Geochemical signature of earthquake-induced surface flooding by mineralized groundwater over the buried Atlántida deposit, northern Chile

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Abstract: At the buried Atlántida deposit (Cu–Au–(Mo)) in the Atacama Desert of Chile, highly saline pockets of fine-grained material 10 cm–3 m in diameter were identified on the alluvial surface using remote sensing and detailed regolith mapping. The median salinity (NaCl dominant) of the saline pockets is 2.2% compared to background alluvial material with a median salinity of 0.01%. Their distribution along mapped fault structures and the highly saline nature of the material suggest they form as an expression of groundwater forced through fractures to the surface during seismic activity. A targeted geochemical survey, oriented parallel to the orientation of the structures (sample spacing 250 m along structural trend) specifically sampling saline pockets on relatively old surfaces, was performed over the deposit. Deionized water extraction of soluble salts and analysis by inductively coupled plasma mass spectrometry revealed strong correlations of increasing salinity and increasing concentrations of porphyry copper pathfinder elements. Elevated responses of Se, Mo, Re and Te normalized to a groundwater volume proxy are present directly over the Atlántida deposit. This suggests the rate of erosion and sedimentation is slow enough in the Atacama Desert to preserve surficial anomalies as saline pockets, formed by periodic seismically induced surface flooding of groundwater along faults extending to surface. Targeted sampling of saline pockets along structural trends using weak leach geochemistry in terrains dominated by transported cover can serve as a routine exploration method for the potential discovery of buried copper porphyries and other styles of mineralization in the Atacama Desert of Chile.

Keywords: exploration; buried deposits; geochemistry; geomorphology; selective leaches; earthquake-induced surface flooding; seismic pumping; saline pockets; Chile

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Porphyry copper deposits are significant contributors of Cu, Au and Mo to the global economy, yet discoveries of large, economically viable deposits in the last 20 years have declined (Kelley et al. 2010). Development of new strategies and practical methodologies to detect and target porphyry copper deposits buried under transported cover is key to future discoveries. The Atacama Desert of Chile hosts some of the largest porphyry copper deposit clusters in the world such as Chuquicamata, Escondida and Collahuasi. However, discovery of new deposits has been hindered by the thick sequence of Neogene and Quaternary gravels which extend through overlying gravels to the surface. Such fault structures are identified using remote sensing revealed distinct geomorphic features on the alluvial surface produced by active structures (Brown et al. 2019). Geochemical anomalies formed by these processes therefore only occur where deep bedrock faults extend through overlying gravels. 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a result of post-gravel deposition fault movement. Saline pockets are interpreted as representing the expression of the effusion of groundwater at the surface by seismic pumping (Brown et al. 2019) (Fig. 3). This study reports results from a geochemical survey at the Atlántida deposit where sample lines were oriented along the trend of fault structures across the project area and targeted saline pockets as the sampling material.

Fig. 1. Map of northern Chile showing large areas of the country covered by gravels. Outcrop in grey and alluvial/colluvial cover in white. The red circle indicates study area: 1, Atlántida. The black circles indicate additional sites where saline pockets have been identified: 2, Papas; 3, Mastodonte; 4, Viento. Black stars represent several of the major porphyry copper clusters: 1, Collahuasi; 2, Chuquicamata; 3, Spence; 4, Gaby Sur; 5, Escondida.

Geology of the Atlántida deposit, Atacama Region, Chile

District geology

Atlántida is a porphyry-skarn Cu–Au–(Mo) deposit located 55 km NNE of Copiapó, Region III (Atacama Region), Chile (Fig. 2). The property (c. 12 km²), previously explored by First Quantum Minerals Ltd, is currently owned by Minera Atlántida. Atlántida is located between the Atacama and Domeyko fault systems within the southern extent of the Central Depression of northern Chile (Bissig & Riquelme 2010). The porphyry is part of the Late Cretaceous porphyry copper belt (Maksaev et al. 2010), including the Inca de Oro mine located 25 km NNE of the Atlántida deposit (Fig. 2). The district geology in the Atlántida region is summarized as comprising dominantly of Cretaceous carbonaceous limestone sequences, and Jurassic to Paleocene volcanic and volcanosedimentary packages younging to the east (Matthews et al. 2006). Miocene to Quaternary gravels fill valleys between outcrops.

Deposit geology

Transported alluvial gravels (25–80 m thick) cover the entire porphyry Cu–Au mineralized zone (Fig. 2). Gravels at Atlántida cover a thin, weakly developed discontinuous leach cap characterized by limonite and hematite; however, no supergene mineralization has accumulated as a result of these leaching processes and sulphides are not reported close to the bedrock–gravel interface (Hope & Andersson 2015; Pizarro 2016). Economic mineralization at Atlántida is reported as 100% hypogene and occurs 200 m below the gravel–bedrock contact extending to at least 600 m below the surface as determined by drilling. Mineralization occurs in association with disseminated and vein-hosted pyrite, with chalcopyrite as the main ore mineral, and minor molybdenite. Mineralization is reported with average grades of c. 0.2% Cu and 0.34 g t⁻¹ Au inclusive of the local skarn with a preliminary resource estimate of 427.1 Mt (Hope & Andersson 2015).

Two main intrusive phases are host to the bulk of mineralization and intrude into volcanic and limestone units. The earlier intrusive phase is tonalitic in composition and is interpreted as pre-mineralization (Hope & Andersson 2015; Pizarro 2016). This phase is intruded by a feldspar-rich granodiorite porphyry, causing brecciated contact zones and highly brecciated areas within the tonalite intrusion (Fig. 4; Hope & Andersson 2015; Pizarro 2016). Local skarn and carbonate replacement polymetallic veins are exposed in the limestone outcrops east and west of the buried porphyry.

Faults mapped in outcrops generally trend north–south, while cross-cutting faults, mainly oriented SW–NE and NNW, occur within the deposit area and control the emplacement of the porphyritic stocks. A SW–NE-trending fault, interpreted as a transfer fault, creates a large valley (Fig. 2) and cross-cuts the porphyry. These cross-cutting faults can be identified by remote sensing (Brown et al. 2019) and in aeromagnetic data (Fig. 4; Hope & Andersson 2015).

Alluvial cover

Gravel cover generally deepens from north to south with depths ranging from 25–80 m. The water table is variable across the property, generally located at 40–50 m below the surface. The alluvial surface consists of unconsolidated gravels of clastic material below a cobble surface with varying occurrences of hard or soft calcare, generally encountered at 20–40 cm depth. Gravel fragments on the current surface covering the deposit, dominated by andesite, are derived from outcrops located 1.5–3 km north and south of the deposit, respectively (Fig. 2). Gravel fragments dominated by skarn derived from the limestone outcrops east and
west of the deposit do not overlie the deposit. The alluvial surfaces lack the common gypcrete and soluble nitrate horizons more commonly found in the northern Atacama Desert.

Field methodology

High-resolution drone imagery (8 cm horizontal resolution) and a digital elevation model (1 m resolution) (Brown et al. 2019) were used for detailed regolith mapping and mapping of reactivated bedrock fault structures extending to, and altering, alluvial landforms on the surface. Field-based conductivity measurements on slurries aided in identifying the saline pockets.

Samples were collected on lines parallel to SW–NE and north–south structural trends (Fig. 2). Regolith maps combined with field assessment were used to ensure samples were taken on the oldest alluvial surfaces and maintained consistent background chemistry by following alluvial fans dominated by specific lithologies. Short sample lines with up to 4 samples spaced at 25–50 m were collected perpendicular to the structural trend. Sample lines were spaced 250 m apart. The peripheral samples along the lines were located up to 150 m away from the main fault zone (Fig. 2). To evaluate background responses, the two sample lines (SW–NE and north–south) were extended up to 2 km away from the area of buried mineralization (Fig. 2).

Saline pockets were specifically targeted for sampling. The upper 5 cm of the pockets were removed to avoid contamination by windblown dust. Samples were extracted from the top 5–30 cm of the material within the pockets, taking care not to sample the adjacent gravel, using nylon tools, and were sieved to <180 µm in the field. Measurements of electrical conductivity in slurries (1:1 deionized water to soil by volume) were performed in the field. Measurements of pH in slurries (1:1 deionized water to soil by volume) were subsequently performed at the University of British Columbia, Canada. Certified reference material along with field duplicates taken from 2 adjacent sample sites, were inserted every 20 samples.

Analytical methodology

Analytical methods utilized are summarized in Table 1. Samples were analysed at Bureau Veritas Ltd in Vancouver, Canada. One gram of the sample was leached with 20 g of deionized water at room temperature (20°C). The sample was centrifuged and the leachate analysed by inductively coupled plasma mass spectrometry (ICP-MS). Select samples were analysed by sequential leach analysis at ALS Laboratories Ltd in Vancouver, Canada. Further select samples were analysed at Bureau Veritas Ltd in Vancouver for organic carbon by combustion furnace and infrared absorption after extraction of carbonate and by hot hydroxylamine hydrochloride/ICP-MS. X-ray diffraction was undertaken at EOAS, University of British Columbia, Canada.

Results

Trace element concentration in saline pockets by deionized water leach ICP-MS

Deionized water leach analyses of samples from saline pockets show elevated concentrations of Na, Cl (Fig. 5a) and Br (Fig. 5b) compared to samples of low-salinity alluvial material. The Br response is similar to that observed in groundwater at the Spence Deposit (Leybourne & Cameron 2008). The high salinity dominantly reflects the presence of halite (NaCl) as confirmed by XRD analyses of twelve samples. XRD analysis of salts, precipitated from the deionized water leachate of saline pocket material by evaporation, indicated the presence of halite, calcium nitrate and calcium chloride. XRD analysis also showed calcite which likely precipitated from aqueous calcium bicarbonate in the leachate (Reddy et al. 1981).

Increased concentrations of porphyry copper pathfinder elements Re, Se, Te and Mo are observed in saline pockets compared to low-salinity alluvial material (Fig. 6). Distinct differences in salinity and metal concentration between saline pockets and low-salinity alluvial material located within 2.5 m of the pockets were observed.
Comparable responses were also observed at four additional similar sites sampled throughout the project area. Concentrations of Re, Te, Se and Mo increase with increasing salinity (Fig. 8). Salinity in the sample is represented as the sum of the molar concentrations of the major cations (Ca$^{2+}$, Mg$^{2+}$, Na$^+$ and K$^+$) by deionized water leach because not all anions, such as nitrate and bicarbonate, were identified in the deionized water leach analysis. Selenium, Re and Te show strong correlations to Cl while a weaker correlation exists between Mo and Cl (Fig. 9). Arsenic and Cu concentrations by deionized water leach are not significantly elevated in saline pockets compared to background samples. Given that the samples are considered to comprise of the evaporated remains of groundwater forced to the surface, it is optimal to treat the results of the deionized water leach/ICP-MS analysis in a similar manner to conventional groundwater analysis. To this extent, trace element results were normalized to the molar sum of the major cations to account for varying concentrations of saline material accumulated within the pockets.

**Vertical soil profiles**

A soil profile of a saline pocket (10–30 cm) (Fig. 10) shows a strong correlation of major cations and Cl with Mo, Re and Se from 10 to 15 cm. Maximum concentrations of Na (1.64%) and Cl (1.85%) are measured to a depth of 10 cm with coincident maximum concentrations of Se (2996 ppb), Mo (15 ppb), Re (7.14 ppb) and Te (9 ppb). Concentrations of Na and Cl both decrease to 0.75% (7534 ppm and 7535 ppm, respectively) at 15 cm, together with decreased concentrations of Se (869 ppb), Mo (8 ppb), Re (2.56 ppb) and Te (2 ppb). Concentrations of Re, Se and Te are consistent from 15–30 cm, while Na and Cl increase to 1.0% and 1.1%, respectively. Concentrations of Mo continue to decrease from 15–30 cm. Normalizing metal concentration to the molar sum of the major cations (Na, Ca, Mg and K) through the vertical profile reveals a fairly consistent metal signature from 10–30 cm, with the exception of Se which decreases down profile.
Sequential leach analyses indicate near-total extraction of Re and Se by deionized water leach (Fig. 11). The labile portion of Mo is extracted by both deionized water (soluble salts) and sodium pyrophosphate (organic matter); however, Mo concentrations decrease with increasing organic carbon contents. Results for Te indicate samples submitted for sequential leach analysis contained concentrations at, or close to, detection limit for all selective extractions, and partial and total digests (medianAquaRegia = 0.05 ppm, median4-acid = 0.04 ppm). This implies Te extracted by deionized water from other highly saline samples (see e.g. Fig. 6) likely reflects an exogenic source. The labile portion of As is dominantly extracted by ammonium acetate (carbonates) and the most labile portion of Cu extracted by hot hydroxylamine hydrochloride (amorphous Fe-oxides; Fig. 11).

Table 1. Analytical methods used: reagents and target phases from each type of analysis, with measurement method and the number of samples in each geochemical analysis

| Geochemical analysis                  | Reagent                     | Target phases                                | Finish                | Number of samples |
|---------------------------------------|-----------------------------|----------------------------------------------|-----------------------|-------------------|
| Deionized water leach                 | Deionized water             | Water soluble salts and loosely adsorbed elements | ICP-MS                | 334               |
| Sequential leach:                     | Deionized water             | Water soluble salts and loosely adsorbed elements | ICP-MS                | 11                |
| Selective extractions                 | Ammonium acetate (buffered to pH 5.2) | Carbonates                                  | ICP-MS                |                   |
|                                       | Cold (60°C) hydroxylamine hydrochloride | Amorphous Mn-oxides and surfaces of Mn- and Fe-oxides | ICP-MS                |                   |
|                                       | Hot (90°C) hydroxylamine hydrochloride | Amorphous Fe-oxides                          | ICP-MS                |                   |
|                                       | Sodium pyrophosphate        | Organic matter                               | ICP-MS                |                   |
| Partial and total digest              | Aqua regia                  | Crystalline Fe-oxides, sulphides              | ICP-MS, ICP-AES       |                   |
|                                       | 4-Acid                      | Silicates, alumin-silicates, boro-silicates   | ICP-MS, ICP-AES       |                   |
| Hot hydroxylamine hydrochloride leach | Hot (90°C) hydroxylamine hydrochloride | Amorphous Fe-oxides                          | ICP-MS                | 12                |
| Total organic carbon                  | Pre-digest with hydrochloric acid (25%) to remove carbonate | Organic carbon                               | Combustion/infrared absorption | 8                |
| X-ray diffraction                     |                             | Crystalline materials                        |                       | 12                |

ICP-AES, inductively coupled plasma atomic emission spectroscopy; ICP-MS, inductively coupled plasma mass spectrometry.

**Discussion**

**Source of metals in saline pockets**

Saline pockets on the surface are interpreted to form as a result of saline groundwater transported to the surface during seismic pumping (Brown et al. 2019). An elevated NaCl and trace element geochemical signature is detected in saline pockets, compared to surrounding alluvial material, throughout the project area, up to 2 km away from the deposit. We propose that as a result of interaction of mineralization with groundwater, trace elements are leached into the groundwater, and the geochemical signature is subsequently diffused outwards. The groundwater is transported to the surface along structures during seismic activity forming highly localized saline pockets containing elevated concentrations of NaCl and trace elements compared to surrounding alluvial material.

![Fig. 5. (a) Na (ppm) v. Cl (ppm) after deionized water leach shows elevated concentrations of NaCl in saline pockets v. surrounding background alluvial material; and (b) box-plot showing elevated Br concentrations in saline pockets compared to background alluvial samples.](http://geea.lyellcollection.org/)
Groundwater sampling was attempted at existing drillholes but proved to be impractical due to previous drilling activities. This inhibits the direct correlation of geochemical signatures observed on the surface to groundwater geochemistry at Atlántida. However, we argue that geochemical signatures observed in saline pockets are formed by the injection of mineralized groundwater to the surface for the following reasons:

1. saline pockets are enriched with elements characteristic of porphyry copper mineralization;
2. increased metal concentrations are restricted to saline pockets which are distributed along structural trends;
3. the relationship between increasing salinity and concentrations of Se, Mo, Re and Te indicates time-accumulated volumes of groundwater pumped to the surface will yield higher concentrations of these elements.

Geochemical and isotopic analyses of the groundwater and surface geochemistry at the Spence Deposit clearly demonstrate the link between the geochemistry of sulphides oxidizing in the presence of groundwater and the formation of surficial geochemical anomalies (Cameron & Leybourne 2005; Leybourne & Cameron 2008). The surficial geochemical signature on the alluvial surface at Spence closely resembles that observed from saline pockets at Atlántida.

**Mobility of metals from groundwater to surface**

Whilst the oxidation of porphyry deposits, particularly those rich in pyrite or chalcopyrite, will generate acidic conditions (pH <4), groundwater in the Atacama Desert is currently dominantly alkaline (pH 7–9) (de Caritat et al. 2007). Elements released from the porphyry that remain soluble and mobile as oxyanions, or neutral hydroxides when pH conditions change from acid to neutral to alkaline, can be transported to the surface. These include elements identified in saline pockets: Se (HSeO3−, SeO42−, SeO32−), Mo (HMoO4−), Re (ReO4−, Re(OH)4(aq)), As (H2AsO4−, HAsO42−, As(OH)3(aq)) and Te (HTeO3−, H2TeO4−, TeO32−, TeO42−) all mobile in oxidizing alkaline groundwater conditions (Howard 1977; Bethke 1994). However, the mobility of these elements in groundwater is complex and may be hindered by adsorption to mineral surfaces, changes in pH or competing ions such as bicarbonate or sulphate (Stollenwerk 2003). For example, in oxidizing alkaline conditions, Fe-oxyhydroxides can play a major role in attenuation of mobile As from groundwater (Nordstrom 2002; Smedley & Kinniburgh 2002). However, Leybourne & Cameron (2008) suggest AsV can travel considerable distances in groundwater at the Spence Deposit due to the redox state of the groundwater close to the FeII/FeIII transition, preventing significant attenuation of As by Fe-oxyhydroxides. In comparison, Re and Mo both display conservative behaviour, with no significant adsorption on to particles (Colodner et al. 1993) and are therefore considered mobile in oxidizing saline groundwater. Copper, which dissolves in groundwater as Cu2+ is considered essentially immobile in alkaline conditions and is further depleted due to the tendency of Cu2+ to adsorb on to Fe-oxyhydroxides and clay surfaces (Dzombak & Morel 1990), or to precipitate as secondary Cu-oxides or Cu-carbonates (Leybourne & Cameron 2008). The changing element mobility in varying Eh–pH environments may be used as vectors towards buried mineralization. For example, due to the low mobility of Cu in alkaline environments, anomalous Cu concentrations on the surface using a weak leach may indicate proximity to source.

**Hydrogeological information concerning the current Eh–pH conditions, or possible mixing of meteoric and saline groundwater**

![Fig. 6. Box-plots of analyses of Cl, Re, Se and Te after deionized water leach of saline pockets (grey) and background alluvial material (black). Open circles represent outlier data and open triangles represent far outlier data.](http://geea.lyellcollection.org/)

![Fig. 7. (a) Surficial conductivity measured at 0.5 m spacing over 5 m intervals across one saline pocket located at the southern end of the north–south-trending sample line and analyses of Cl after deionized water leach; and (b) concentrations of Te, Re, Mo, Se and As from the saline pocket and two background alluvial samples located 2.5 m on either side of the saline pocket after deionized water leach.](http://geea.lyellcollection.org/)
sources at Atlántida, is not available. However, groundwater studies at Inca de Oro, located 25 km NNE from Atlántida, report mean pH values of 7.42 and Eh (mV) of 385–415, which is comparable to measurements at Spence (mean pH of 7.32 and Eh (mV) of −100–250) and Mantos Blancos (mean pH of 7.41) (Leybourne & Cameron 2008; Reich et al. 2008; Soto 2010). This suggests oxidizing and alkaline groundwater conditions in the Inca de Oro–Atlántida area, allowing for Mo, Re, Se, Te and As to be present as mobile oxyanions.

Upon reaching the surface and commencement of evaporation under hyper-arid conditions, elements may be incorporated into secondary mineral phases depending on the Eh–pH conditions. The pH of saline pocket samples is neutral to alkaline, ranging from 7–10.5. The near-total extraction by deionized water leach of Se and

![Fig. 8. Plots of analyses of Re, Se, Te and Mo v. the molar sum of cations Na⁺, K⁺, Mg²⁺ and Ca²⁺ after deionized water leach.](image)

![Fig. 9. Plots of analyses of Re, Se, Te and Mo v. Cl after deionized water leach.](image)
Re (Fig. 11) indicates that these elements are preserved on the surface in the same water-soluble form in which they were transported to the surface, without significant incorporation into secondary mineral phases.

Organic carbon analyses of saline pocket material indicate extremely low organic carbon contents (0.2–0.8%), similar to organic carbon contents measured in the hyper-arid core of the Atacama Desert (Ziolkowski et al. 2013; Azua-Bustos et al. 2015; Robinson et al. 2015). The low organic content indicates that Mo extracted by the sodium pyrophosphate leach is likely Mo solubilized from another water insoluble mineral phase, for example ferrimolybdate (Jones 1957), besides those extracted earlier in the sequential extraction sequence (i.e. not associated with carbonate nor amorphous Fe–Mn-oxides) under the alkaline nature (pH 10) of the leach. This may contribute to the weaker correlation observed between Mo and increasing sum of cations and Cl by deionized water leach.

Sequential leach results indicate As, despite being mobile as an oxyanion, is sequestered by carbonates near the surface (Fig. 11) (Goldberg & Glaubig 1988). Adsorption of As on secondary mineral phases clarifies why low concentrations of As are extracted from saline pockets by the deionized water leach. Any labile fraction of Cu, derived from an exogenic source or released from the weathering of clasts on the surface, is dominantly adsorbed on to Fe-oxyhydroxides (Fig. 11) as a result of the high affinity for cation adsorption in alkaline environments (Dzombak & Morel 1990).

Assuming no major redistribution of elements to secondary mineral phases other than As, analysis by deionized water leach of material from saline pockets allows for the recreation of the geochemical signature of the groundwater interacting with mineralization. Concentrations of elements, leached by deionized water, from saline pockets which have not been dominantly incorporated into secondary mineral phases (i.e. Se, Mo, Re and Te), can hence be used to vector towards buried mineralization in the same way groundwater data are used to vector to mineralization (e.g. Casa Grande porphyry in Arizona (Ficklin et al. 1981); Bathurst Mining Camp in Canada (Leybourne et al. 2003); Spence porphyry deposit in Chile (Leybourne & Cameron 2008)).

Data processing: normalization of metal signatures from saline pockets to groundwater volume proxy

As groundwater interacts with mineralization, releasing porphyry copper pathfinder elements, the concentration of elements leached from the porphyry into groundwater will increase proximally, yet the volume of groundwater pumped to the surface during seismic events may not be equal across all saline pockets (Fig. 12), resulting in concentration variability reflecting volumes rather than concentrations.

The volume of groundwater which reaches the surface controls the salinity and concentration of elements at the surface (Figs 8 and 10) and can be represented as the sum of the major cations analysed.

**Fig. 10.** Vertical soil profiles of a saline pocket (10–30 cm): (a), Na, Mg, Ca, K and Cl (ppm) after deionized water leach; (b), Mo, Re, Se and Te (ppb) after deionized water leach; and (c), Mo, Re, Se and Te normalized to the molar sum of cations.

| 0 | 500 | 1000 | 1500 | 20000 |
|---|-----|------|------|-------|
| Na | 10  | 15   | 20   | 25    |
| Mg | 20  | 25   | 30   | 35    |
| Ca | 0   | 5    | 10   | 15    |
| K  | 0   | 5    | 10   | 15    |
| Cl | 0   | 5    | 10   | 15    |

| 0 | 1000 | 2000 | 3000 |
|---|------|------|------|
| Mo | 0    | 5    | 10   |
| Re | 0    | 5    | 10   |
| Se | 0    | 5    | 10   |
| Te | 0    | 5    | 10   |

**Fig. 11.** Sequential leach results: (a) Na, Mg, Ca, K and Cl (ppm) after deionized water leach; (b) Mo, Re, Se and Te (ppb) after deionized water leach; and (c) Mo, Re, Se and Te normalized to the molar sum of cations.
by deionized water leach. Element concentrations must therefore be normalized to the varying groundwater volume flux reaching the surface and forming the pockets. The concentrations of each metal (Se, Mo, Re and Te) were normalized to the molar sum of the major cations at each site separately and expressed as percentiles. The percentiles of Se, Mo, Re and Te were summed and re-expressed as a percentile. Summed normalized responses of Se, Mo, Re and Te are elevated directly over mineralization (Fig. 13). Normalizing the response to the sum of molar cations ensures that anomalous concentrations are not simply a result of a larger groundwater flux...
Fig. 12. Conceptual models for (a) transport of trace elements to the surface and varying volumes of groundwater flux to the surface; and (b) the requirement for normalization of metal signature to a proxy for groundwater flux. Major cations and anions in groundwater: Cl$,\ NO_3^-, SO_4^{2-}, CO_3^{2-}, Ca^{2+}, Mg^{2+}, K^+, Na^+, H^+, OH^-$ and $H_3O^+$ omitted for simplicity of illustration. Metals are soluble as neutral hydroxides or oxyanions at neutral–alkaline pH.
and tightens the geochemical response to directly over the target (Fig. 13). No information concerning groundwater source, flow direction, rate of flow and fault-controlled changes to groundwater hydrology is available at Atlántida. This methodology is therefore based on the assumption that groundwater is homogeneous throughout the Atlántida area.

Arsenic and copper signatures above Atlántida

Analyses by ICP-MS after ammonium acetate leach of select samples over Atlántida show slightly elevated responses of As normalized to Ca over mineralization (Fig. 14a). This may indicate an elevated concentration of As in the groundwater proximal to the deposit, that upon reaching the surface, is incorporated into carbonates as a result of the highly alkaline surficial environment. Concentration levels are, however, still low, with a poor anomaly to background contrast.

Analyses of Cu extracted from Fe-oxides in saline pockets using a hot (90°C) hydroxylamine hydrochloride leach do not show a clear response over mineralization (Fig. 14b). Analysis of Cu by cold (60°C) hydroxylamine hydrochloride leach, extracted from Mn-oxides and surfaces of Mn- and Fe-oxides shows elevated responses of Cu/Mn over mineralization (Fig. 14c), yet very low concentrations of Cu are extracted using this method (maximum concentration of 1.3 ppm Cu). These results likely indicate Cu is not present in significant concentrations in the groundwater, possibly due to its reduced solubility in alkaline conditions. Saline pockets may therefore not be significantly enriched in Cu compared to background concentrations, potentially resulting in poor anomaly to background contrast.

Comparison of surficial geochemical results from other buried deposits in Chile

Distribution of elements in the vertical soil profiles above the Spence Deposit by ICP-MS after deionized water leach and enzyme leach reveal increasing concentrations with depth (30–100 cm) of elements which are soluble (NaCl) and those that form oxyanions in aqueous solution (As and Se) (Cameron & Leybourne 2005). They observed that elements which dissolve as cations (Cu²⁺, Ag²⁺ and Pb²⁺) are concentrated in the upper 30 cm. The interpretation of this behaviour is the redistribution of elements at the surface by infrequent rains (Cameron & Leybourne 2005). Sampling depth at Atlántida did not exceed 40 cm therefore no direct comparisons to element distribution at the Spence Deposit can be made. However, the vertical soil profiles at Atlántida show increased concentrations of soluble elements (Mo, Re, Se, Te, Na and Cl) from 10–15 cm depth, potentially due to evaporation of injected groundwater at the surface.

Surficial geochemical responses observed throughout northern Chile, including at the Spence Deposit (Cameron & Leybourne 2005), Mantos Blancos (Palacios et al. 2005), Radomiro Tomic, Mansa Mina (Cameron et al. 2010) and Gaby Sur (Cameron et al. 2004) are characterized by highly localized, elevated concentrations of halogens (Cl, Br and I) and Na occurring with high concentrations of porphyry copper pathfinder elements such as As, Se, Mo, V and Re. Geochemical responses from the Spence Deposit and Gaby Sur were directly correlated with fracture zones in the gravels identified afterwards by trenching (Cameron et al. 2000). Anomalous samples from Mantos Blancos and Mansa Mina were directly correlated with mapped bedrock faults extending through
Influenced by the depth of mineralization, leach cap thickness, ore grade and the thickness of overlying barren rock. The depth of mineralization, low-grade ore (c. 0.2% Cu) and alkaline conditions at Atlántida may therefore contribute to the lack of a strong Cu response observed on the surface.

Mineralization at Atlántida is reported as 100% hypogene with no evidence for significant supergene enrichment (Hope & Andersson 2015). Cameron et al. (2010) suggest deposits having undergone supergene enrichment can later be subjected to additional metasomatism of Cu-oxides by saline groundwater infiltration resulting in the precipitation of atacamite (Cameron & Leybourne 2005; Cameron et al. 2007; Reich et al. 2008, 2009). Atacamite, a Cu chloride (Cu₂Cl(OH)₃), is highly soluble in meteoric groundwater (Reich et al. 2008). For example, atacamite was dissolved from a large section of the central oxide zone at Radomiro Tomic by infiltration of meteoric groundwater during transport of alluvial gravels (Cameron et al. 2010). Interaction of meteoric groundwater and atacamite would lead to increased Cu concentrations in groundwater compared to water–rock interactions with Cu-sulphides. Increased concentrations of Cu may then allow for appreciable Cu concentrations to reach the surface by seismic pumping of groundwater, even from considerable depth. For example, at Mantos Blancos, where the oxide zone near the surface contains atacamite yet the water table is currently present at 400 m depth, groundwater transport along faults has created salt efflorescence along fault structures at the surface. Salt efflorescence which occurs directly over mineralization can exceed 1000 ppm Cu and has a distinct green coloration resulting from a mixture of atacamite and chalcocite (Palacios et al. 2005; Cameron et al. 2010). Thus, the absence of a Cu-oxide zone or supergene enrichment blanket at Atlántida has likely also contributed to the weak geochemical response of Cu at the surface. Anomalous concentrations of Cu extracted on the surface using a weak leach may therefore potentially provide information regarding depth and type of Cu mineralization (hypogene v. supergene).

Exploration recommendations

This study demonstrates a targeted geochemical sampling strategy may significantly improve the potential for the discovery of buried deposits in the Atacama Desert. This strategy is based on evidence from several sites suggesting that groundwater is forced to the surface during seismic events along permeable fractures, forming discrete saline pockets at the surface. Sampling saline pockets over the visible extent of structures at the surface, identifiable using remote sensing and regolith mapping (Brown et al. 2019), is necessary.

Regular grid pattern geochemical programmes (e.g. 1 sample per 250 m or 500 m), a standard practice used by industry, rely on chance to sample on structural trends. Grid sampling using partial leach geochemistry in areas dominated by transported cover does not consider variable background chemistry, metal transport, predictive chemistry or signal preservation. These are all important components required for effective application of partial leach geochemistry for the discovery of buried deposits in covered terrains.

Based on work at Atlántida, we recommend a number of measures for designing an effective geochemical survey for application at a regional, district or target scale.

1. Use of remote sensing, regolith mapping and geomorphic markers of faulting to map the physical extent of fault features on the surface. Remote sensing at high-resolution can also identify distinct saline pockets distributed along structural trends.
2. Use of total dissolved solids/conductivity for identification of saline pockets in the field.
3. Sample grids (e.g. 250 × 250 m) can be oriented parallel to the orientation of structural trends, where within a grid cell...
a saline pocket can be identified and specifically sampled as the target medium. Sample lines with 25–50 m spacing (sampling saline pockets) should be oriented perpendicular to structural trend, extending up to 150 m from the main fault zone. Sample on relatively older alluvial surfaces to allow for signal accumulation, avoiding young channels or recently deposited material on older surfaces. Use a weak digestion (e.g. deionized water leach) to extract labile, exogenic signatures. Consider element mobility and predictive chemistry of porphyry weathering by rock–groundwater interaction. These elements will include Mo, As, Te and Re, soluble as oxyanion/neutral hydroxide complexes in alkaline conditions, in contrast to the low mobility of Cu in alkaline conditions. Data interpretation requires normalization of metal concentration to total major cations as a proxy for groundwater volume. Notably, normalization of samples taken outside saline pockets and targeted sampling has the potential to be widely applicable in the Chuquicamata (Brown 2002). Saline pockets have been identified at four other unique opportunity to sample the geochemistry of the groundwater, sensing and deionized water extraction geochemistry provides a environments, and signal preservation on the surface. Sampling of porphyry copper pathfinder elements in changing Eh directly over mineralization, indicating targeted sampling of saline pockets along structural trends. Geochemical –50 m spacing –7873/03-012

Conclusions

The localized nature of geochemical responses on the surface observed at Atlántida emphasizes the importance for targeted sampling of saline pockets along structural trends. Geochemical results and geomorphic observations indicate the rate of erosion is low enough in the Atacama Desert (e.g. Carretier et al. 2018) to preserve the surficial anomalies formed as saline pockets by mineralized groundwater forced to the surface during seismic activity. Geochemical signatures of Se, Mo, Re and Te, normalized to a proxy for groundwater volume, show elevated responses directly over mineralization, indicating targeted sampling of saline pockets along structures can be used to vector toward buried mineralization. The magnitude of anomalous Cu responses on the surface may provide information concerning the depth of mineralization, or perhaps the type (hypogene v. supergene) of Cu mineralization below. To be effective, targeted sampling must employ an understanding of element transport, predictive chemistry of porphyry copper pathfinder elements in changing Eh–pH environments, and signal preservation on the surface. Sampling of saline pockets along structural trends identified using remote sensing and deionized water extraction geochemistry provides a unique opportunity to sample the geochemistry of the groundwater, potentially interacting with buried mineralization, by only sampling on the surface. Saline pockets have been identified at four other sites throughout the Atacama Desert extending as far north as Chiquicamata (Brown et al. 2019), demonstrating that this type of targeted sampling has the potential to be widely applicable in the Atacama Desert of Chile, and potentially other desert environments in active tectonic terrains, for the discovery of buried porphyry deposits.

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