discussed here were collected in 1999 from drill holes using a bailer. Chloride contents show two types of groundwater: low-salinity water east and up gradient of the long axis of the deposit, and saline water west and down gradient from the axis. Over the middle of the deposit is a zone of mixed waters (Fig. 4b). There is more than an order of magnitude difference in the Cl content of the two waters; the low-salinity waters average 356 mg/l, whereas the saline waters average 11,600 mg/l. The maximum for the saline water is 21,200 mg/l, compared to seawater with 19,000 mg/l Cl. In Table 1, saline water sample 1004 west of the deposit is
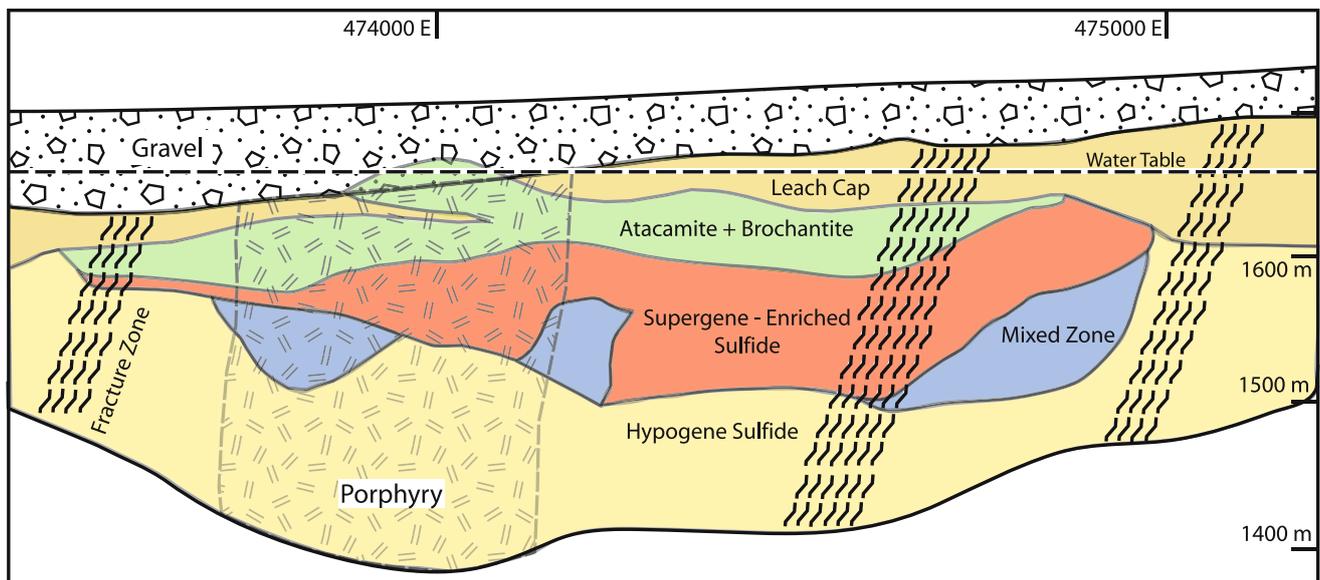

Fig. 3 West–east section through the southern part of the Spence deposit at 747,900 N. Eastings in meters. Porphyry is intruded into andesitic country rock both in the form of a *large mass*, as shown, and as dykes in the central of the three fracture zones. From a section prepared by RioChilex in 1999
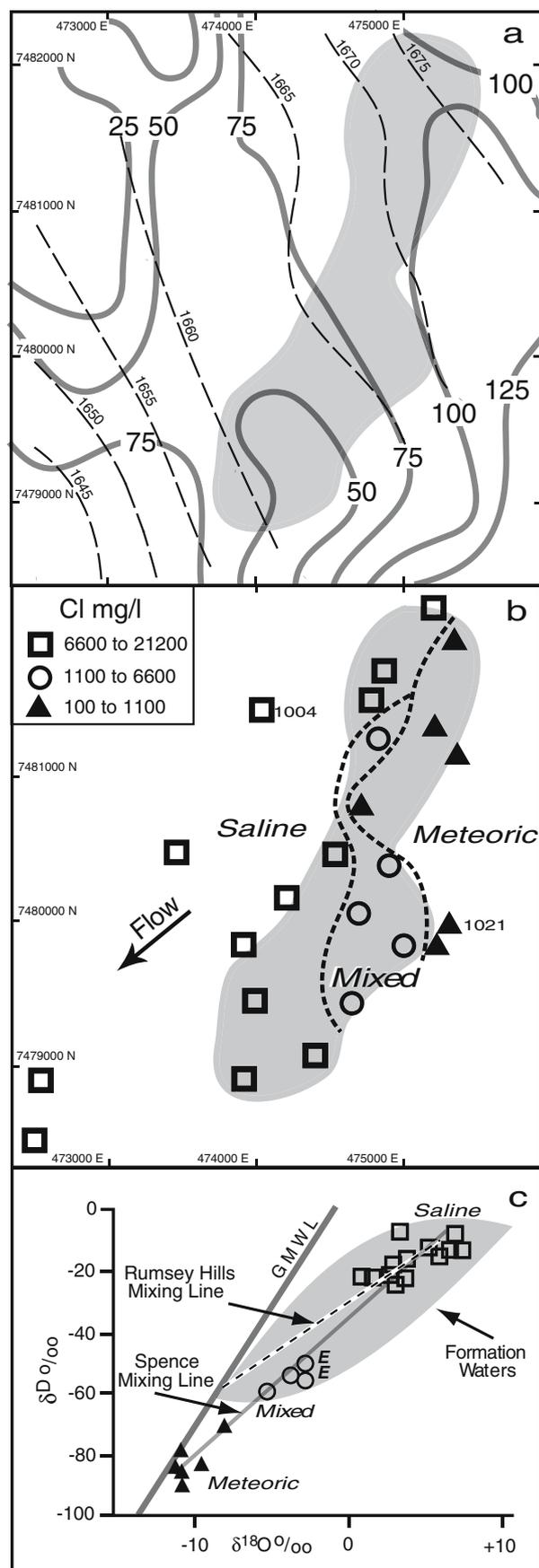
◄ **Fig. 4** **a** Thickness in meters of the Miocene gravel cover over and peripheral to the Spence deposit (*solid contours*). Data courtesy of BHP-Billiton. The elevation of groundwater table is shown in meters (*interrupted lines*). The *shaded outline* is the approximate extent of economic copper mineralization. **b** Distribution of groundwaters of different origin and salinity in and around the Spence deposit. *Dotted lines* show boundaries between saline, meteoric, and mixed waters. The water table lies within the basal gravels, except at the southern part of the deposit, where it lies within the deposit. Data for samples 1004 and 1021 are listed in Table 1. **c** Plot of δD vs $\delta^{18}O$ for groundwaters at Spence relative to the Global Meteoric Water Line (GMWL). *Shaded area* is the field for deep formation waters (after Taylor 1974). The data for the mixing line for Rumsey Hills, California spring waters is from Davisson et al. (1994). The letters *E* show saline waters from the supergene zone in the La Escondida mine (Alpers and Whittemore 1990)

compared to low salinity water 1021 from the east. The saline water is enriched by an order of magnitude or more in the elements As, Br, Ca, I, Li, Mg, Na, Se, and Sr. Sulfur isotope values for the two waters are tightly grouped and different, being heavier for the low-salinity waters (Leybourne and Cameron 2006). Within the deposit area, saline, low-salinity, and mixed waters are all enriched in Cu, up to 1,200 μg/l. On a δD vs $\delta^{18}O$ plot (Fig. 4c), the low-salinity waters plot near the global meteoric water line (GMWL), whereas the saline waters plot well to the right in the field of deep-sourced formation waters, i.e., basinal brines (Cameron and Leybourne 2005). Leybourne and Cameron (2006) considered whether the isotope trend is due to mixing of two waters of different origin or is due to evaporation of the lower salinity water. Considering data for the isotopes and conservative elements, the trend is most compatible with binary mixing of two distinct waters. Moreover, it is difficult to conceive of 75% evaporation taking place only in the immediate vicinity of the deposit, and different sulfur isotope compositions cannot be generated by evaporation. We suggest that the saline waters are basinal brines rising though the deposit along fracture zones, such as those shown in Fig. 3 (Cameron et al. 2002). The waters entering the deposit area from the east are meteoric waters. In northern Chile, precipitation is significant only above 3,000 m, i.e., in the Precordillera and Andes east of Spence. Spence is at 1,700 m. Values of $\delta^{18}O$ for precipitation decrease with altitude; in northern Chile, the range is from −5 to −7‰ at 2,500 m, decreasing to −20‰ above 4,000 m (Aravena et al. 1999). The meteoric waters entering Spence from the east have a range in $\delta^{18}O$ from −8 to −11‰ (Cameron and Leybourne 2005), consistent with derivation from precipitation at higher altitudes. The combined saline and meteoric waters reach the surface in a salar (dried salt lake) 5 km southwest of Spence. Saline waters dominate down-flow from the deposit, indicating that their inflow is greater than that of the meteoric water. The composition of the waters shown in Fig. 4 are plotted on the equilibrium diagrams for copper

Table 1 Comparison of selected elements in saline water 1,004 and meteoric water 1,021 from the Spence deposit (for locations, see Fig. 4) and meteoric water RT1 from Radomiro Tomic. Waters were filtered through a 0.45 μm filter

Sample	Spence Saline 1004	Spence Meteoric 1002	Radomiro Tomic Meteoric RT1
pH	7.52	7.14	6.70
mg/l			
TDS	24,918	1,900	
Cl[c]	9,006	170	1,744
HCO$_3$	145	181	
SO$_4$[c]	5,686	920	5,438
B[b]	39.6	5.0	50.2
Br[b]	11.8	0.4	2.4
Ca[a]	727	47	426
I[b]	19.6	1.3	
K[a]	81.5	13	37.4
Mg[a]	245	5.8	375
Na[a]	7,757	564	2,853
Si[a]	8.1	4.5	13.5
μg/l			
As[b]	73.2	<10	<10
Ba[b]	41	12	<20
Cu[b]	14.3	28.9	828
Fe[a]	<500	<500	<500
Li[b]	3,913	362	813
Mn[b]	880	216	29
Mo[b]	24.2	53.6	701
Ni[b]	34	6	<20
Rb[b]	116	20	34
Se[b]	503	<50	
Sr[b]	10,931	342	6,569
V[b]	41	2.7	<10
Zn[b]	46.2	<10	88

[a] Analyzed by ICP-OES
[b] Analyzed by ICP-ES
[c] Analyzed by ion chromatography
HCO$_3$ by wet chemistry

minerals (Fig. 5) developed by Woods and Garrels (1986). Groundwater compositions were speciated and mineral saturations calculated with the computer code PHREEQC (Parkhurst 1995) using the WATEQ4F thermodynamic database (Ball and Nordstrom 1991). The saline waters are predominantly in the atacamite–brochantite fields, the two minerals that comprise the oxide zone. Some of the mixed waters also plot in these fields, but the meteoritic waters lie in the tenorite and malachite fields. In the absence of saline waters that rise along fracture zones in the deposit, the flow of meteoric water from the east would have caused the replacement of atacamite that occurs within the gravels (Fig. 3), and possibly, atacamite within the deposit. In a later section, we show how meteoric water flowing through the Radomiro Tomic deposit has caused replacement of atacamite by other copper minerals.

Soil geochemistry

At Spence, there are fracture zones in the gravels above the deposit, interpreted to be the result of reactivation of faults that cut the deposit (see Fig. 3). Soils above these fracture zones are anomalous in the same elements as found in the saline groundwaters, including Cl and Br (Cameron and Leybourne 2005); we proposed that saline water was pumped to the surface during earthquakes (Cameron et al. 2002). The rising saline waters incorporate elements present in the deposit, such as Cu, As, and Se, so that these too are anomalous in the soils above the deposit. Elements reaching the surface have been redistributed by the rare rainfall, with cations, such as Cu, more concentrated above 40 cm depth, and anions, more concentrated at 40 cm and below.

Comparison with saline waters at Rumsey Hills, California: evidence for chloride loss in saline waters passing through Spence deposit

Surface flows of saline waters occur within forearc basins, resulting from fluid overpressures caused by tectonic compression. One example is perennial saline springs in the Rumsey Hills, California (Davisson et al. 1994). Nearby petroleum exploration wells blew out at 600 m depth due to overpressure. The Rumsey Hills saline water shows a linear mixing line with meteoric water, shown together with the Spence data on the δD vs δ^{18}O plot (Fig. 4c). The isotopic composition of the saline waters from Spence and the Rumsey Hills are similar. Davisson et al. (1994) present evidence that the saline water is seawater modified as a result of albitization of plagioclase at depth within the underlying Cretaceous sedimentary rocks:

$$CaAl_2Si_2O_8 + 4SiO_2 + 2Na^+ = 2NaAlSi_3O_8 + Ca^{2+}$$

This is estimated to occur at temperatures of 70 to 120°C, although the springs are relatively cool at 13 to 26°C. The reaction results in a 1:2 exchange between Ca and Na, with Ca becoming enriched relative to Cl in the deeper, more saline waters. To quantify the Na–Ca exchange during albitization, Davisson et al. (1994) calculated a "Na deficit" and a "Ca excess," defined as the deviations of the measured cation concentrations from those expected for a linear dilution between seawater and freshwater, where:

$$Na\ deficit = 1/22.99\big((Na/Cl)_{seawater}Cl_{measured} - Na_{measured}\big)$$

$$Ca\ excess = 2/40.08\big(Ca_{measured} - (Ca/Cl)_{seawater}Cl_{measured}\big)$$

In these equations, Cl is used to normalize the concentrations of cations, as it is conservative, i.e., water–rock reactions neither consume nor produce Cl. The Na deficit vs

Fig. 5 Compositions of different types of groundwater at Spence relative to the stability fields for copper oxides, carbonates, and sulfates after Woods and Garrels (1986), who also provide data for seawater and average river water. The dimorph of atacamite, paratacamite [$Cu_4Cl_2(OH)_6$], precipitates under acidic conditions, atacamite in more alkaline conditions
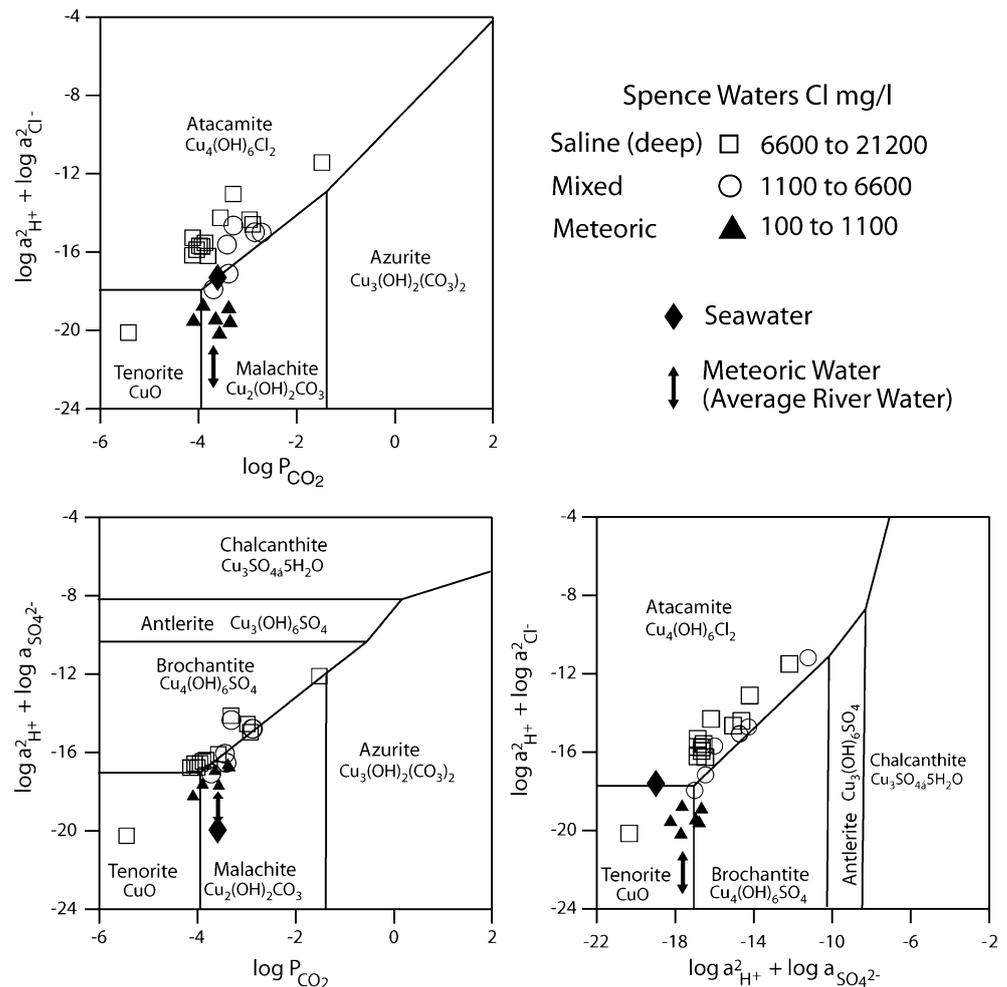
the Ca excess produces a linear plot for the Rumsey Hills samples (Fig. 6). In a later paper, Davisson and Chriss (1996) applied these equations to the Na, Ca, and Cl concentrations in 800 samples of basinal fluids from around the world, which they considered to be modified seawater. The host lithologies varied from carbonates to granites. These samples plot on a similar trend to the Rumsey Hills samples, reflecting a net cation exchange ratio of 2 Na for 1 Ca.

These data by Davisson and colleagues establishes a consistent relationship between Na, Ca, and Cl concentrations in basinal fluids from a wide variety of environments. Whereas Cl used to normalize Na and Ca in the above equations is conservative when water interacts with silicate rocks at moderate temperatures, Cl is not necessarily conservative when it migrates through an assemblage containing copper oxides. Depending on fluid-oxide equilibria and Cl concentration, Cl may be added to the assemblage, forming atacamite, or existing atacamite may be removed. As formulated in the above equation, the Na deficit is a positive number that increases as Na is lost relative to Cl. The Rumsey Hills samples follow the slope
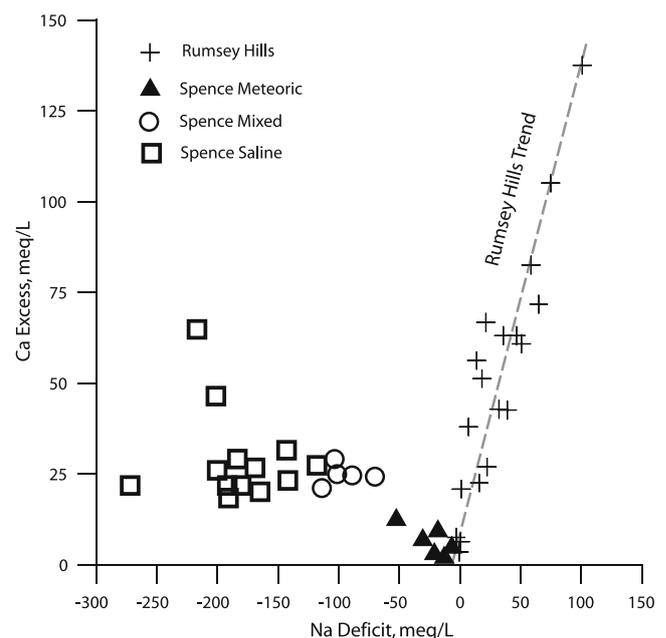

Fig. 6 Plot of Na deficit vs Ca excess for Rumsey Hills, California, waters (Davisson et al. 1994) and for Spence waters. See text for details. For classification of Spence waters, see Fig. 4

required by the 2:1 Na:Ca exchange ratio, whereas the Spence saline and mixed samples are entirely different, with negative values for the Na deficit, implying loss of Cl relative to Na (Fig. 6). This is also shown on a Na vs Cl plot (Fig. 7a) in which the Rumsey Hills samples plot below the seawater dilution line, whereas the Spence samples plot above it. For the atacamite-brochantite oxide assemblage at Spence, formation of atacamite causing loss of Cl from the basinal fluid can only result from the replacement of brochantite by atacamite. This should lead to addition of SO_4 to the basinal fluid emerging from the top of the deposit. For the saline samples, there is a trend of decreasing Cl with increasing SO_4 (Fig. 7b). Thus, it is possible that the ore zone at Spence is currently not passive but may be reacting with the basinal fluids passing through the deposit. With mining of the deposit about to start, this may be more thoroughly explored.

Other deposits

Radomiro Tomic

The most comprehensive studies of the distribution of atacamite in Chilean porphyries are at Radomiro Tomic, by Cuadra and Rojas (2001), Brimhall et al. (2001), and Arcuri and Brimhall (2003). At Radomiro Tomic, there is 2,330 Mt of 0.59% Cu, of which 850 Mt at 0.62% Cu is oxide ore (Ossandon et al. 2001). The deposit is hosted within the Chuqui Porphyry (32.7 Ma, Cuadra et al. 1997), which was

intruded through a Lower Jurassic to Middle Cretaceous marine and non-marine sedimentary sequence. The most important structural feature in northern Chile, the north-trending West Fissure, part of the Domeyko Fault Zone (Fig. 1), is 1 km west of the deposit. Dextral movements on this fault formed a related system of faults in the deposit area, including faults trending north and northeast. Sericitic alteration at Radomiro Tomic has been dated at 31.8± 0.3 Ma (Cuadra et al. 1997); supergene alunite from the adjacent Chuquicamata deposit ranges from 19 to 15 Ma (Sillitoe and McKee 1996). The Radomiro Tomic deposit is covered by alluvial gravels, with a tuff near their top dated by K–Ar at 9.7±0.7 Ma (Cuadra et al. 1997). Whereas the gravel surface is flat, bedrock, including the oxide zone, slopes westward, with some abrupt changes indicating possible faults. On the east margin of the deposit, there is 30 m of gravel cover, 150 m on the west. Cuadra and Rojas (2001) provide a comprehensive description of the distribution of oxide minerals, atacamite, copper clays, chrysocolla, and copper wad. They divide the oxide ore into upper and lower zones (Fig. 8), based on the proportions of Cu-bearing minerals. Atacamite accounts for 40% of the Cu content of the upper zone and 70% of the lower zone. In the upper zone, atacamite covers preexisting copper minerals or fills fractures; it is the last-forming mineral. In the lower zone, it is present in veins or is disseminated. In an interval extending from the water table down ~50 m (Fig. 8), atacamite is absent, but all other copper minerals increase in amount, and total Cu reaches a maximum. In the upper part of the upper oxide zone, directly below the gravels, the
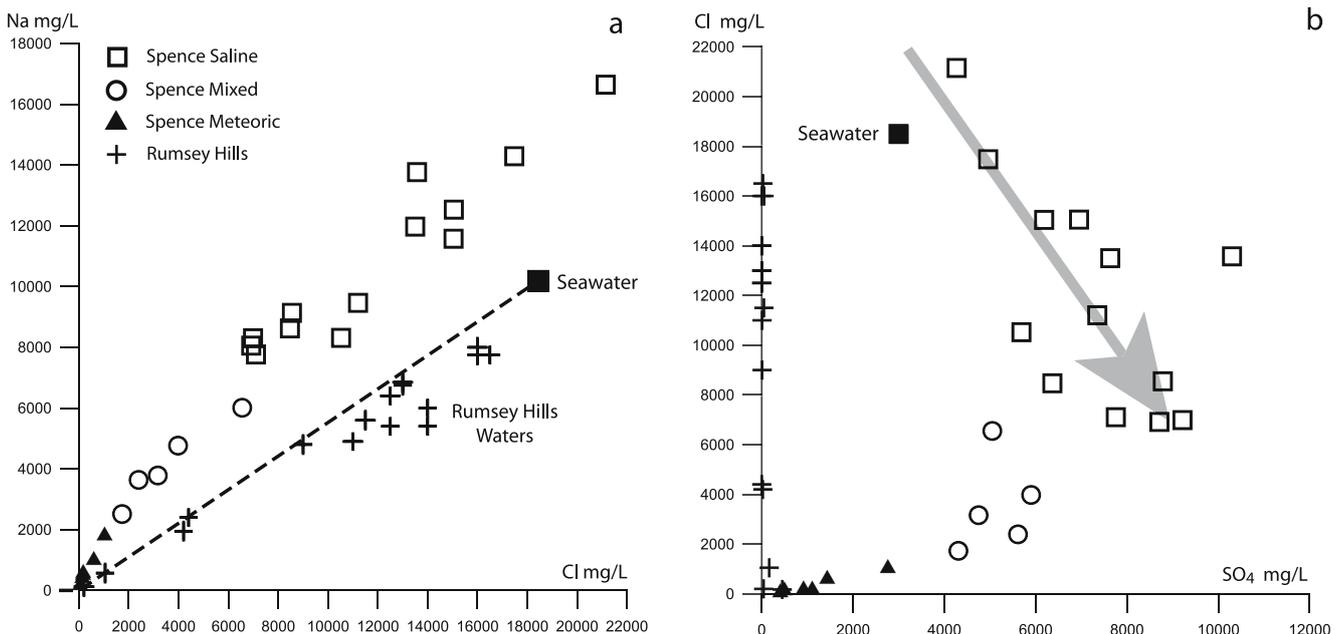

Fig. 7 a Plot of Na vs Cl for Spence and Rumsey Hills waters relative to seawater dilution line. For classification of Spence waters, see Fig. 4. (**b**) Plot of Cl vs SO_4 for Spence and Rumsey Hills waters. Note that for Spence saline waters, there is a trend to declining Cl with increasing SO_4

Fig. 8 Idealized section through the Radomiro Tomic deposit. Chrysocolla zone in gravels and water sample RT1 are at "A." Atacamite is preserved above the water table because of lack of recharge in the hyperarid climate and in the lower oxide zone because it is bathed in saline water. The flow of an upper layer of meteoric water removes atacamite, replacing it with other copper minerals
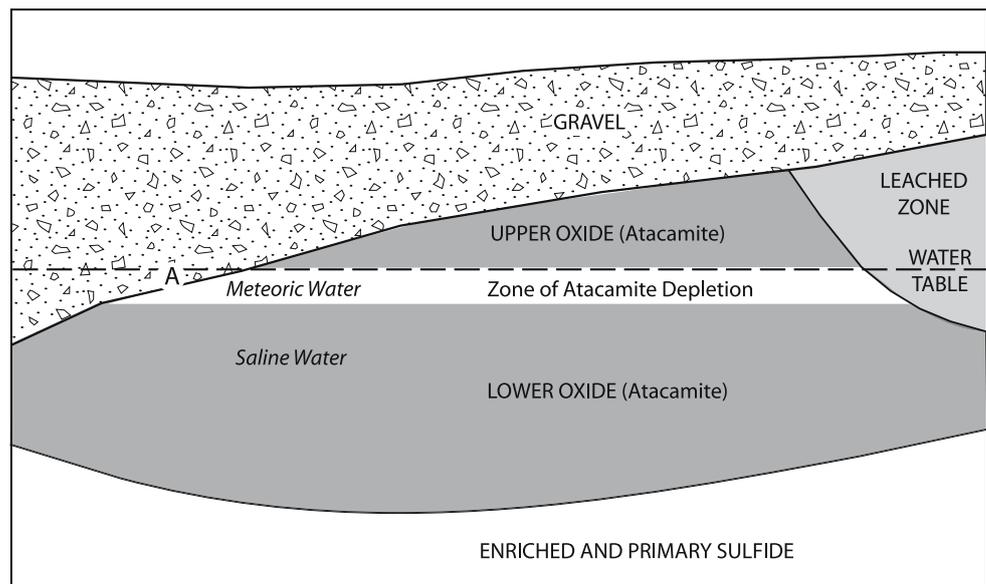
Cl/Cu ratio is 0.33 to 0.80, whereas in the zone of atacamite depletion, it is 0.00 to 0.10. As the stoichiometric ratio for atacamite is ca 0.28, the upper part of the oxide zone has excess Cl, possibly in the form of salts. Sylvite and thenardite occur along parts of the gravel/bedrock contact. In places, along northwest and east–west trending paleo-channels, the gravels are mineralized by exotic Cu minerals, chrysocolla, atacamite, and copper wad.

During a visit to the pit by the senior author in 1999, the characteristic dark green color of atacamite was most marked at the top of the oxide zone, directly under the gravel contact (Fig. 9a). Down the slope created by the irregular topography of the deposit, this coloration becomes less intense, and near the water table, is replaced by the light blue of chrysocolla. The chrysocolla zone extends several tens of meters into the gravels (Fig. 9b). Water dripping from the pit wall at this location was collected as sample RT1 (Table 1). Analyses showed this to be low-salinity meteoric water, but with high concentrations of Cu and Mo. This low-salinity water may be "floating" on denser saline waters at depth. Two samples of water collected by Cuadra and Rojas (2001) from a deeper exploration shaft contain 7,200 mg/l Cl, compared to 1,744 mg/l for the sample near the water table (Table 1). The gravels are well indurated and mostly form vertical pit walls, but in places, there are zones of fracturing where the gravels have slumped into the pit (Fig. 9a). The exposed oxide zone was fractured at many locations (Fig. 9c), and some fractures may be iron stained.

Arcuri and Brimhall (2003) measured Br and δ^{37}Cl in atacamite from the deposit as tracers for the source of Cl. They found elevated Br contents, 22 to 180 ppm, and δ^{37}Cl values near 0‰ and similar values for atacamite from the nearby Chuquicamata and Mina Sur deposits. These data

rule out a magmatic source, as biotite-bearing protore samples from the deposit have <2 ppm Br and δ^{37}Cl values of 0.1 to 2.5‰. Analyses of local meteoric water also show that waters of this type were not a source. The most likely source is Upper Jurassic sediments, part of the succession that lies below the deposit, with values of 22 to 24 ppm Br and δ^{37}Cl of −0.8 to + 0.5‰. Arcuri and Brimhall (2003) suggest that supergene enrichment was coincident with regional uplift that exposed the Upper Jurassic sediments, which were leached by meteoric water that conveyed Cl and Br to the deposit. Atacamite from small, distal deposits, up to 25 km away from Radomiro Tomic, have different compositions, 9 to 23 ppm Br and δ^{37}Cl of −0.3 to −2.6‰, more similar to Lower Jurassic rocks. On a regional basis, the Br–Cl geochemistry of atacamite is, thus, variable, which to Arcuri and Brimhall (2003) argued against a meteoric Cl source, which would have given rise to more homogeneous values.

Before mine development, soil samples were collected by Minera Mount Isa at 40 cm depth and 100-m intervals on a 7-km west–east traverse across the deposit. These were analyzed at Actlabs by Enzyme Leach-ICP-MS, which measures water-soluble constituents (Cameron et al. 2004). The results show anomalies for Cl and Br directly over the deposit (Fig. 10). This figure also shows data for Cl in soils sampled at 10 to 20 cm depth at Spence. There are Cl anomalies above the Spence deposit and also over a fracture zone, 1 km east of the deposit that lies above barren basement. The soils above the deposit are anomalous in Cu, As, Br, I, and a number of other elements (Cameron and Leybourne 2005). At Radomiro Tomic, the soils above the deposit are anomalous in As and I, but not Cu. The absence of Cu may be due to the deeper sampling depth, 40 cm at Radomiro Tomic, compared to 10–20 cm at Spence.

Fig. 9 **a** General view of Radomiro Tomic pit, February 1999. *Green colour* is atacamite. There is considerable relief on the top of the oxide zone, being highest to the right of the slumped gravels. **b** Chrysocolla mineralization extending into gravels from zone of atacamite depletion to the right. Water of meteoric origin dripping from the pit wall was collected as sample RT1 (Table 1). **c** Vertically fractured oxide zone containing atacamite. Substantial amounts of atacamite are occluded within micro-fractured feldspar and biotite (Brimhall et al. 2001), indicating its information during tectonism
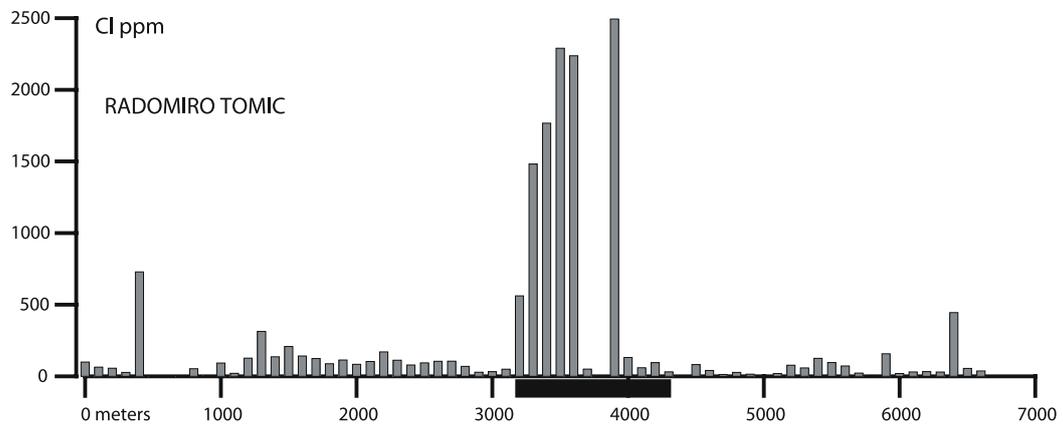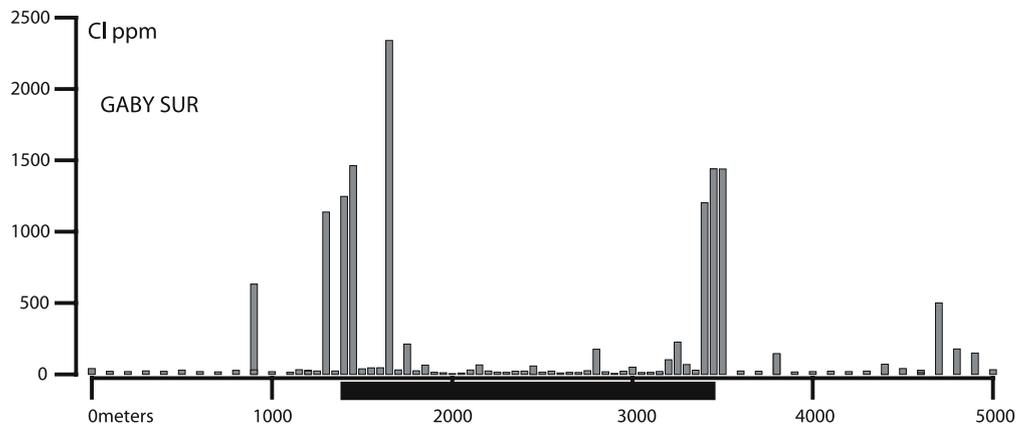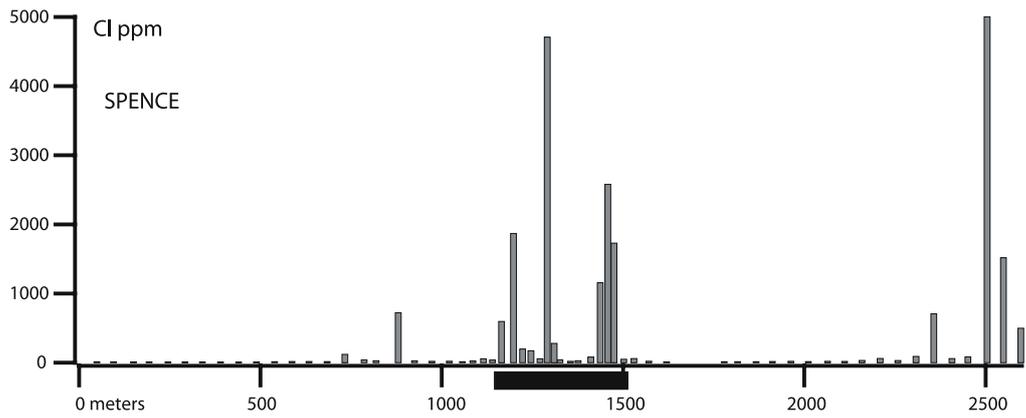
Gaby Sur

Codelco's Gaby Sur porphyry deposit contains 584 Mt of oxide ore grading 0.41% Cu. The copper oxide zone, up to 180 m thick, is underlain by hypogene sulfides. The deposit lies in a graben, delimited by high-angle boundary faults and is covered by up to 40 m of gravel, containing a tuff dated at ca 9.6 Ma (Camus 2001). The upper 20 m of the gravel is cemented by calcrete, making it impermeable to water where unfractured. Water is found only below the basement unconformity, where drill holes intersect major faults. Soils from 10 to 30 cm depth were sampled in 1999 along a 5-km long undisturbed east–west traverse across the deposit (Cameron et al. 2004). Analyses by Enzyme Leach-ICP-MS show distinct anomalies for NaCl in the soils above both boundary faults (see Cl data, Fig. 10) and

coincident anomalies for elements similar to those found to be anomalous at Spence, including As, Se, and Cu. In soil pits, the calcrete-cemented gravels can be seen to be fractured in these saline zones, similar to the fracturing of the gravels above Spence and Radomiro Tomic.

Mantos Blancos

The Mantos Blancos copper deposit, in the Coast Range near Antofagasta, occurs within a bi-modal igneous complex of Upper Jurassic—Early Cretaceous age (Ramirez et al. 2006). An enriched oxide zone, including atacamite (or para-tacamite) and chrysocolla, is present near the surface. Chavez (1983, 2000) noted the similarity in the oxide assemblage to Radomiro Tomic. The oxide ore contains 10 Mt of 1.47% Cu and 14 Mt at 0.78% Cu; also, 20 Mt of

sulfide ore grading 1.65%. The deposit is bounded by two major faults, the Tercera and Marina faults. Both have been active since the time of ore formation, with substantial lateral and vertical displacement. The Tercera fault truncates oxide and sulfide zones with approximately 2,000 m of post-mineral dextral displacement; the Marina Fault has several hundred meters of displacement (W. Chavez, personal communication). Alluvium and colluvium in the area of the deposit is cemented by halite-rich caliche ranging from a few centimeters in thickness to 3 m (Chavez 1983).

Palacios et al. (2005) carried out local and regional soil geochemical studies over and around Mantos Blancos and a similar deposit, Sierra Miranda, 25 km to the north. Much of the surfaces in this region, including slopes and hilltops, have a layer of gypcrete, 10 to 30 cm in depth or thicker, deposited from marine fogs, "camanchaca" that have moved in from the coast. Normalized to the Cl content of seawater, fog condensates are enriched in Ca and SO_4 by approximately an order of magnitude (Schemenauer and Cereceda 1992). In most locations in northern Chile, gypcrete soils contain only trace amounts of NaCl (see plots of Cl in soils peripheral to the Spence, Gaby Sur, and Radomiro Tomic deposits, Fig. 10). A biotite-rich lapilli layer in the gypcrete was dated by K/Ar at 2.97 ± 0.07 and 2.87 ± 0.03 Ma (Chavez 1985).

Palacios et al. (2005) collected salt samples (gypsum + anhydrite + halite), which were dissolved in aqua regia, then analyzed by atomic absorption spectrometry. Results at Mantos Blancos showed "spike" anomalies for Cu up to 1,200 ppm on hills and slopes 250 to 300 m vertically above known mineralization, contrasting with background concentrations over barren rocks. The depth to the water table is more than 250 m. The spikes correspond to the surface projection of known faults that intersect mineralization at depth. There is a good correlation between Cu and Na where the concentration of Cu is high. Drilling on Cu anomalies in the southern part of the Sierra Miranda district located copper oxide mineralization below 125 m of leached bedrock and gravels (Palacios et al. 2005). These authors report salt efflorescence at the surface along major faults. In places, these have a green coloration, which X-ray diffraction showed to be atacamite and chalcantite. These surface occurrences of copper minerals may extend several hundreds of meters, depending on the importance of the faults and the size of the mineralized bodies. The internal texture and structures within the efflorescences suggest explosion bubbles, which could indicate that a mixture of liquid plus air or gas has reached the surface.

Discussion

Atacamite is a major constituent of the oxide zones of several large copper deposits in the hyperarid Atacama Desert (Fig. 1). For this mineral to be a primary product of supergene oxidation, as is widely supposed, the agent for supergene oxidation would have to be saline water. This is at odds with the accepted model of oxidation by meteoric water from rainfall percolating through the deposits. To account for this, Arcuri and Brimhall (2003) proposed that salt-bearing rocks that form part of the succession below the Radomiro Tomic deposit were uplifted and the dissolved salts incorporated into the meteoric water that then caused supergene oxidation. Atacamite that might have formed during supergene oxidation would have been exposed to percolating meteoric water during two periods. The first was during the long period of supergene oxidation. For porphyry copper deposits in the central Atacama Desert, this extended from 44 to 9 Ma, reaching a maximum at 21 to 14 Ma (Arancibia et al. 2006). Similar age ranges have been reported for exotic mineralization (Mote et al. 2001). Individual deposits can show a wide range of ages for supergene oxidation (Hartley and Rice 2005), including Spence, from 44 to 21 Ma (Rowland and Clark 2001). Supergene oxidation during this time required significant rainfall, >10 cm/year by the estimate of Clark et al. (1990). As a primary product of supergene oxidation during the period 44 to 9 Ma, atacamite would have been exposed to repeated periods of rainfall and percolation.

The second period when preexisting atacamite would have been exposed to percolating meteoric water was during gravel deposition, when stream waters flowed over the deposits. Spence, Radomiro Tomic, and Gaby Sur are directly covered by thick alluvial gravels of Miocene age. The top of the oxide zone at Radomiro Tomic has a relief of more than 100 m in gravel. Gravels were deposited in stages, the stream flow gradually rising up the zone and coming into direct contact with atacamite. Given the ready solubility or replacement of atacamite when it is in contact with meteoric water, the atacamite now present at Radomiro Tomic cannot have been any older than the end of gravel deposition. This deposit presents in microcosm the conditions that constrain the presence or absence of this mineral in northern Chile. In the upper oxide zone above the water table, atacamite is preserved because, in a hyperarid climate, there is no recharge to the groundwater by meteoric water. At the water table and for 50 m below, meteoric water is percolating through the oxide zone and has removed atacamite, replacing it with other copper minerals. Finally, atacamite is preserved in the lower part of the oxide zone because the layer of meteoric water "floats" on deeper layers of saline water.

In the model considered here, atacamite was formed as a replacement of a primary oxide assemblage after the onset of hyperaridity at about 9 Ma. An increasingly arid climate favors the generation of saline meteoric water by evaporation. Locally in northern Chile, within closed basins, saline groundwaters occur in salars. If saline groundwaters that formed as a result of evaporation came into contact with copper mineralization, then atacamite could have replaced copper oxide minerals. However, over much of the region, neither the groundwater nor the soil are saline. At Spence, in soils away from the fracture zones, samples have <50 ppm Cl and low values are also the norm on the other soil traverses shown in Fig. 10. Deep groundwaters in the Central Depression are predominantly of low salinity because they are derived from precipitation in the Andes (Magaritz et al. 1990); they serve as a source of drinking water. In addition to the meteoric waters entering Spence from the east, which average 356 mg/l Cl, we have analyzed groundwater samples from five exploratory drill holes through ca 300 m of gravel in the Pampa del Tamarugal, 60 km northwest of Chuquicamata; these have chloride concentrations from 97 to 550 mg/l Cl. Over much of the region, groundwaters are at too great a depth for capillary rise and evaporation, the maxima for different substrates being 0.15 m for coarse sand, 0.3 m for medium sand, 1 m for fine sand, 1 to 10 m for silt, and 10–30 m for clay (Jumikis 1967).

Sedimentary rocks, such as that of the Domeyko Basin underlying the Atacama Desert, progressively dewater, releasing saline formation waters. In wet climates, these mix and are diluted by larger volumes of meteoric water. Porphyry deposits are mostly developed along faults, and it is faults that are the conduits for dewatering. Moreover, many deposits are covered by gravels, which are often permeable in better sorted channels at their base. This provides a further conduit for the dispersal of the saline formation waters, where they may reach other mineralization lying along the unconformity. At Spence, saline basin waters rising through the deposit disperse 5 km through the basal gravels to a salar. These waters have compositions within the stability field of atacamite and brochantite, and atacamite–brochantite mineralization is continuous from the deposit into the basal gravels (Fig. 3). Isotope data identify these as formation waters; saline groundwaters with similar isotopic character (Fig. 4) were sampled by Alpers and Whittemore (1990) from the Escondida deposit.

Although much of the saline water emerging from the basement at Spence flows away through the basal gravels, we suggest that, during earthquakes, saline water was forced to the surface through a fracture zone in the gravels (Cameron et al. 2002). The soils above this fracture zone are anomalous in NaCl, Cu, and elements that are enriched in the saline water. At other deposits, too, there is similar evidence for pumping of saline waters to the surface (e.g., at Gaby Sur and Radomiro Tomic: Fig. 10). In soils directly above the West Fissure, south of Chuquicamata, there is a chloride anomaly of 17,000 ppm Cl (Cameron et al. 2004), a value that exceeds that of the anomalies shown in Fig. 10. At Mantos Blancos, in gypsum–halite material, Palacios et al. (2005) found Cu anomalies that correspond with faults that cut mineralization. Salt efflorescences at the surface along major faults, which over copper mineralization contain atacamite and chalcantite, indicate that Cu was brought to the surface in saline waters.

At Radomiro Tomic, in addition to Cl, the soils above the deposit are enriched in Br, which Arcuri and Brimhall (2003) found to be a diagnostic constituent of the atacamite in the deposit. Bromine and $\delta^{37}Cl$ analyses for atacamite at Radomiro Tomic are most comparable to salts in Upper Jurassic strata, part of the basement below the deposit. Atacamite from other occurrences in the district is different, with Br and $\delta^{37}Cl$ compositions similar to Lower Jurassic strata. We agree with Arcuri and Brimhall (2003) that the likely source of the Cl and Br in the atacamite at Radomiro Tomic and elsewhere in the district is in the sedimentary rocks in the basement. Whereas Arcuri and Brimhall (2003) proposed uplift of the sedimentary units and the dissolution of their salts into the meteoric waters that caused supergene oxidation, we propose that basinal brines were pumped up through the deposit after the onset of hyperaridity.

The situation for the older deposits of different type in the Coastal Cordillera (Mantos Blancos, Sierra Miranda, and Michilla) is likely different. In addition to differences in age and deposit type, the Coastal Cordillera has had a hyperarid climate for a longer time. Dunai et al. (2005) estimate that the surface has not been disturbed since 25 Ma. However, the origin of atacamite in these older deposits is likely to be similar in that saline water has been pumped to the surface along faults from a deep water table, in the case of Mantos Blancos greater than 250 m (Palacios et al. 2005).

Conclusions

Supergene enrichment of copper porphyry deposits required significant rainfall, and for atacamite to form as a primary product of supergene enrichment required that water percolating through the deposit be saline. The climatic and tectonic conditions for supergene enrichment of porphyry deposits in northern Chile extended over a long period from 44 Ma to the onset of hyperaridity at 9 Ma. Oxide zones containing atacamite formed during this period would have experienced continued percolation of meteoric waters. Further interaction with meteoric water would have occurred when alluvial gravels were laid over the oxide

zones. Experimental evidence shows that atacamite is very rapidly dissolved or is replaced by other copper minerals when it is exposed to low-salinity waters. Thus, we suggest that the atacamite found in the oxide zone of many porphyry deposits in northern Chile, is not a primary product of supergene oxidation but formed by replacement of other copper oxide minerals after the climate of the region became hyperarid. Saline waters can form in a hyperarid climate by the evaporation of meteoric water. In this paper, we consider another source for saline water: basinal brines expelled during dewatering of sedimentary rocks underlying the Atacama Desert. Porphyry deposits were formed along faults, and it is faults that serve as a conduit for dewatering. At Spence, we have previously shown that saline water with the isotopic composition of deep formation water is rising through the deposit. The composition of these saline waters falls within the stability fields of the atacamite–brochantite assemblage of the oxide zone at Spence.

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