Geoscience Canada

Economic Geology Models 1.
Geochemical Exploration and Metallogenic Studies, Northern Chile

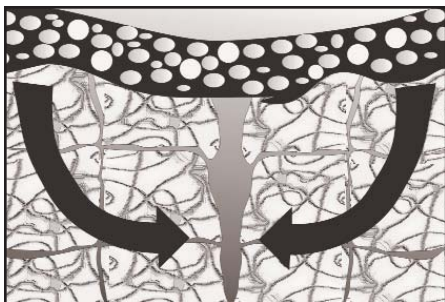## Eion M. Cameron, Matthew I. Leybourne, Carlos Palacios et Martin Reich

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Résumé de l'article

La recherche décrite ici et initiée en 1998 visait à mettre au point des méth-odes d'exploration de gisements de porphyres cuprifères enfouis sous d'épaisses couches lithifiées de graviers dans le désert d'Atacama au Chili. Des données préliminaires indiquent que des eaux souterraines salines minéralisées ont été poussées épisodiquement jusqu'à la surface, à travers des zones de fractures, à l'occasion de séismes, créant ainsi des anomalies au-dessus de gisements minéraux. Une recherche subséquente appuyée par la *Canadian Mining Industry Research Organization* (CAMIRO) qui a porté sur la composition de l'eau souterraine et des anomalies de surface, a permis de confirmer l'existence d'un lien entre les deux. Les résultats de travaux subséquents permettent de croire que ces anomalies géochimiques sont l'expression en surface d'un processus commun à l'évolution métallogénique de nombreux gisements. L'intrusion porphyrique et la minéralisation hypogène sont tributaires de failles, auxquelles s'est ensuite ajouté un enrichissement supergène sous climat semi-aride. Après l'enfouissement au Miocène par des graviers, le climat est devenu hyper-aride; selon les estimations le climat serait devenu hyperaride entre le Miocène moyen (11-14 Ma) et le Pliocène (~3-5 Ma). Depuis, l'assèchement des eaux salines du socle le long de failles persistantes a entraîné une conversion de l'assemblage original d'oxydes de cuivre supergène - lequel s'était formé en état d'équilibre en milieu d'eau météorique et qui était dépourvu d'atacamite - en un assemblage contenant de l'atacamite [Cu2Cl(OH)3], ce minéral de cuivre typique du Chili du nord. Cette interprétation est corroboré par des études montrant que la salinité des inclusions fluides dans l'atacamite est semblable à celle de l'eau souterraine locale et que l'atacamite est significativement plus jeune que l'altération supergène coexistante.

SERIES

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Geochemical Exploration and Metallogenic Studies, Northern Chile

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SUMMARY

Research was initiated in 1998 on geochemical methods of exploration for copper porphyry deposits buried under thick, lithified piedmont gravel cover in the Atacama Desert, Chile. Early data suggest that mineralized, saline groundwater has been episodically forced up through fracture zones to the surface during earthquakes, creating geochemical anomalies above ore deposits. Follow-up research supported by the Canadian Mining Industry Research Organization (CAMIRO) examined the composition of both groundwater and surface anomalies, confirming a link between the two. Further work suggests that the geochemical anomalies are the surface expression of a process common to the metallogenic evolution of many deposits. Porphyry intrusion and hypogene mineralization are controlled by faults, and are followed by supergene enrichment in a semi-arid climate. After burial by Miocene gravels, the climate changed to hyper-arid; estimates of the onset of hyperaridity vary from mid-Miocene (11–14 Ma) to Pliocene (~3–5 Ma). Since then, saline dewatering of the basement along long-lived faults has converted the original supergene copper oxide assemblage, formed in equilibrium with meteoric water and lacking atacamite, to one containing atacamite [$Cu_2Cl(OH)_3$], the copper mineral especially associated with northern Chile. This interpretation is supported by studies showing that the salinity of fluid inclusions in atacamite is similar to that of local groundwater and that atacamite is considerably younger than the co-existing supergene alteration.

SOMMAIRE

La recherche décrite ici et initiée en 1998 visait à mettre au point des méthodes d'exploration de gisements de porphyres cuprifères enfouis sous d'épaisses couches lithifiées de graviers dans le désert d'Atacama au Chili. Des données préliminaires indiquent que des eaux souterraines salines minéralisées ont été poussées épisodiquement jusqu'à la surface, à travers des zones de fractures, à l'occasion de séismes, créant ainsi des anomalies au-dessus de gisements minéraux. Une recherche subséquente appuyée par la *Canadian Mining Industry Research Organization* (CAMIRO) qui a porté sur la composition de l'eau souterraine et des anomalies de surface, a permis de confirmer l'existence d'un lien entre les deux. Les résultats de travaux subséquents permettent de croire que ces anomalies géochimiques sont l'expression en surface d'un processus commun à l'évolution métallogénique de nombreux gisements. L'intrusion porphyrique et la minéralisation hypogène sont tributaires de failles, auxquelles s'est ensuite ajouté un enrichissement supergène sous climat semi-aride. Après l'enfouissement au Miocène par des graviers, le climat est devenu hyperaride; selon les estimations le climat serait devenu hyperaride entre le Miocène moyen (11-14 Ma) et le Pliocène (~3-5 Ma). Depuis, l'assèchement des eaux salines du socle le long de failles persistantes a entraîné une conversion de l'assemblage original d'oxydes de cuivre supergène - lequel s'était formé en état d'équilibre en milieu d'eau météorique et qui était dépourvu d'atacamite - en un assemblage contenant de l'atacamite [$Cu_2Cl(OH)_3$], ce minéral de cuivre typique du Chili du nord. Cette interprétation est corroboré par des études montrant que la salinité des inclusions fluides dans l'atacamite est semblable à celle de l'eau souterraine locale et que l'atacamite est significativement plus jeune que l'altération supergène coexistante.

INTRODUCTION

Most near-surface base- and precious-metal mineralization has likely already been discovered. Continued exploration for metal resources requires

extending the search for undiscovered mineralization into the third dimension, especially in areas of thick cover (Cameron et al. 2004). Geochemical exploration for base- and precious-metal mineralization has become increasingly focused on the use of relatively weak leaches of soils, sediments, or till that overly mineralization. The use of these weak leach methods is predicated on the observation that high signal/noise geochemical anomalies develop over mineralization that may be buried by as much as 200 m of overburden (Hall et al. 1996; Cameron et al. 2004). In many cases, however, the utility of geochemistry in exploring for deeply buried mineralization is hampered by a lack of understanding of the processes by which ore-associated species migrate through overburden on meaningful timescales. Many mechanisms have been postulated to account for surface geochemical anomalies, including upward diffusion, advection, electrochemical cells, vapour-transport, barometric pumping, and seismic pumping (Hamilton 1999; Cameron et al. 2004).

To better understand the processes of metal migration, and therefore to better interpret the results of large-scale soil geochemical surveys, the Canadian Mining Industry Research Organization (CAMIRO), with the support of 26 companies and commercial laboratories, sponsored a six-month scoping study (Deep-Penetrating Geochemistry (DPG), Phase I) in 1997. The Deep Penetrating Geochemistry Phase I comprised: i) theoretical considerations for the movement of elements from depth to surface, ii) a review of relevant analytical methods, with emphasis on partial leaches, and iii) a presentation of case studies contributed by the company sponsors, including surveys over buried mineralization in Ontario, Manitoba, Northwest Territories, Alaska, Wisconsin, Nevada, Arizona, Chile, Peru, Queensland, and Spain (Cameron 1998). Deep Penetrating Geochemistry Phase II (28 company sponsors) was initiated in 1999, and focused on field and laboratory studies in a variety of geological and climatic terranes in Ontario, Nevada, and northern Chile. The Ontario study (additional support from the Ontario Geological Survey)
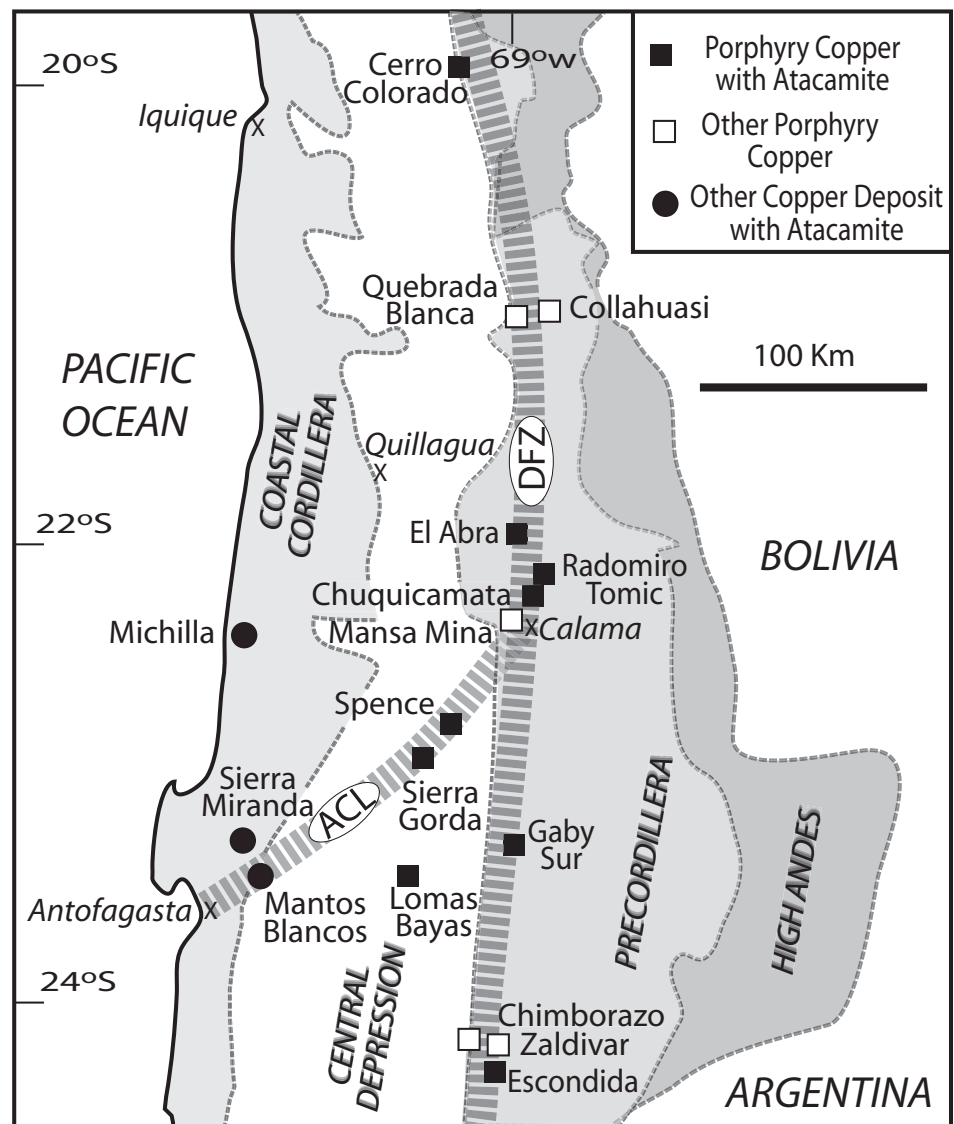
Figure 1. Major physiographic divisions and distribution of copper deposits in northern Chile, including those containing atacamite in the oxide zone. DFZ is the Domeyko Fault Zone and ACL is the Antofagasta–Calama Lineament. The land between the High Andes and the coast is the hyper-arid central Atacama Desert.

made substantial advances in developing methods for detecting mineralization under thick clay cover and understanding the processes that created these anomalies (Hamilton et al. 2004a, b). Work on the Mike deposit, Nevada, was described by Cameron et al. (2005). Studies in northern Chile looked at a number of porphyry copper deposits, and emphasised the Spence deposit.

The purpose of this paper is to provide an overview of the DPG Phase II research in northern Chile and subsequent investigations that grew out of that research. Deep Penetrating Geochemistry Phase I suggest-

ed that in a hyper-arid, tectonically active terrane such as northern Chile, movement of water by seismic activity should be a viable mechanism for the production of surficial geochemical anomalies (Cameron 1998). The northern Chile DPG Phase II research was designed to: i) collect soil samples over several areas of known mineralization and subject these samples to a variety of weak leaches, ii) collect groundwater samples, where possible, to determine the genetic link, if any, between soil geochemical anomalies and groundwater chemistry, and iii) use these data to interpret the process(es) of porphyry copper-associated metal migration, and

more specifically to determine if seismic pumping was a viable mechanism for metal transfer. The DPG Phase II research indicated that, not only was seismic pumping a viable mechanism, but that it might also provide an alternative explanation for the formation of atacamite [$Cu_2Cl(OH)_3$], the most characteristic supergene oxide mineral of northern Chile. Therefore, further work was initiated to better constrain the origin and timing of formation of atacamite.

GEOLOGICAL AND HYDROLOGICAL BACKGROUND

The study area in northern Chile encompasses a large part of the Atacama Desert, the driest major desert on the planet (Fig. 1). Hyperaridity is pervasive throughout the Coastal Cordillera and Central Depression, changing to less arid conditions with increasing altitude and rainfall in the Precordillera. Rainfall minima occur near the boundary between the Central Depression and the Coastal Cordillera; at Quillagua (Fig. 1), the annual average rainfall is 0.5 mm. The Coastal Cordillera is a Carboniferous–Early Triassic magmatic arc that contains numerous copper deposits, of which the largest is the Early Cretaceous Mantos Blancos deposit (Ramirez et al. 2006; Oliveros et al. 2008). The basement of the Central Depression contains Jurassic and Cretaceous sedimentary–volcanic sequences, the former comprising rocks of both marine and non-marine origin, and including evaporites. From the late Oligocene through the middle Miocene, a large volume of sediment sourced from the Precordillera was deposited in the Central Depression, obscuring much of the basement; most prominent of these Tertiary sediments are early to middle Miocene piedmont gravels. The Precordillera consists of Triassic to Eocene fault-bounded blocks.

A Paleocene–early Eocene belt of porphyry copper deposits, including the Spence deposit, is situated within the Central Depression, and a late Eocene–early Oligocene belt is hosted by rocks of the Precordillera. These deposits are structurally controlled. In the Precordillera they occur along the Domeyko Fault Zone (DFZ), whereas the Spence deposit is spatially associat-

Figure 2. Photograph of the ground surface directly above the Spence deposit, looking west. A gypcrete crust of non-pedogenic origin is near-ubiquitous in this area but has been removed by an unusual period of sheetflood erosion, revealing the bare piedmont gravel surface.

ed with the Antofagasta–Calama Lineament (ACL, Palacios et al. 2007; Fig. 1). During the structural and geomorphological evolution of the Precordillera, some deposits have been exhumed and exposed at the surface. Copper was extracted from Chuquicamata in pre-Inca times, and El Abra lies near the summit of a mountain. Conversely, some systems, such as Radomiro Tomic, Spence and Gaby Sur, are in structural depressions covered by thick gravels. Most exploration is now focused on methods of detecting deposits lying under this gravel cover.

Northern Chile

Since the early 1990s, most geochemical exploration programs in the Atacama Desert have employed selective leach analytical methods, designed to extract mobile element components that have migrated from deposits in solution. Proprietary selective leaches, such as Enzyme Leach[SM] and MMI[TM]-A (Mobile Metal Ion, suite A (base metals)) have been used extensively in covered terrains. The Enzyme Leach[SM] method dissolves water-soluble salts plus loosely adsorbed metals, and allows determination of up to 50 elements by ICP-MS. The MMI[TM]-A method measures four base metals, Cu,

Zn, Cd and Pb, producing higher concentrations than Enzyme Leach[SM] because it uses an acidic extraction method to dissolve minerals, including carbonates.

Examination of data, acquired from soils overlying thick piedmont gravels above known deposits, provided the opportunity to evaluate the geochemical processes occurring within, and below, cover sequences. These data included soils collected at 200-m intervals over the Spence deposit, soon after its discovery by Rio Algom in 1997. The Spence deposit, covered by 50 to 100 m of gravel, was discovered by systematic grid drilling along favourable structural trends. The surface at Spence lacks the non-pedogenic gypcrete crust that is widespread throughout the Atacama Desert because it had been removed by sporadic sheet flood erosion. A lapilli tuff layer in gypcrete near Mantos Blancos was dated by the K–Ar (biotite) method at 2.97 ± 0.07 and 2.87 ± 0.03 Ma (Chavez 1985). If this timing is relevant to the Spence deposit, it provides a maximum age for the former erosional surface.

Initially, the coarse surface material (Fig. 2) provided little encouragement that geochemical studies would prove useful. Neither Enzyme
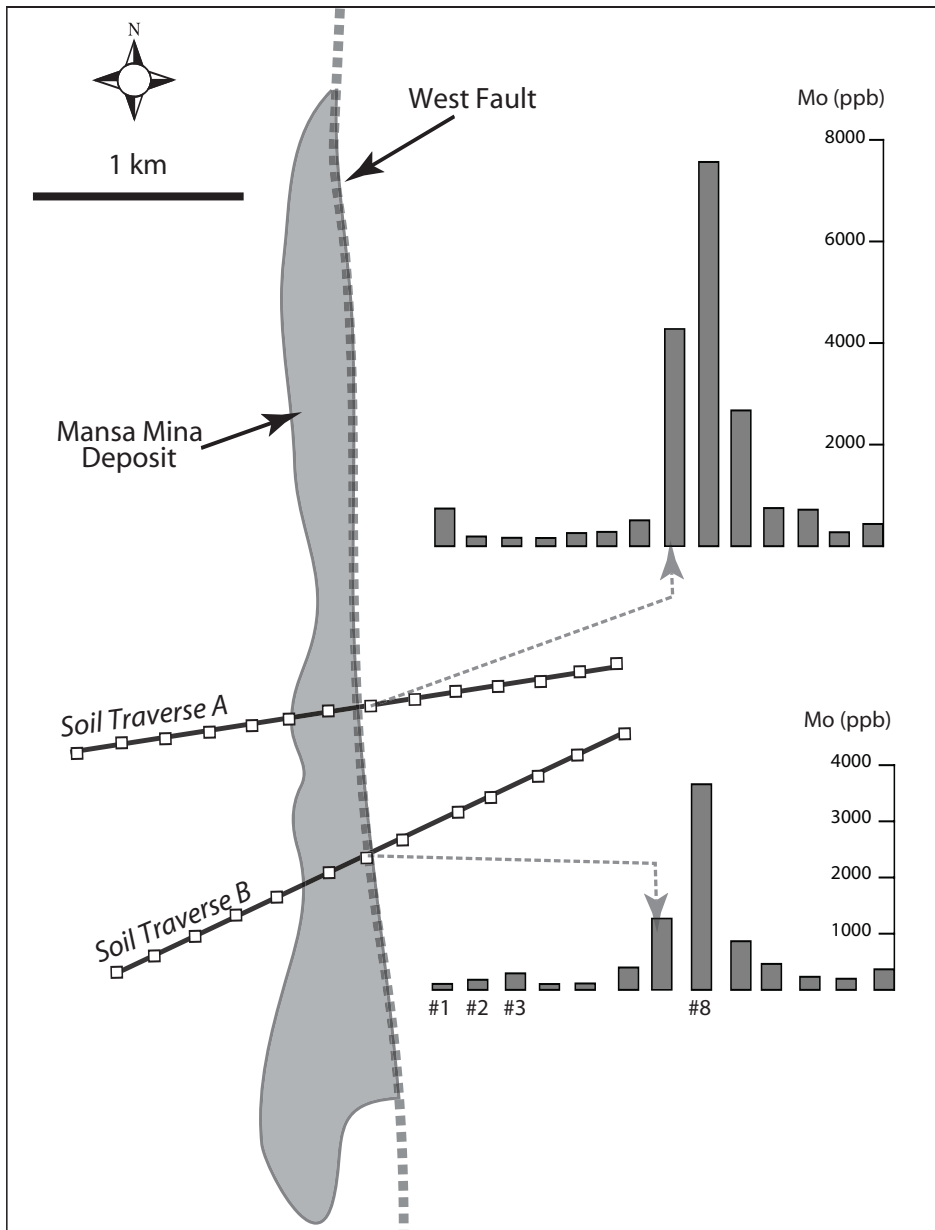
Figure 3. Data for Mo analyzed by Enzyme Leach[SM], from soil samples on two traverses across the Mansa Mina deposit, 4 km south of Chuquicamata, Chile. Data provided courtesy of Noranda Ltd. About 50 m of gravel overlies the deposit west of the West Fault, whereas up to several hundred metres of gravel cover lies east of the fault. On line B, data for sample #8 have been compared to the average of data from samples #1 to #3 (see text for details).

Leach[SM] nor MMI[TM]-A analyses from the 1997 soil survey revealed significant anomalies for Cu. Nevertheless, there were scattered Enzyme Leach[SM] anomalies for a suite of elements, principally Cl, I, Br and Mo. The presence of the three halogens suggested that saline groundwater had reached the surface.

Enzyme Leach[SM] data for soils above other deposits show anomalies for the same elements. These include surveys over the Fortuna de Cobre porphyry prospect adjacent to Lomas Bayas, and over the Radomiro Tomic deposit. Two soil geochemical traverses by Noranda over the Mansa Mina deposit provided the best clue to the origins of the Enzyme Leach[SM] anomalies. Mansa Mina (Sillitoe et al. 1996) is a faulted slice of porphyry mineralization, possibly from nearby Chuquicamata. The principal fault of the DFZ, the West Fault, forms its

eastern boundary (Fig. 3). About 50 m of gravel overlie the deposit west of the fault, and gravel thickness increases to several hundred metres east of the fault. Samples from above, and immediately east of the fault, are strongly anomalous in several elements, including Mo (Fig. 3). Enrichment factors were determined for the most anomalous sample on Line B (Fig. 3) compared to average values of the most distal samples to the west; elements showing the highest ratios are Cl (64); Mo (19); Se (13); I (12); Br (9); and Cu (6). The location of the anomalies suggests that they are related to the fault.

EARTHQUAKE-INDUCED FORCING OF SALINE GROUNDWATER TO THE SURFACE

A scoping study by Cameron (1998) suggested a number of possible processes to explain the Cl, I, Br, and Mo soil geochemical anomalies. Vapour transport is not an option, because the principal constituent of the anomalies, NaCl, is non-volatile. Capillary transport of groundwater was also rejected as a significant mechanism for metal transport at the Spence deposit. Maximum depths for capillary rise are 0.15 m for coarse sand, 0.3 m for medium sand, 1 m for fine sand, and 1 to 10 m for silt (Jumikis 1967), whereas the depth to the water table at the Spence deposit is between 43 and 88 m. The most likely mechanism was identified as forcing of basement waters to the surface during earthquakes (Cameron et al. 2002). In interseismic periods, extension in basement rocks can cause cracks to open, drawing in water. During an earthquake, cracks close under compression, expelling water, which migrates to the faults and then to the surface (Muir-Wood 1994). Because of limited permeability in basement rocks, migration towards faults is slow; thus, unusual flows of waters in springs, streams and rivers persist for weeks or months after an earthquake. For example, in the desert areas of Iran, after earthquakes, surface soils have become waterlogged along fault lines (Tchalenko 1973; Tchalenko and Berberian 1974). Northern Chile is a region of high seismicity and, although the Atacama Desert does occasionally receive some
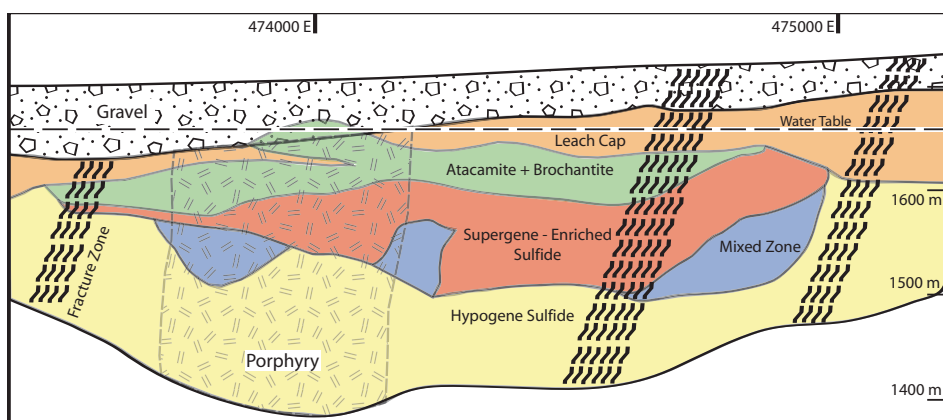
Figure 4. West–east section through the southern part of the Spence deposit at 7479000 N. Eastings are in metres. Porphyry is intruded into andesitic country rock both in the form of a large mass, as shown, and as dykes in the central of the three fracture zones (wavy broken lines). Modified from a section prepared by Rio Algom in 1999.
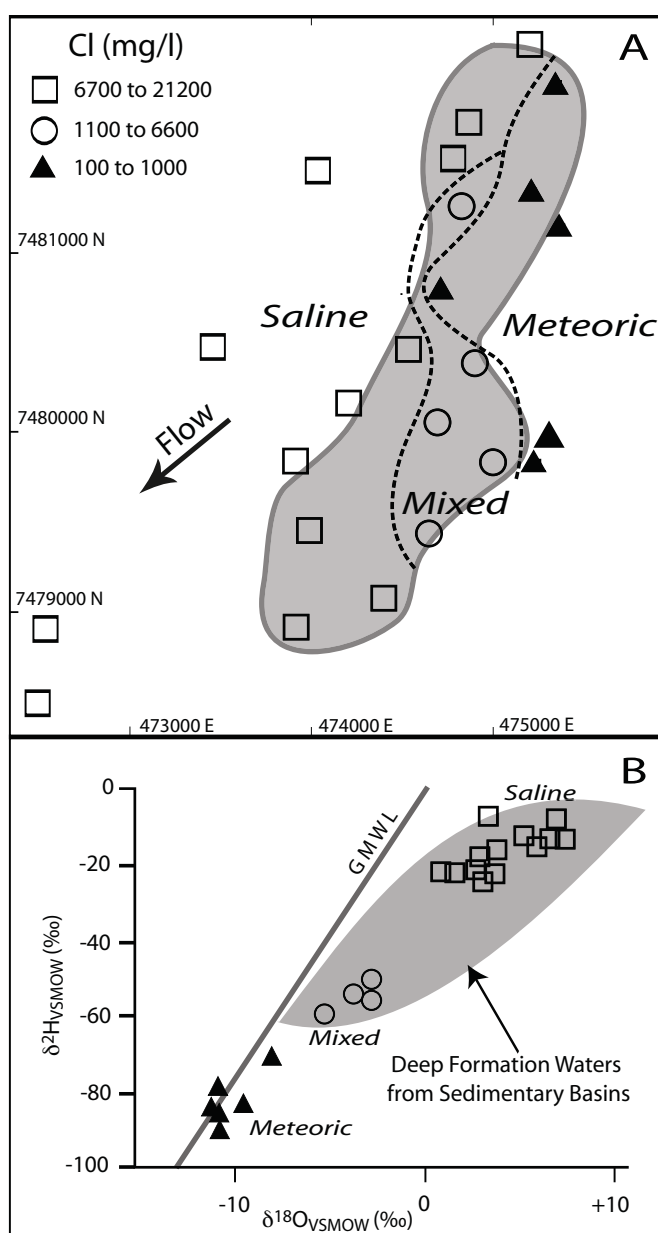

rainfall, which can redistribute elements at the surface, the rate of erosion is mostly too low to disperse anomalies derived from seismic-related flooding once they have formed.

The Spence deposit was chosen to test the seismic pumping hypothesis. Porphyry intrusion and hypogene mineralization in andesite host rocks occurred along a north-northeast axis during the Paleocene. Dating of alunite shows that supergene alteration extended over a long period from 44 to at least 21 Ma (Rowland and Clark 2001). Copper minerals are atacamite and brochantite in the oxide zone; chalcocite, covellite, and pyrite in the enriched zone; and chalcopyrite, bornite, molybdenite, tennantite, and pyrite in the hypogene zone. Spence has reserves of 313 Mt grading 1.08% Cu and mining commenced in 2006. The topography of the deposit area controlled the variable thickness (50 to 100 m) of the gravel cover and the location of the water table, which is within the basal gravels to the north and within the oxide zone to the south (Fig. 4). The gravels are indurated and have a fine-grained matrix that renders them impermeable, except where fractured or where layers of better-sorted material occur near their base. South of the hypogene deposit, exotic copper oxide minerals are present in the basal gravels (Fig. 4), indicating that weathering-related lateral copper mobility con-

Figure 5. (*adjacent*) A) Distribution of groundwaters of different origin and salinity in and around the Spence deposit (shaded area). 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. B) Plot of δ^2H_{VSMOW} vs $\delta^{18}O_{VSMOW}$ for groundwaters at the Spence deposit relative to the Global Meteoric Water Line (GMWL). VSMOW – Vienna Standard Mean Ocean Water, a reference standard for comparing hydrogen and oxygen isotope ratios. Shaded area is the field for deep formation waters (after Taylor 1974).
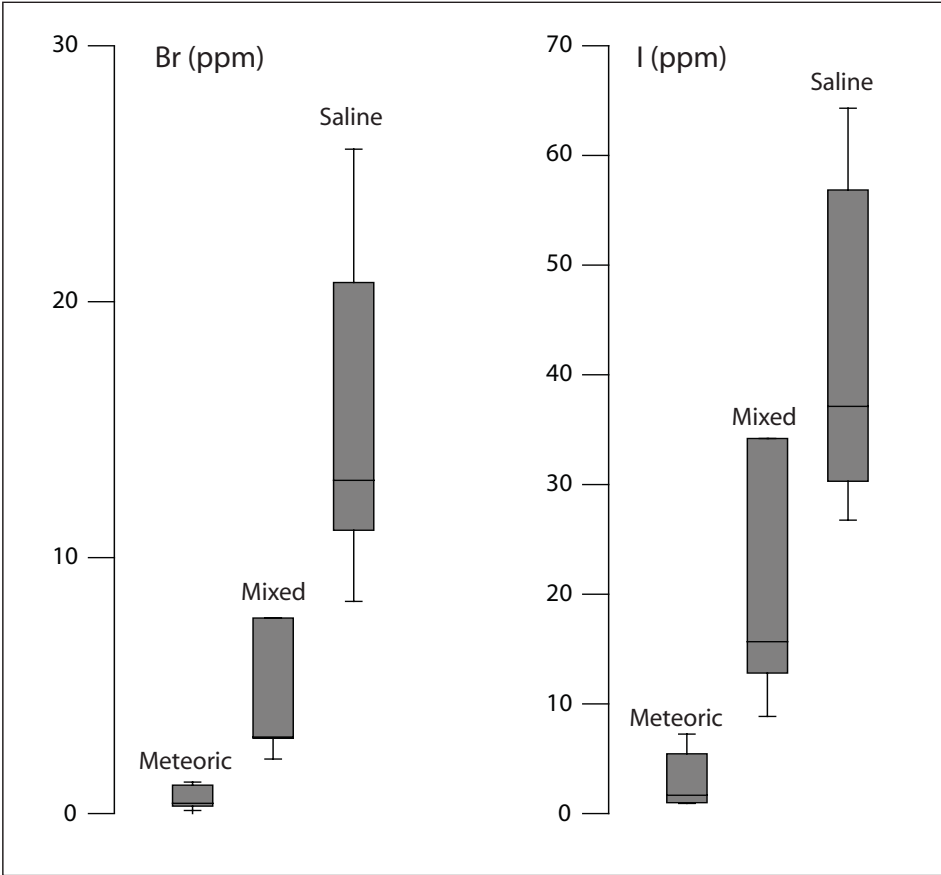
Figure 6. Box and whisker plots for Br and I in Spence deposit groundwaters. For locations and classification of saline, meteoric and mixed waters, see Figure 5A.
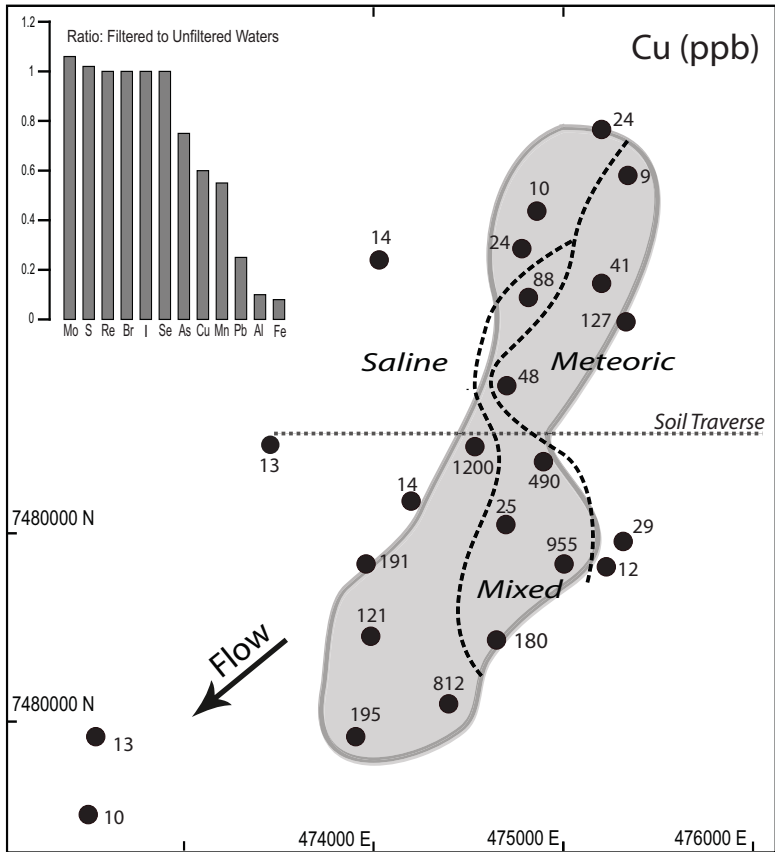
tinued after supergene oxidation and gravel deposition.

Groundwater, which was clear and contained no visible suspended phase, was sampled from drill holes in 1999 and 2000. Details of sampling, sample preparation, and analytical methods are given by Leybourne and Cameron (2006a). Fresh water flows into the deposit from the northeast and mixes with saline water found within and down-flow of the deposit (Fig. 5A). Data for δ^2H and $\delta^{18}O$ (Fig. 5B) help identify the source of the meteoric and saline waters. The more dilute meteoric waters plot close to the Global Meteoric Water Line (GMWL; Fig. 5B). Comparison of our Spence groundwater data with $\delta^{18}O$ data for precipitation in the Andes (Aravena et al. 1999), suggests that the meteoric waters come from elevations of 3500 m or greater in the Precordillera or the Andes (Cameron and Leybourne 2005); regional migration of high Andes recharge has been demonstrated elsewhere in the Atacama Desert using ^{14}C dating of groundwater (Magaritz et al. 1990). The saline waters within and down-flow of the Spence deposit are interpreted to be formation (basinal brine) water flowing up from basement, presumably along fracture zones identified during drilling. Inflow of formation waters into the Spence deposit exceeds that of meteoric water, because saline water is dominant down-flow of the deposit.

Many elements have substantially higher concentrations in Spence saline waters than in the meteoric waters (Leybourne and Cameron 2006a, 2008). Among those that show the greatest differences are Br, I (Fig. 6), Re, and Se. Bromine and iodine were earlier identified as major constituents of the anomalies developed in gravels above some copper porphyry deposits in northern Chile. The pres-

Figure 7. (*adjacent*) Plot of Cu (ppb) in Spence deposit groundwaters filtered through 0.45 μm filters in the field. Inset shows the average ratios of filtered vs. unfiltered concentrations for selected elements.

ence of these halogens is interpreted as evidence for generation of the anomalies by formation waters of deep, basement origin that have been pumped to the surface along faults or fracture zones.

At the Spence deposit, copper is enriched in all groundwater types, but is generally restricted to the deposit area (Fig. 7). Copper is not dispersed away from the deposit, because it is readily adsorbed to Fe-, Mn- and Al-oxy-hydroxides, and may form secondary Cu minerals (Cameron and Leybourne 2005; Leybourne and Cameron 2008). A histogram of element ratios in filtered (< 0.45 μm) vs. unfiltered water (Fig. 7) shows much higher concentrations of Al and Fe in the unfiltered samples, because these elements are present as colloidal Fe and Al oxy-hydroxides. These oxy-hydroxides have a negative charge, which adsorbs cations such as Cu^{2+}, and readily precipitate as coatings, fixing the Cu. In contrast, elements having filtered to unfiltered ratios near unity are not present in particulate form. These elements, Mo, S, Re, Br, I, and Se, dissolve in the weakly acidic to mildly alkaline groundwater as anions, which are not adsorbed by negatively charged oxy-hydroxides. Accordingly, Mo and other anions are dispersed in groundwater away from the deposit. Molybdenum is a ubiquitous minor constituent of copper porphyry mineralization. Because of its relatively high mobility under moderately oxidizing conditions (Stollenwerk 1995; Hodge et al. 1996), it is widespread in the groundwater of this region. For example, Mo has dispersed 65 km westward of the El Abra deposit to create intense Mo anomalies in soils within the Central Depression (Leybourne and Cameron 2006b).

Soil samples were collected on an east–west traverse across the Spence deposit (Fig. 7). Molybdenum and Br anomalies identify two locations where saline water of deep origin has reached the surface (Fig. 8), one directly over the deposit (Deposit Fracture Zone), and the other 1 km to the east (Eastern Fracture Zone). Trenching at these two locations showed the indurated gravels to be cut by vertical fractures, whereas a background location to the west of the deposit lacked fractures (Cameron et al. 2004); these fracture zones result
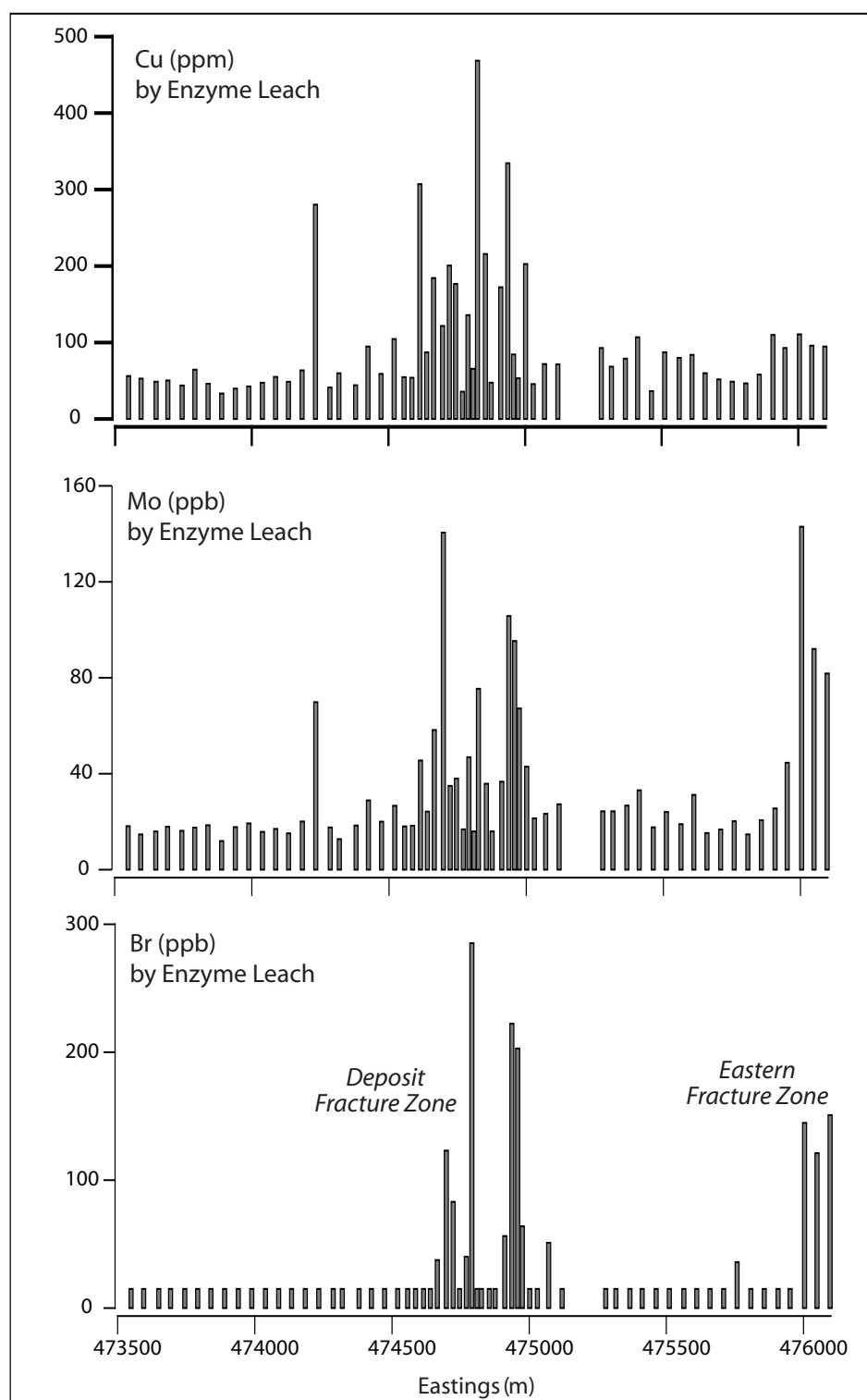

Figure 8. Plots of Cu, Mo and Br, all by Enzyme Leach[SM] analysis, in a west–east soil traverse across the centre of the Spence deposit at 7480500 N. Soils were collected at depths of 10-20 cm.

from reactivation of basement faults. As saline waters were pumped to the surface during earthquakes, they carried dissolved and adsorbed Cu to the surface above the deposit, but this did not happen at the Eastern Fracture

Zone, where drilling has shown the basement rocks to be barren. Molybdenum is anomalous above both fracture zones (Fig. 8). Given the mobility of Mo, this suggests that Mo-bearing mineralization is present up-gradient from
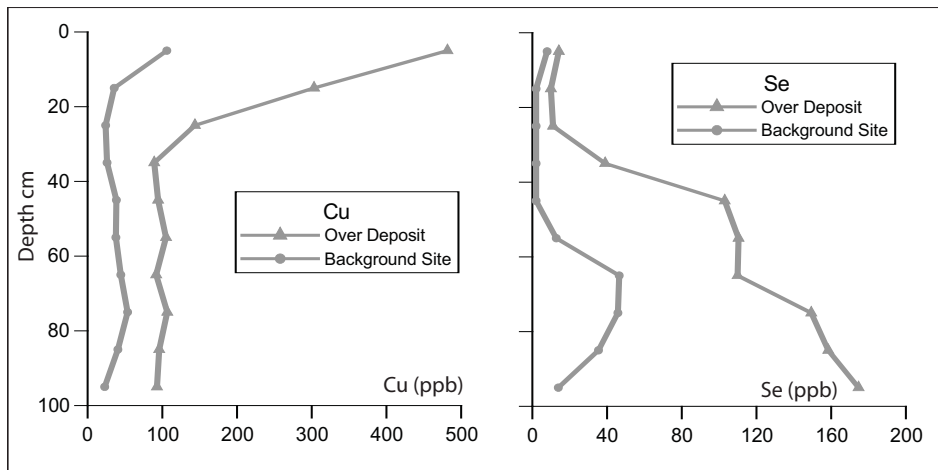
Figure 9. Plot of Cu and Se in soil profiles directly over the Spence deposit and at a background site west of the deposit. All analyses were performed by Enzyme Leach[SM].

these locations. Molybdenum and other mobile porphyry indicator elements thus provide a method of exploration using groundwater. This is possible because supergene-enriched porphyry deposits lie along the basement unconformity, above which the basal gravels, as at Spence, commonly represent an aquifer that can readily be sampled during mineral exploration.

After reaching the surface, elements transported by mineralized groundwater are redistributed by the occasional rains and subsequent surface flow. Mimicking their behaviour in groundwater, elements dissolving as anions, such as Se, are moved to depth (Fig. 9), whereas cations, including Cu, are retained near the surface by adsorption on oxide coatings. By normal soil processes, Cu is then incorporated into different minerals, notably carbonate (Cameron et al. 2004). Part of the objective of the CAMIRO program was to compare the effectiveness of different selective leaches by measuring the anomaly-to-background contrast for each leach. In Chile, at the Spence, Gaby Sur and Mansa Mina deposits, all soil samples were analyzed using up to five selective leaches plus an aqua regia leach. Whereas the Enzyme Leach[SM] (equivalent to a water-soluble metals leach) yields large anomalies over Spence, leaches that dissolve

Figure 10. View of the Radomiro Tomic deposit pit, in February 1999, showing the upper part of the oxide zone covered by a variable thickness of piedmont gravels. Green colour is atacamite.

the carbonate minerals, such as ammonium acetate and MMI™-A, provide greater anomaly contrast (Cameron et al. 2004). The profile for Cu (Fig. 9) reveals why samples collected in 1997 were not anomalous for Cu over Spence: they were sampled at a depth of ca. 40 cm, whereas sampling depth in 1999 was 10 to 20 cm.

FORMATION OF ATACAMITE
Supergene enrichment of porphyry copper deposits in the Atacama Desert occurred before the climate became hyper-arid. Supergene enrichment by meteoric waters therefore occurred over an extended period, starting around 44 Ma. Estimates of termination of supergene processes vary from mid Miocene (11–14 Ma; Alpers and Brimhall 1989; Sillitoe and McKee 1996; Mote et al. 2001) to as recently as the early Pliocene (3–5 Ma; Hartley and Rice 2005; Arancibia et al. 2006). It has been assumed that supergene oxide assemblages that formed prior to the onset of hyperaridity have been preserved since that time. However, a corollary of our hypothesis of seismic pumping of groundwater to surface through mineralized rock is that water-deposit interaction, and resultant supergene and exotic mineralization processes, may not have ceased.

Passage of saline formation waters through an oxide zone, as at Spence, would have caused these assemblages to change. Cupric hydroxy assemblages re-equilibrate rapidly within days or weeks when solution compositions change (Woods and Garrels 1986). Northern Chile is unique in having atacamite [$Cu_2Cl(OH)_3$], which requires Cl-rich saline water for its formation, as a component of the oxide zone of many porphyry copper and other copper deposit types (Fig. 1). Aside from northern Chile, its most characteristic occurrence is on the sea floor, where it forms as a product of weathering of copper sulfides (Hannington 1993). Elsewhere, because it is rapidly dissolved or replaced by other copper minerals when it is exposed to meteoric water, atacamite is rare. MacFarlane et al. (2005) passed a slow flow of water through powdered atacamite-bearing ore and found that all Cl and most of the Cu was removed in less than an hour.

A photograph of the open pit at Radomiro Tomic (Fig. 10), taken in 1999 when the upper part of the oxide zone was being mined, shows the characteristic emerald green of atacamite, the most abundant copper mineral of the oxide zone (Cuadra and Rojas 2001). The deposit forms a basement hill covered by piedmont gravels, which vary in thickness from 30 m to 150 m. A tuff near the top of the gravels was dated at 9.7 ± 0.7 Ma by K–Ar (biotite) (Cuadra et al. 1997). When the photograph (Fig. 10) was taken, the water table was near the base of the pit. Below this, meteoric water flows across the deposit, 'floating' on deeper, denser, saline water (Cameron et al. 2007). In a zone 50 m below the water table, atacamite has been removed, and replaced by other copper minerals (Cuadra and Rojas 2001).

Atacamite has been considered to be a primary product of supergene oxidation, both generally in the region (Chavez 2000), and specifically for this deposit (Arcuri and Brimhall 2003). However, during the long period of supergene oxidation, at least episodic rainfall must have fallen; Clark et al. (1990) suggest >10 cm/year, compared to the present <10 mm/year. Under these conditions, any atacamite that may have periodically formed would have been removed by percolating meteoric water during episodes of rainfall. Hence, in contrast to a primary supergene origin for the atacamite, Cameron et al. (2007) proposed that supergene copper oxide minerals were later replaced by atacamite following the onset of hyper-arid climatic conditions. Equilibrium diagrams show that atacamite is stable in saline waters at Spence (Leybourne and Cameron 2008), and an antipathetic relationship between SO_4 and Cl in these waters suggest that brochantite is currently being replaced by atacamite (Cameron et al. 2007). At Radomiro Tomic and Spence, atacamite has been deposited in the basal gravels. In addition, there are Cl–Br–I anomalies in soils above both deposits, indicating that saline waters have reached the surface. Hyperaridity is required for the formation and preservation of supergene atacamite; it is preserved above the water table at Radomiro Tomic because there is no recharge through

the vadose zone. At Spence, when a wetter climate prevailed, there would have been a greater inflow of meteoric waters through the oxide zone. When these wet conditions ended and a hyper-arid climate began is much debated. It was previously thought to have followed the main period of supergene enrichment that ended at 14 Ma, but recent dating of post-14 Ma supergene events, along with other evidence (Hartley and Rice 2005; Arancibia et al. 2006), suggest that hyperaridity started at around 4 Ma. In the case of the Radomiro Tomic deposit, the onset of hyperaridity must have been later than the 9.7 Ma date for the gravels.

Reich et al. (2008), using samples from Spence and Mantos Blancos, demonstrated that the salinity of fluid inclusions in atacamite overlaps that of the local groundwater (Fig. 11), which is what one would expect if atacamite forms through the interaction of saline groundwater and pre-existing copper oxides. This comparison is given greater significance by the substantially different groundwater salinity at the two locations. At Spence, the saline waters are flowing through the oxide zone, whereas at Mantos Blancos they are at much greater (400 m) depth. This implies that saline waters could only have contacted the pre-existing oxide minerals by being episodically forced to the surface, i.e. by seismic activity.

Palacios et al. (2005) showed that Cu-bearing saline waters have reached the surface around Mantos Blancos, where rocks are well exposed, not covered by gravels. 'Spike' Cu anomalies up to 1200 ppm, and correlated anomalies for Na on hills and slopes 250 to 300 m above known mineralization, contrast with background concentrations over barren rocks and correspond to the surface projection of known faults that intersect mineralization at depth. Palacios et al. (2005) also report salt efflorescences at the surface along major faults; in places, these efflorescences have a green colouration that was shown (by X-ray diffraction) to be related to the presence of atacamite and chalcantite. The distribution of these copper minerals locally extends several hundreds of metres, depending on the importance of the faults and the size of the
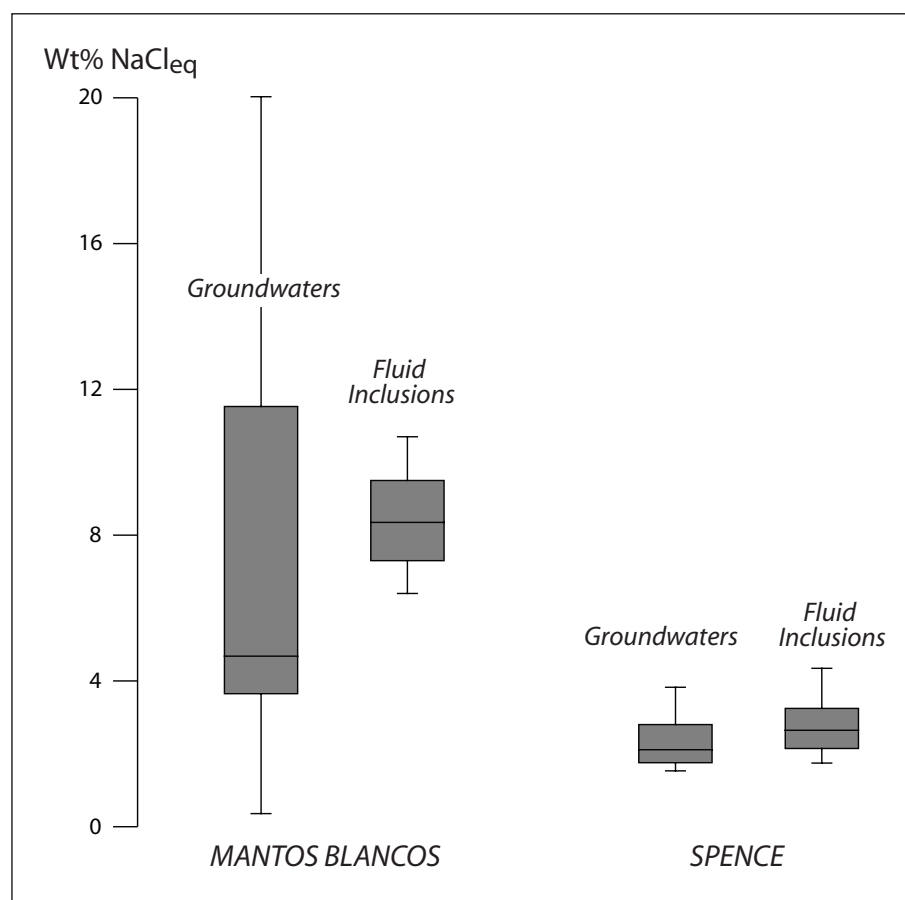
Figure 11. Box and whisker plots comparing the salinity of fluid inclusions in atacamite with that of local groundwater in the vicinity of the Mantos Blancos and Spence deposits. The salinity of fluid inclusions at Spence (n = 43), fluid inclusions at Mantos Blancos (n = 48) and groundwaters from Mantos Blancos (n = 32) are from Reich et al (2008). The salinity of groundwaters at Spence are for the saline waters (n = 13) shown in Figure 5A.

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.

If atacamite forms by seismic pumping of saline groundwater to surface, the implication is that this mineral may be young, potentially much younger than other supergene copper minerals in the oxide zones of copper deposits in the Atacama Desert. It is therefore significant that new U–Th disequilibrium data for gypsum-atacamite intergrowths from several deposits in northern Chile indicate formation ages of ~ 240 ka to as young as ~ 80 ka (Reich et al. 2009).

CONCLUSIONS

Although use of weak partial leaches of soils is common in mineral explo-ration, a lack of understanding of the processes by which surface anomalies form from deeply buried mineralization has hampered effective utilization of exploration geochemical data. This study around the copper deposits in northern Chile, over the last ten years, has shown that groundwater sampled in, and around, the Spence porphyry copper deposit has a geochemical signature similar to soil geochemical anomalies overlying mineralization at the deposit. The trace metal, metalloid, and isotopic geochemistry of the groundwater clearly demonstrates water-deposit interaction. The genetic link between the soil anomalies and groundwater supports the hypothesis that surface geochemical anomalies are generated by movement of water to surface during seismic events. The hyper-arid climate of northern Chile is conducive to preservation of these geochemical anomalies directly over mineralization. Groundwater at the Spence deposit is saline within and down-flow of the deposit, and is geochemically and isotopically similar to formation waters recovered from sedimentary basins elsewhere. This finding led to the hypothesis that one of the main supergene copper minerals, atacamite, may not be the product of Miocene to Pliocene supergene enrichment processes, but could be better explained as a later replacement of earlier supergene copper minerals. The saline groundwater at the Spence and Mantos Blancos deposits is at or near saturation with respect to atacamite. An origin for atacamite that links it to seismically pumped saline groundwater is consistent with our fluid inclusion studies of atacamite from several deposits in northern Chile, and with U–Th disequilibrium age dating of gypsum intergrown with fracture-zone atacamite. These studies have important implications for geochemical exploration, supergene mineralization models, and interpretations of climate change in northern Chile.

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