



Stable isotopic composition of soil calcite (O, C) and gypsum (S) overlying Cu deposits in the Atacama Desert, Chile: Implications for mineral exploration, salt sources, and paleoenvironmental reconstruction



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ABSTRACT

Soils overlying two porphyry Cu deposits (Spence, Gaby Sur) and the Pampa del Tamarugal, Atacama Desert, Northern Chile were collected in order to investigate the extent to which saline groundwaters influence “soil” chemistry in regions with thick Miocene and younger sediment cover. Soil carbonate (calcite) was analyzed for C and O isotopes and pedogenic gypsum for S isotopes. Soil calcite is present in all soils at the Spence deposit, but increases volumetrically above two fracture zones that cut the Miocene gravels, including gravels that overlie the deposit. The C isotope composition of carbonate from the soils overlying fracture zones is indistinguishable from pedogenic carbonate elsewhere at the Spence deposit; all $\delta^{13}\text{C}_{\text{VPDB}}$ values fall within a narrow range (1.40–4.23‰), consistent with the carbonate having formed in equilibrium with atmospheric CO_2 . However, $\delta^{18}\text{O}_{\text{VPDB}}$ for carbonate over both fracture zones is statistically different from carbonate elsewhere (average $\delta^{18}\text{O}_{\text{VPDB}} = 0.82\text{‰}$ vs. -2.23‰ , respectively), suggesting involvement of groundwater in their formation. The composition of soils at the Tamarugal anomaly has been most strongly affected by earthquake-related surface flooding and evaporation of groundwater; $\delta^{13}\text{C}_{\text{VPDB}}$ values (-4.28‰ to -2.04‰) are interpreted to be a mixture of dissolved inorganic C (DIC) from groundwater and atmospheric CO_2 . At the Spence deposit, soils only rarely contain sufficient SO_4 for S isotope analysis; the SO_4 -bearing soils occur only above the fracture zones in the gravel. Results are uniform (3.7–4.9‰ $\delta^{34}\text{S}_{\text{CDT}}$), which is near the middle of the range for SO_4 in groundwater (0.9–7.3‰). Sulfur in soils at the Gaby Sur deposit (3.8–6.1‰ $\delta^{34}\text{S}_{\text{CDT}}$) is dominated by gypsum, which primarily occurs on the flanks and tops of hills, suggesting deposition from SO_4 -rich fogs. Sulfate in Gaby Sur deposit gypsum is possibly derived by condensation of airborne SO_4 from volcanic SO_2 from the nearby Andes. At the Gaby Sur deposit and Tamarugal anomaly, pedogenic stable isotopes cannot distinguish between S from porphyry or redeposited SO_4 from interior salars.

The three sites studied have had different histories of salt accumulation and display variable influence of groundwater, which is interpreted to have been forced to the surface during earthquakes. The clear accumulation of salts associated with fractures at the Spence deposit, and shifts in the isotopic composition of carbonate and sulfate in the fractures despite clear evidence of relatively recent removal of salts indicates that transfer from groundwater is an ongoing process. The interpretation that groundwaters can influence the isotopic composition of pedogenic calcite and gypsum has important implications for previous studies that have not considered this mechanism.

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1. Introduction

The Atacama Desert is recognized as being the driest on Earth and has been arid or semi-arid since perhaps the Jurassic (Alpers

and Brimhall, 1988; Hartley et al., 2005). The timing of climate change to hyperaridity has recently been debated, with interpretations ranging from Late Oligocene to Pliocene (Alpers and Brimhall, 1988; Hartley and Chong, 2002; Hartley et al., 2005; Dunai et al., 2005; Clarke, 2006; Garzzone et al., 2006; Ghosh et al., 2006; Rech et al., 2006; Reich et al., 2009). The change to hyperaridity is significant for a number of reasons including cessation of significant

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supergene enrichment of porphyry mineralization (Arancibia et al., 2006), reduction in surface erosion and preservation of surface landscapes on the scale of millions of years (Alpers and Brimhall, 1989), and accumulation of salts in soils (Rech et al., 2003b).

There continues to be debate over the origin of salts (i.e., sulfates, nitrates and chlorides) that have accumulated in the hyper-arid Atacama Desert (e.g., Ewing et al., 2006, 2007, 2008; Michalski et al., 2004). Sources of salts that have been considered previously include marine aerosols, non-marine aerosols, weathering of volcanic rocks in the active part of the Andean arc, volcanic emissions, organic remains from lakes, and guano (summarized by Rech et al. (2003b)). Bao et al. (2004) used $\Delta^{17}\text{O}$ anomalies in soil gypsum to suggest that SO_4 sources should be classified as primary (derived from rock weathering, marine aerosols, and presumably redistributed from salars) and secondary (biological or volcanic emissions). Based on the major and trace element composition of soils and groundwaters associated with several porphyry Cu systems in the Atacama Desert, previous studies have suggested that soils overlying deeply buried mineralization are influenced by the movement of groundwater to surface during seismic events (Cameron et al., 2004, 2002; Cameron and Leybourne, 2005; Cameron, in press). Detailed studies around the Spence deposit (Fig. 1) have shown that seismically migrated fluids include a significant component derived from deep basinal brines that are modified by water–rock interactions with hypogene and supergene mineralization (Cameron and Leybourne, 2005; Leybourne and Cameron, 2006a, 2008). Earthquake-induced groundwater flow, therefore, brings isotopically and chemically distinct fluids to the surface, with the potential to influence the development and accumulation of surface salts especially carbonates, sulfates and halides mostly in localized areas around fracture systems.

Carbonate is found in soils from arid to sub-humid climatic regions, typically where the soil $\text{pH} \geq 7$. Soil carbonate is mostly comprised of CaCO_3 , but there may also be smaller amounts of MgCO_3 . Where sufficient carbonate is present, it may cement the clastic constituents of the soil to form hard layers called calcrete or caliche. The O and C isotopic compositions of pedogenic carbonate have been used as paleoenvironmental proxies because of equilibration between soil zone CO_2 and soil water; the isotopic composition of soil gas and water is in turn controlled by vegetation and climate patterns (Cerling, 1984, 1991; Quade et al., 1989, 2007; Kaakinen et al., 2006; Breecker et al., 2009). However, in hyperarid climates such as the Atacama Desert of northern Chile, poor to non-existent soil development complicates reconstruction of climate information. For example, Rech et al. (2006) studied paleosols in the Calama Basin and showed that soils formed ca. 20 Ma were calcic vertisols, with gleyed horizons and root traces consistent with significantly wetter climates (>200 mm/a precipitation). By contrast, gypsisols interpreted to be ca. 13–8 Ma are consistent with rainfall of ~ 20 mm/a, nominally greater than much of the core of the Atacama Desert at present (Rech et al., 2006). Thus, the relationship between soil zone CO_2 and pedogenic calcite is complicated by low P_{CO_2} in Atacama Desert “soils” (Rissmann, 2003; Rissmann et al., in preparation).

In this paper the results are presented of a stable isotopic study of soil carbonate (C, O) and gypsum (S) firstly for samples collected over two porphyry Cu deposits (Spence and Gaby Sur deposits) buried by Miocene and younger gravels and secondly for samples from an apparently unmineralized but geochemically anomalous portion of the Pampa del Tamarugal (the Tamarugal anomaly; Leybourne and Cameron, 2006b). The objectives of this study are to: (1) determine if groundwaters interacting with porphyry mineralization influence the isotopic composition of authigenic soil minerals overlying mineralization; (2) determine if the S isotope composition of soil SO_4 could be used to distinguish between SO_4 of porphyry origin from SO_4 deposited from coastal fog; and (3)

determine the extent to which atmospheric CO_2 influences the isotopic composition of soil carbonate in hyperarid climates.

2. Geological setting and field observations

The Atacama Desert of northern Chile hosts the world's largest Cu resource. Weathering of the primary (hypogene) sulfide mineralization in giant porphyry Cu deposits has produced several hundred meters of higher grade caps of secondary Cu sulfides, oxides, hydroxides, carbonates, sulfates and chlorides. This supergene mineralization is a reflection of the history of groundwater flow, tectonics, landscape, and climate of the Atacama Desert (Alpers and Brimhall, 1988; Sillitoe and McKee, 1996; Clarke, 2006).

The Spence porphyry Cu deposit was discovered by RioChilex in 1996–1997 by grid drilling through piedmont gravels that cover the deposit, which displays a typical supergene-enriched sequence (Fig. 2). The deposit is situated some 50 km SW of Calama, at an altitude of ~ 1700 m above sea level. Mineralization is associated with three quartz–feldspar porphyry bodies intruded along a NE axis into andesitic volcanic rocks. Intrusions are cut by tourmaline–quartz–sulfide hydrothermal breccias. The irregular deposit surface is covered by 30–180 m of gravels.

The Gaby Sur porphyry Cu deposit (~ 35 Mt of Cu), located 43 km SE of the Spence deposit, was discovered by Codelco in 1997 (Fig. 1). The Gaby Sur deposit lies at an altitude of ~ 2700 m above sea level in a broad valley that slopes SW at 40 m/km. A supergene-enriched zone of Cu oxides up to 180 m thick is underlain by hypogene sulfides. The deposit is completely covered by up to 40 m of gravel. The deposit lies in a graben, delimited by high-angle boundary faults.

The Pampa del Tamarugal is a broad plain between the mountains of the Coast Range to the west and the Sierra de Moreno (part of the Precordillera) to the east (Fig. 1). The study area is 50 km west of the giant Chuquicamata porphyry Cu deposit, at an altitude of ~ 1100 m above sea level (Fig. 1). The Pampa is largely underlain by Quaternary piedmont and alluvial gravels, which the Rio Loa has incised to a depth of about 50 m. North of the study area is an abandoned Cu mine (Mina Campamento), associated with exposed andesite and granitic bedrock through the gravels. A soil geochemical survey by Noranda established an extensive Cu anomaly, over 100 km², previously defined as the Tamarugal anomaly (Leybourne and Cameron, 2006b). Despite the large soil Cu anomaly, drilling only intersected unmineralized andesitic basement below 262–338 m of gravel and other clastic sediment. The water table in the Tamarugal anomaly is at ~ 50 m.

2.1. Surface features

At the Gaby Sur deposit, the upper 20 m of gravel is variably cemented by calcrete, making it impermeable to water where unfractured. Water is only found in the basement below the gravels, where drill holes intersect major faults (Cameron et al., 2004). The Gaby Sur deposit is most typical of ground cover in the Atacama Desert (Fig. 3B). Immediately below a cobble surface, soils developed on the piedmont gravels have a variable thickness of gypsum mixed with clastic sediment, below which there is commonly hard or soft calcrete. This gypsum-rich surface is classified here as the “old” surface. Over a minority of the area of Gaby Sur, there is a younger “new” surface, which is present in areas that are slightly lower topographically, and likely reflects the action of sheetwash, during a period of higher rainfall in the nearby mountains. Erosion caused the upper horizon of the “old” surface, containing gypsum, to be removed and replaced by solely clastic material, again capped by a pebble surface, but with pebbles smaller than those of the “old” surface. Gypsum is soft and soluble, so

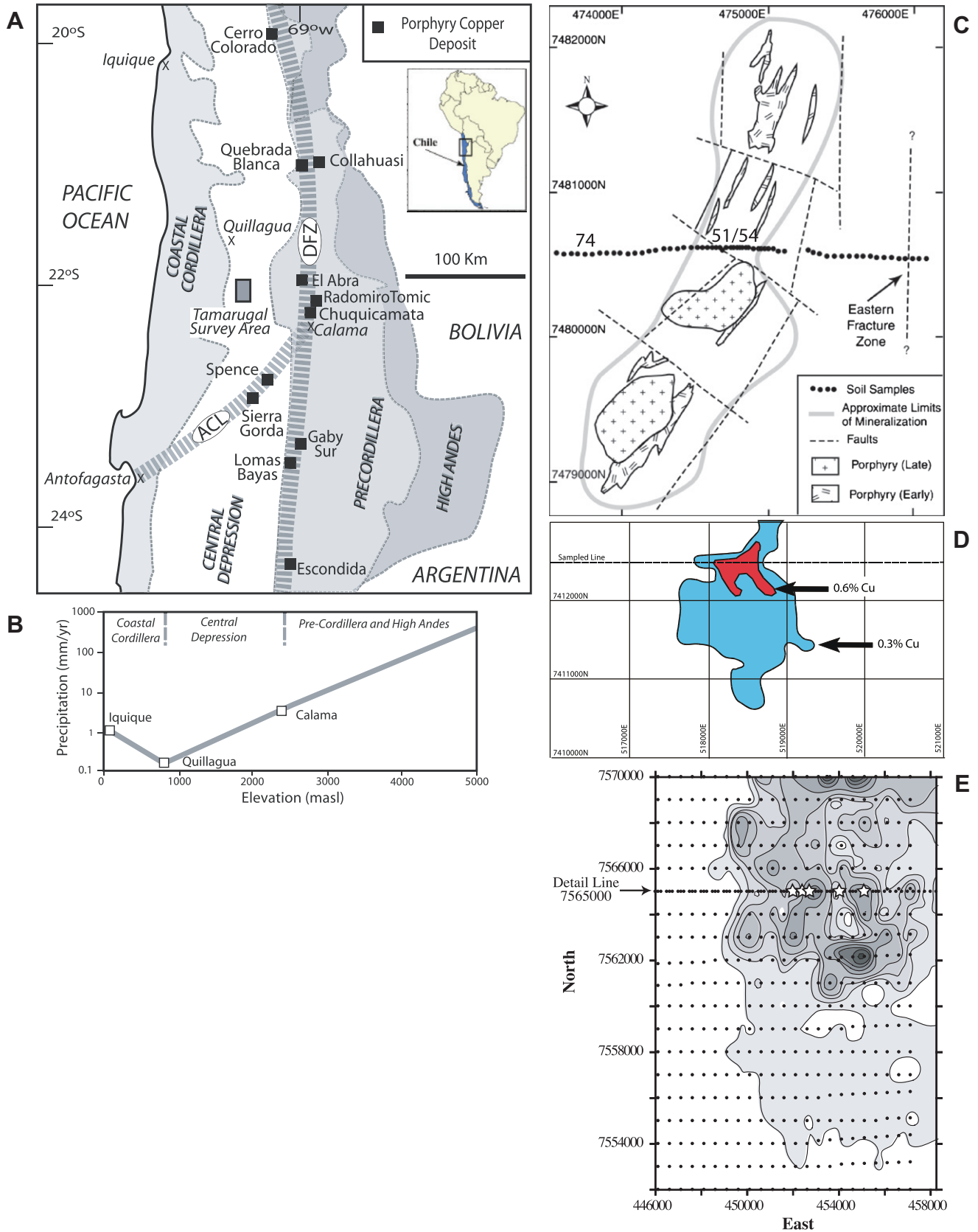


Fig. 1. (A) Location of the study areas. DFZ refers to the Domeyko Fault Zone and ACL is the Antofagasta–Calama Lineament. (B) Profile of changes in rainfall with elevation; precipitation data from (Houston and Hartley, 2003). (C) Plan map of the Spence Deposit, showing the location of the soil traverse, and profiles 51, 54, and 74. (D) Plan map of the Gaby Sur deposit, defined by Cu content of the supergene zone, showing location of the soil traverse. (E) Tamarugal anomaly, as defined by Cu contents of soils in MMI leach, showing location of the soil traverse.

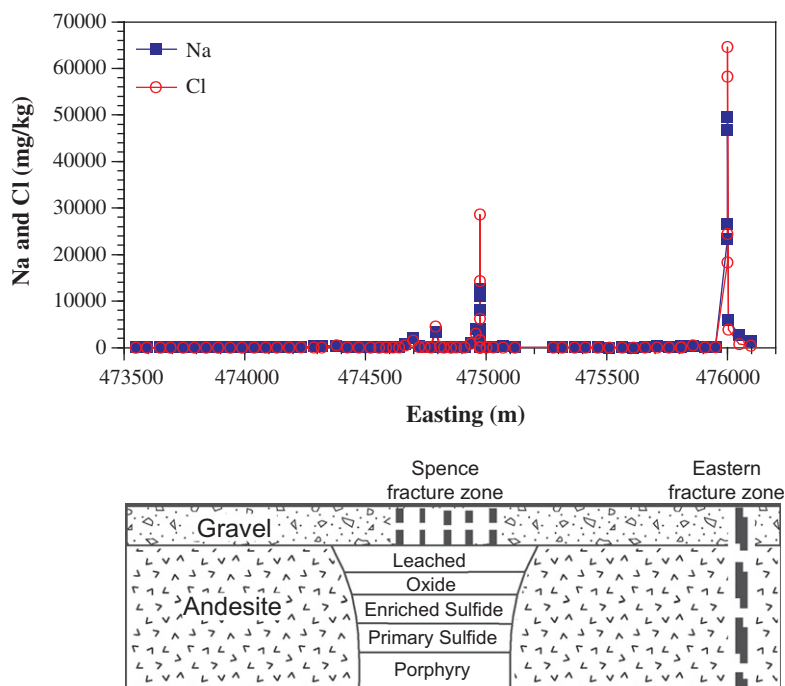


Fig. 2. Idealized east to west cross section of the Spence Deposit, showing the locations of the fracture zones through gravels overlying mineralization and to the east of the deposit. Note that the Spence deposit has a classical supergene enrichment profile (leached cap, oxide zone, supergene sulfide zone, hypogene sulfide zone). Also shown are the Na and Cl concentrations in deionized water leaches of the soils overlying the deposit.

was readily removed during sheetwash erosion. By contrast, hardpan calcrete is resistant and insoluble and has been retained below this “new” surface. Although the terms “old” and “new” are used, both surfaces may be several million years old, and during sampling vertical fractures were observed that penetrate both the older and newer surfaces. At the Spence deposit, and at Gaby Sur, partly caliche-cemented fractures were observed in the gravels, which are coincident with anomalous porphyry-associated metals and metalloids. Fractures have up to 1 cm void space and extend to within 5–10 cm of the surface. In 2000 at the Spence Deposit, a backhoe was used to excavate L-shaped sets of trenches in the gravels, 5 m long N–S and E–W, and 1.5 m in depth. Trenches in the fracture zone directly over the Spence deposit were characterized by common fractures (~1 fracture/m) oriented both E–W and N–S. Trenches excavated over the Eastern fracture zone also revealed E–W fractures (~1 fracture/m) and more common N–S fractures (~2 fractures/m). By contrast, the trenches excavated in geochemical background to the west of the deposit were poorly fractured, with only one N–S fracture over the 5 m trench. These fractures are distinct from the typical polygonal fractures in soil seen commonly in the Atacama Desert (in this study, polygonal fractures were mostly observed at Gaby Sur).

By contrast to the Gaby Sur deposit, at the Spence deposit there is no gypsum horizon and the occurrence of calcrete is rare. Of the >100 sample pits dug along a 2.5 km east–west traverse centered on the deposit, only one pit showed a significant calcrete hardpan layer. The absence of gypsum accumulation is attributed to local erosion of the “old” surface, by sheetwash from mountains to the east (Fig. 3A). Elsewhere in the immediate area, there is a gypsum horizon, including on the slopes and tops of hills. There are no obvious NO_3 accumulations along the Spence soil traverse, although within a few km westwards is one of the richest areas of nitrate deposits in Chile.

At the Pampa del Tamarugal, a polymictic pebbly lag surface, a few cm thick, is underlain by “chusca”, a horizon comprised of powdery, fine-grained, salts including gypsum, nitrates and halite

(Fig. 3C). The salts are only visible where the surface has been disturbed, e.g., vehicle tracks (Fig. 3C) (Leybourne and Cameron, 2006b). The salt horizon is of variable thickness (up to several tens of cm). On a satellite image of the survey area (Leybourne and Cameron, 2006b), the most intense portion of the Cu geochemical anomaly appears to be undisturbed. To the west, there has been erosion of the surface, including the salt, in the flood plain of the River Loa. To the south, the surface has been partially disrupted by streams from an alluvial fan.

3. Methods

3.1. Field methods

Soil samples at the Spence deposit were collected at 10–20 cm depth and 50 m intervals along an undisturbed east–west traverse over the centre of the deposit, where gravels range from 50 to 100 m in thickness. Additional samples were collected from zones of higher NaCl content, based on field measurement of the conductivity of soil + deionized water slurries. Several deeper profiles were obtained by trenching using a backhoe. Trenches were dug both over Cu mineralization, over the eastern fracture zone, and in unfractured gravels distal from the deposit. Samples were sieved to <177 μm , and were treated by a variety of selective leaches, including deionized water, Enzyme Leach, ammonium acetate, hydroxylamine hydrochloride, and aqua regia (for details, see Cameron et al., 2004). Groundwaters were also sampled at the Spence Deposit, within the deposit, and upflow and downflow of the deposit. Full sampling and analytical details on the groundwaters have been presented elsewhere (Leybourne and Cameron, 2006a, 2008). Soils were sampled from the Gaby Sur deposit along an undisturbed east–west traverse across the deposit, with samples at 50 m intervals over the deposit and 100 m intervals on the flanks. Soils were sampled based on horizons with the most Fe-oxide (i.e., most well developed oxide zone, in this area typically

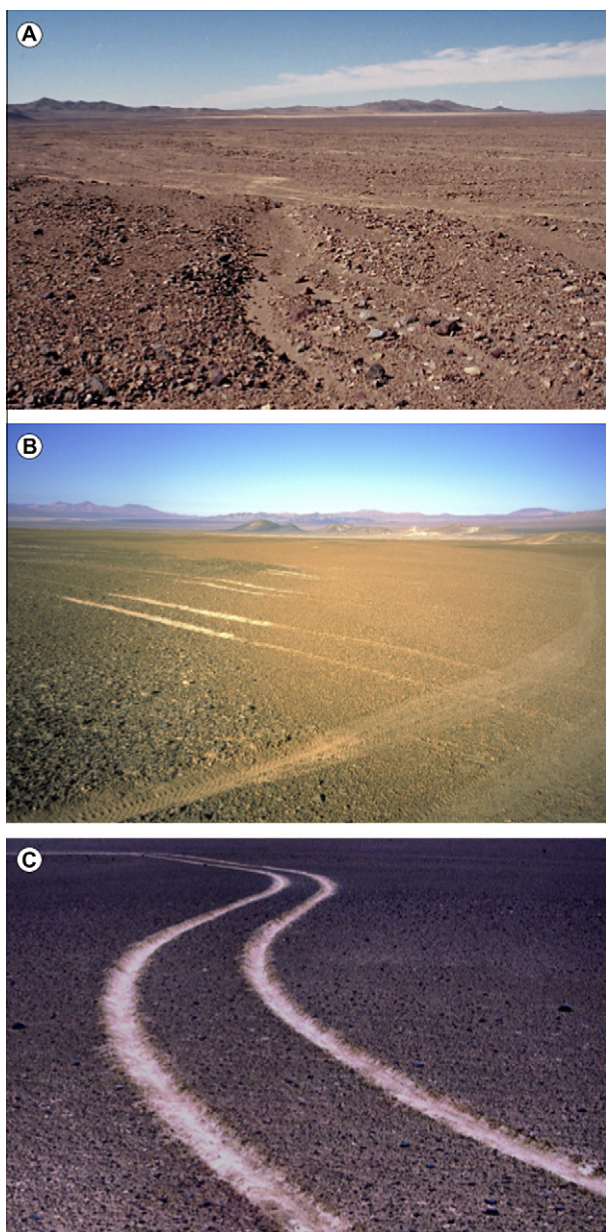


Fig. 3. Photographs showing the different surfaces at the three study areas: (A) Spence deposit shows an erosional surface, (B) Gaby Sur deposit, showing the “old” surface with abundant gypsum (left side of image with deeper tire tracks) and the “new” washout surface lacking gypsum (right side of image), and (C) Tamarugal anomaly in the Pampa del Tamarugal, showing abundant soft salt (exposed by truck tires) below the pebbly lag surface.

minimal at best), with sample depths variable between 10 and 35 cm. Twenty soil samples were collected at the Tamarugal anomaly on Line 7565000N extending from 453460 to 455400E, crossing the large Cu anomaly described in Leybourne and Cameron (2006b). Sites were at approximately 100 m intervals, avoiding areas disturbed by drilling. Samples were taken from 40 cm depth.

3.2. Analytical methods

Stable isotopes were measured at the G.G. Hatch Isotope Laboratories in the Department of Earth Sciences, University of Ottawa. Samples were weighed into exetainers, 0.1 mL of H_3PO_4 was added to the side, and the exetainers were capped and He-flushed while horizontal. Reaction at 25 °C for 24 h (calcite) was followed by

extraction in continuous flow. Isotope ratios were measured using mass spectrometry on a Delta XP and a Gas Bench II (ThermoFinnigan). Routine precision (2σ) on a pure carbonate analysis is 0.1‰. The ^{18}O fractionation factor used for the calcite– H_2PO_4 reaction was 1.01025 (Friedman and O’Neil, 1977). Carbon is reported in ‰ as $\delta^{13}\text{C}_{\text{VPDB}}$, where the results are referenced to the Vienna Pee Dee Belemnite (VPDB) standard. The O isotope ratio measured in carbonate, is also referenced to this standard as $\delta^{18}\text{O}_{\text{VPDB}}$. The O isotopes in water are referenced to Vienna standard mean ocean water (VSMOW) as $\delta^{18}\text{O}_{\text{VSMOW}}$. The relationship between VPDB and SMOW is expressed as: $\delta^{18}\text{O}_{\text{VPDB}}\text{‰} = 0.97 \cdot \delta^{18}\text{O}_{\text{VSMOW}} - 29.98$ (Table 1). Samples for S isotope analysis were weighed into tin capsules with tungstic oxide (or vanadium pentoxide), loaded into a Costech elemental analyzer (EA), and flash combusted at 1800 °C. Helium carrier gas was used to remove released gases, which were then cleaned and separated. The resulting SO_2 gas was carried into a DeltaPlus isotope ratio mass spectrometer (ThermoFinnigan) for analysis. Sulfur isotope values are reported in ‰ as $\delta^{34}\text{S}_{\text{CTD}}$, where the results are referenced to the Canyon Diablo Troilite (CTD) standard. Analytical precision is $\pm 0.2\text{‰}$.

Details of the methods used for the geochemical analysis of the soils are presented elsewhere (Cameron et al., 2004). Briefly, for the deionized water extraction, 20 mL of water were added to 2.5 g sample and tumbled in a roller for 3 min every 15 min for 1 h. After settling for 10 min, the leach was centrifuged for 8 min at 2500 rpm, and decanted. Enzyme Leach and MMI-A are patented and proprietary leaches, respectively, described by Hall (1998). However, both leaches are relatively weak, with Enzyme Leach similar to deionized water (Cameron et al., 2004) and MMI somewhat more aggressive, extracting the adsorbed and carbonate fractions in addition to the water soluble fraction. For ammonium acetate (i.e., NH_4OAc) at pH 5 (AA5), which dissolves carbonate minerals, a 1 g sample was digested by 40 mL of 1.0 M NH_4OAc /pH 5.0 for 2 h, then centrifuged and the solution diluted with water 50:1. Cold hydroxylamine in weak acidic solution dissolves Mn oxides (HX Mn). For this, 1 g of sample was treated with 25 mL of a solution with 0.1 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 0.04 M HNO_3 for 30 min at room temperature. For a limited number of samples involving sequential leaches at the Spence deposit, ammonium acetate at pH 7 (AA7) was also used and a more aggressive hydroxylamine leach (HX Fe), which dissolves Fe as well as Mn oxides; hot 0.25 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 0.25 M HCl. An aqua regia leach was also used, which dissolves all secondary minerals in soils. After dissolution, all leach solutions were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) and, for elements at high concentrations, by inductively coupled plasma optical emission spectroscopy (ICP-OES). Note that because the MMI-A and hydroxylamine leaches are acidic, they also dissolve carbonates. Thus, in a non-sequential leach mode, HX Mn dissolves the water-soluble salts and elements within carbonates, as well as elements present in Mn oxides.

4. Results

4.1. Spence deposit

Soil Na and Cl contents dissolved by deionized water show peaks at two sites: (a) directly over the Spence deposit and (b) 1-km to the east. These represent fracture zones in the gravel, which are interpreted to be the upward propagation of basement faults (Cameron et al., 2002) (Fig. 2). There are also peaks for Ca and S in the soils above these zones (Fig. 4).

All $\delta^{13}\text{C}$ values fall within a relatively narrow range between 1.40‰ and 4.23‰ for both ‘Type A’ (from soils not associated with fracture zones) and ‘Type B’ (from soils above fracture zones) carbonates, i.e., the carbonates above the fracture zones are

Table 1
Isotopic and elemental compositions of soils from the Spence and Gaby Sur deposits, and the Tamarugal anomaly.

Sample	Easting	Depth	Na (ppm)	Cu (ppb)	S (wt%)	$\delta^{34}\text{S}_{\text{CTD}}$ (‰)	Ca (%)	$\delta^{18}\text{O}_{\text{VPDB}}$ (‰)	$\delta^{13}\text{C}_{\text{VPDB}}$ (‰)
<i>Spence deposit</i>									
EMC030	476049		4550	96	0.15	3.9	4.08	1.55	3.57
EMC031	476004		7850	111	0.74	4.9	3.00	-0.09	3.25
EMC033	475907		55	110	0.05		1.31	-2.61	2.83
EMC034	475857		342	58	0.04		1.09	-0.30	3.87
EMC037	475758		188	49	0.20	4.8	3.95	2.09	4.23
EMC039	475659		94	60	0.04		1.04	-6.52	1.40
EMC044	475412		40	107	0.04		1.36	-1.69	3.77
EMC050	475030		134	46	0.04		1.05	-2.10	3.00
EMC051	474975		3820	53	0.70	4.7	2.38	-0.53	2.90
EMC088	474958		3620	84	0.17	4.5	2.54	-0.36	3.18
EMC052	474937		960	334	0.10	3.7	2.41	2.90	3.58
EMC086	474855		59	216	0.05		1.18	-1.62	3.11
EMC055	474791		3520	136	0.05		0.90	-1.76	3.33
EMC057	474698		2880	122	0.05	4.3	2.09	0.15	3.01
EMC062	474425		50	95	0.05		1.30	-2.12	3.04
EMC068	474134		30	49	0.04		1.23	-2.72	2.59
EMC079	473595		45	53	0.04		1.29	-0.86	3.59
EMC507	474959	95				4.76		-1.86	3.24
EMC515	474959	95				5.63		-2.37	2.47
EMC525	474959	95				5.29		-0.29	3.04
EMC559	474939	95				4.27		-3.86	3.39
EMC570	474939	5				3.40		-7.53	2.16
EMC574	474939	45				4.97		-3.79	3.02
EMC579	474939	95				5.51		-0.40	2.67
EMC607		95				5.09		0.06	3.64
<i>Salar southwest of the Spence deposit</i>									
S004					2.86	3.80	0.63		
S005					2.85	3.80	0.63		
S006					1.27	3.40	0.64		
S007					1.01	3.20	0.16		
S008					2.19	2.90	0.23		
					0.99	4.50	0.18		
<i>Gaby Sur deposit</i>									
EMC125	517200		30	15	4.90*	4.9	9.49	-4.42	6.30
EMC126	517250		35	14	9.50*	5.9	9.57	-5.79	7.69
EMC127	517300		5080	54	2.61	6.1	4.58	-8.63	0.23
EMC128	517350		25	10	12.60*	5.3	9.27	-5.51	8.04
EMC129	517400		5400	65	1.29	5.7	2.78	-8.13	-0.73
EMC130	517450		5980	71	0.25	7.5	2.22	-0.79	2.77
EMC131	517500		50	13	10.80*	5.2	9.52	-6.68	6.69
EMC132	517550		55	11	3.6	5.3	6.62	-2.89	6.01
EMC133	517600		64	10	9.20*	6.1	8.69	-7.75	3.86
EMC134	517650		8790	92	0.23	4.4	1.10	-0.94	3.50
EMC135	517700		50	6	9.05*	3.8	8.71	-4.91	7.63
EMC136	517750		144	8	12.10*	4.1	8.43	-6.16	5.78
EMC137	517800		79	10	4.95*	5.8	8.21	-1.67	5.83
<i>Tamarugal anomaly</i>									
EMC610	453460	40	0.96	175	3.1	3.3	3.62	-5.07	-4.28
EMC611	453558	40	5.49	553	6.7	2.7	2.27	-5.34	-3.38
EMC612	453658	40	1.56	190	3.7	2.2	3.25	0.26	-3.37
EMC613	453757	40	1.26	184	2.4	3.4	3.00	-4.48	-3.18
EMC614	453853	40	3.51	328	6.1	2.0	4.02	-5.04	-3.41
EMC615	453963	40	0.34	141	2.3	3.6	3.59	-4.40	-3.13
EMC616	454050	40	0.18	44	5.1	3.2	4.01	-2.56	-2.04
EMC618	454243	40	7.43	949	6.5	2.8	1.13	-5.57	-3.65
EMC619	454332	40	6.14	1110	8.7	3.5	2.47	-5.39	-3.72

* contains significant amount of gypcrete.

isotopically indistinguishable from those interpreted to have formed by “normal” soil processes, involving atmospheric CO_2 (see Section 5) (Figs. 4 and 5A and C). For $\delta^{18}\text{O}_{\text{VPDB}}$ values of soil carbonates, there is a statistically significant difference between the type ‘A’ and ‘B’ carbonates, at the 99% confidence level (i.e., $p < 0.001$; Fig. 5A). The ‘Type B’ samples above the fracture zones range from -0.5‰ to 2.9‰ , whereas the ‘Type A’ samples range from -6.5‰ to -0.3‰ .

Only a small number of soil samples above the Spence deposit contained sufficient SO_4 for a determination of the S isotope value; all are type B soils (Fig. 5D). The $\delta^{34}\text{S}$ values have little variation, in the range $3.7\text{--}4.9\text{‰}$ and there is no statistically significant

difference between the samples collected over the Spence fracture zone and those collected over the Eastern fracture zone (Fig. 4A). In Spence deposit groundwaters, there is a statistically significant negative correlation between $\delta^{18}\text{O}_{\text{VSMOW}}$ and $\delta^{34}\text{S}$ values (Fig. 6) (Leybourne and Cameron, 2006a). The soils above both fracture zones plotted in terms of these isotope ratios, fall within the groundwater array (Fig. 6).

To investigate vertical variations in geochemistry of the soils, three sets of trenches were dug, two in the deposit fracture zone (sites 51 and 54) and one in a background area to the west (site 74). Six profiles in total were sampled from sites 51 and 54. These

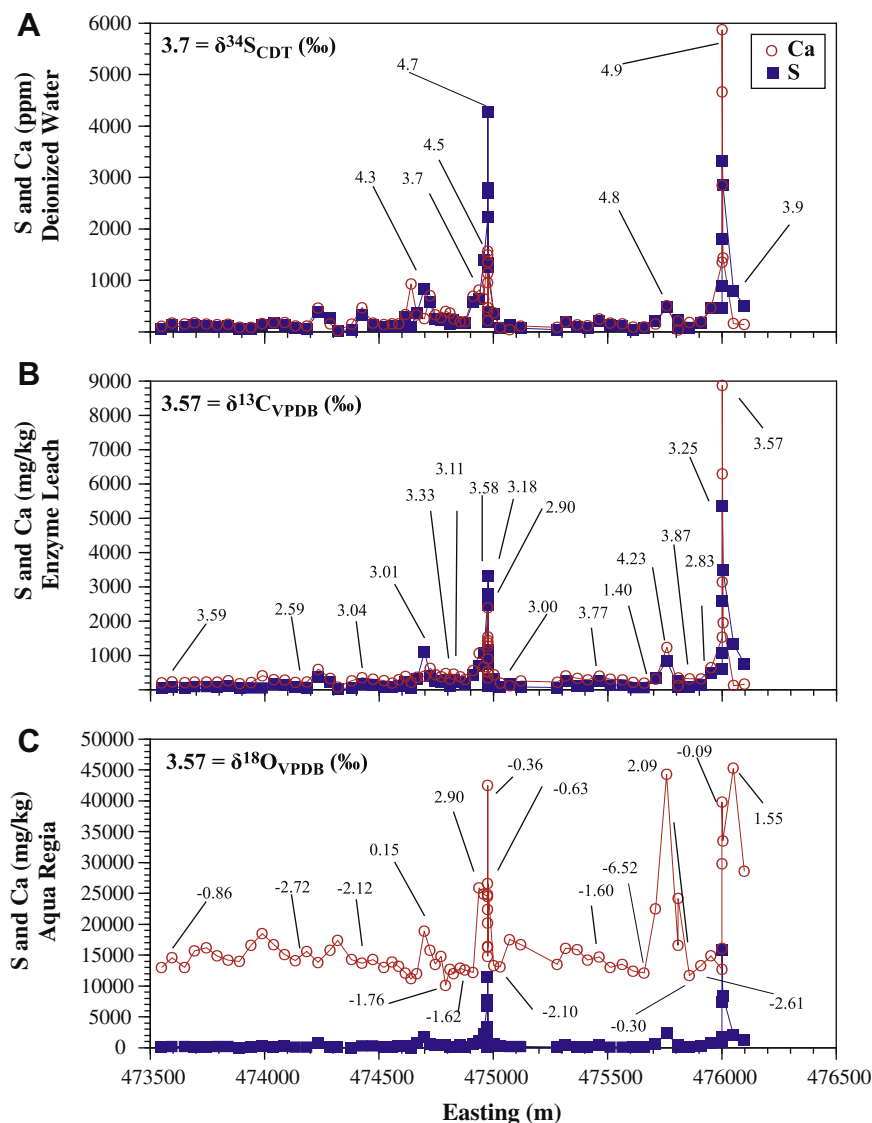


Fig. 4. Results for $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ for selected soil samples from an east–west traverse across the Spence deposit superimposed on plots showing the contents of Ca and S by (A) deionized water leach, (B) enzyme leach, and (C) aqua regia. Numerical values inside each plot are $\delta^{34}\text{S}$ (‰) for total S (A), $\delta^{13}\text{C}$ (‰) for carbonate (B), and $\delta^{18}\text{O}$ (‰) for carbonate, respectively. See Fig. 2 for idealized cross section of the Spence Deposit showing fracture zones.

profiles are at 10 cm intervals from 0–10 cm to 90–100 cm (Fig. 7). The median values for water-soluble S for these six profiles are 490 ppm S in the 0–10 cm interval, increasing downwards to 1629 ppm S at 90–100 cm depth. For the background profile (site 74), water-soluble S was 170 ppm in the 0–10 cm interval, decreasing to 61 ppm S in the 90–100 cm depth interval. Species associated with groundwater-deposit interaction show different depth profiles (Fig. 7). Species dissolved as metal cations, such as Cu, show peaks in the surface soils, and decrease with depth. By contrast, more water-soluble (labile) species, including S (not shown), Se and Na show maximum contents at 80–100 cm depth (Fig. 7). A limited number of samples at sites 51 and 74 were also analyzed for the isotopic composition of carbonate and sulfate (Table 1). There are no systematic trends observed in the data, which are broadly consistent with values seen in the surface profiles.

4.2. Gaby Sur deposit

Over both boundary faults, there are distinct anomalies for water-soluble Na and Cl and for Cu by Enzyme Leach (Fig. 8).

There are also peaks for elements similar to those found at the Spence deposit: As, I, Mo, Se and Re (Se shown in Fig. 9). In soil pits, the calcrete-cemented gravels are fractured in these saline zones, also similar to the Spence deposit. For the isotope study, soil samples were selected from a traverse along a line 517200E to 517800E. This interval brackets the anomalous and non-anomalous soils that lie above the boundary fault to the west of the Gaby Sur deposit. The soils at the Gaby Sur deposit differ from those at the Spence deposit in that many samples contain gypsum, consistent with elevated S concentrations, up to 126,000 ppm (12.6% S) compared to 7400 ppm S at the Spence deposit. Gypcrete, of presumed atmospheric origin, is widely present throughout the Atacama Desert. Four samples contain elevated salt (Na) and Cu (Fig. 9). $\delta^{13}\text{C}$ values for carbonate have a greater range (-0.7‰ to $+8\text{‰}$) than those for the Spence deposit (Figs. 5 and 9). $\delta^{18}\text{O}_{\text{VPDB}}$ values also have a wider range (-8.6‰ to -0.8‰) in the soils at the Gaby Sur deposit than at the Spence deposit (Fig. 5). Only a small number of samples containing gypsum at Gaby Sur were analyzed for $\delta^{34}\text{S}$, with values ranging from 3.8‰ to 6.1‰.

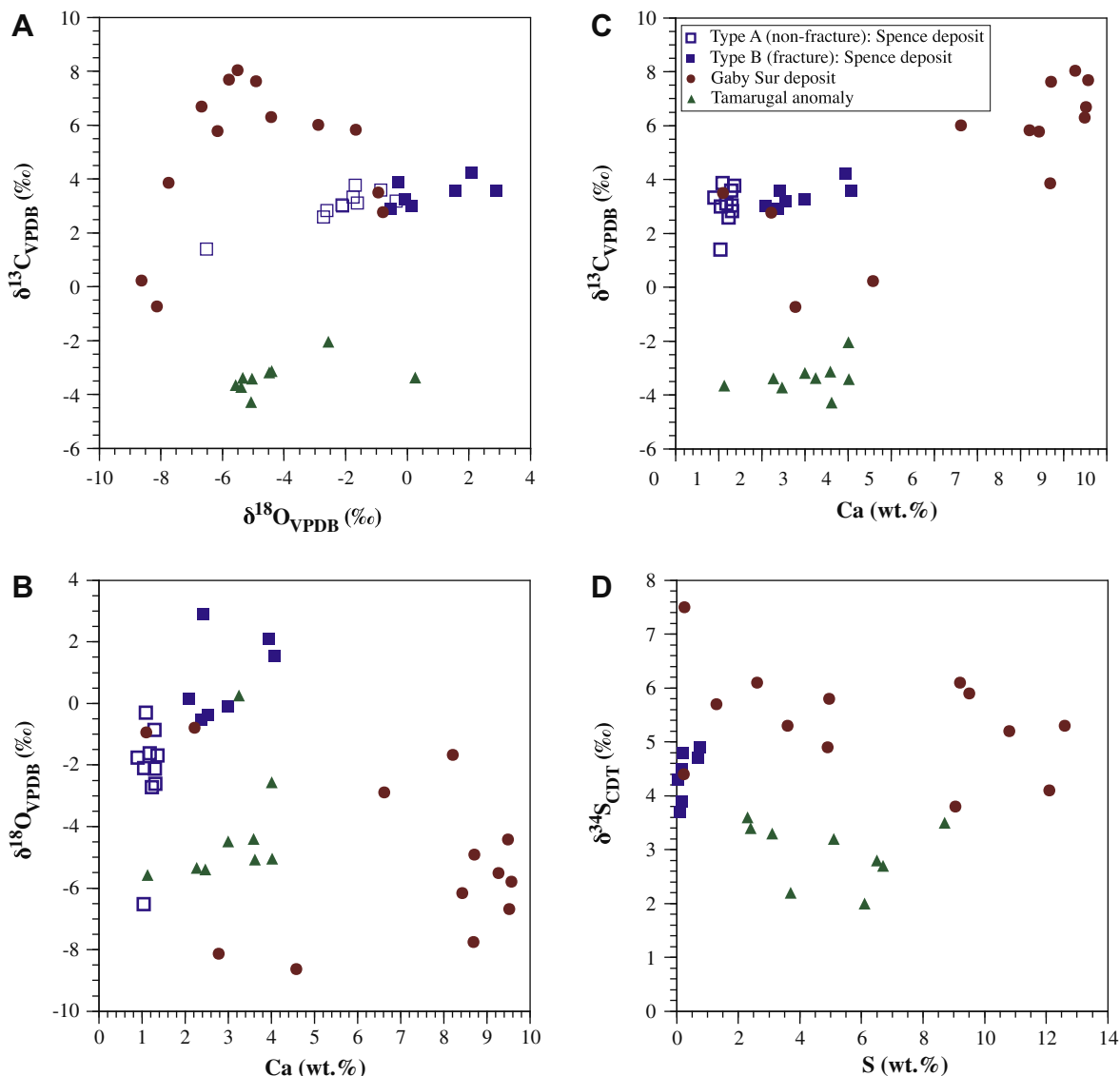


Fig. 5. Plots of (A) $\delta^{13}\text{C}$ vs. $\delta^{18}\text{O}$, (B) $\delta^{13}\text{C}$ vs. Ca, (C) $\delta^{18}\text{O}$ vs. Ca and, (D) $\delta^{34}\text{S}$ vs. S for pedogenic carbonate and sulfate from the Spence deposit, Gaby Sur deposit, and Tamarugal anomaly.

4.3. Pampa del Tamarugal

Isotope measurements were carried out on selected soil samples from a line across the Tamarugal anomaly, defined by Leybourne and Cameron (2006b). In addition to halite, the samples contain varying amounts of gypsum (i.e., elevated S; Table 1). Results show that Tamarugal anomaly samples have higher salt contents than those from either the Spence or Gaby Sur deposits, with up to 7.4% Na, or ~19% NaCl (Table 1). Sulfur is comparable in concentration to the soils at the Gaby Sur deposit (Table 1), but is more evenly distributed than the latter. The most significant feature of the Tamarugal anomaly soils compared to those at the Spence and Gaby Sur deposits is the depletion of $\delta^{13}\text{C}$ in soil carbonates from the Tamarugal anomaly (Figs. 5 and 10). The Tamarugal anomaly soils have $\delta^{18}\text{O}$ values that are lower than Type A soils at the Spence deposit, but broadly similar to those at the Gaby Sur deposit (-5.6‰ to 0.3‰), and $\delta^{34}\text{S}$ lower than both of these deposits ($2.0\text{--}3.6\text{‰}$) (Fig. 5).

4.4. Partial leaches

Based on the soil isotope data presented above, there appear to be quite different controls on accumulation of salts and respective isotopic signatures for each deposit. These differences are also reflected in the differential accumulation of various species in the soils (Fig. 11). Accumulations of salts derived entirely from atmospheric deposition would not be expected to have anomalous accumulation of metals and metalloids associated with porphyry Cu mineralization. Previous studies have suggested that S/Se values are elevated where associated with sedimentary sources/marine sources (away from metal deposits) and decrease towards the deposits, owing to the increased contribution of magmatic/hydrothermal sources with low S/Se (Cameron et al., 1995). For the water leach, soils at the Spence deposit show an inverse relationship between S/Se and Cu content, consistent with significant accumulation of SO_4 in the soils from groundwater (Fig. 11A), and consistent with higher Cu/S values than for the Gaby Sur Deposit

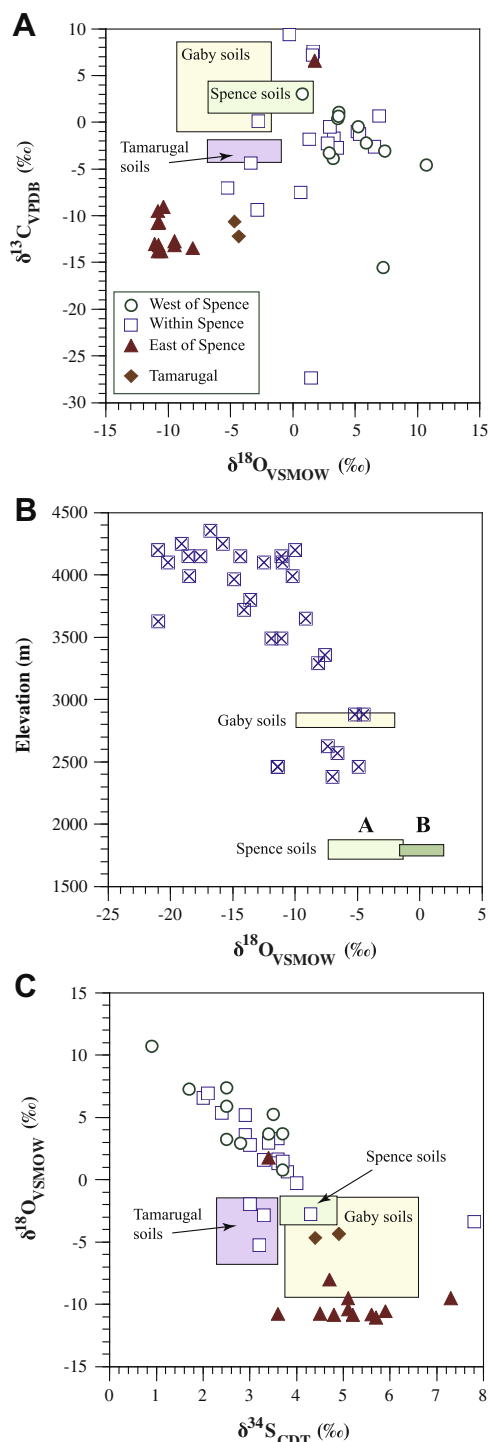


Fig. 6. (A) Plot of $\delta^{13}\text{C}$ vs. $\delta^{18}\text{O}$ for groundwaters from within the Spence deposit and east (upflow) and west (downflow) of the deposit (data from Leybourne and Cameron, 2006a). Similar values for Tamarugal anomaly waters are also shown (data from Leybourne and Cameron, 2006b). Boxes show the range of composition for soil carbonates from the Spence deposit, Gaby Sur deposit, and Tamarugal anomaly (Aravena et al., 1999). (B) Squares show $\delta^{18}\text{O}_{\text{VSMOW}}$ vs. altitude for rain in northern Chile (Cerling et al., 1999). For the Spence deposit, boxes show range for 'Type A' and 'Type B' carbonates, and for the Gaby Sur deposit, all carbonates. The measured values of $\delta^{18}\text{O}$ for the carbonates have been converted to the equivalent values of $\delta^{18}\text{O}$ for waters using the regression line from Cerling (1984). (C) Plot of $\delta^{18}\text{O}$ vs. $\delta^{34}\text{S}$ for Spence deposit groundwaters (data from Leybourne and Cameron, 2006a). Superimposed is a box containing the range in values for carbonate- and sulfate-bearing soils above the Spence and Eastern fracture zones and for the soils at the Gaby Sur deposit and Tamarugal anomaly. The measured values of $\delta^{18}\text{O}$ for the carbonates have been converted to the equivalent values of $\delta^{18}\text{O}$ for waters using the regression line from Cerling (1984).

and Tamarugal anomaly (Fig. 11D). Soils above the Gaby Sur deposit mostly have elevated S/Se values and relatively low labile Cu contents, with the exception of those directly over fractures (Fig. 11). Both the Spence deposit and the Tamarugal anomaly have elevated As and S contents with higher As/S values than the Gaby Sur deposit (Fig. 11B). Although I is commonly associated with the accumulation of marine aerosols, I is also abundant in saline groundwaters and groundwaters associated with geothermal/hydrothermal systems. Soils above the Gaby Sur Deposit have low abundances of I and Cu compared to those above the Spence deposit and at the Tamarugal anomaly (Fig. 11C).

5. Discussion

5.1. Origin of soil calcite

Typically, soil carbonate forms in relatively dry soils (arid to sub-humid climates) dominated by grass and mixed grass/shrub environments where evaporation or evapotranspiration of soil water leads to supersaturation with respect to calcite (Cerling, 1984; Cerling and Quade, 1993). These environmental conditions result in soil pH values ≥ 7 , and pedogenic carbonate is most common where rainfall is < 75 cm/a (Cerling, 1984). Although complicated by a variety of processes, the O isotope composition of soil carbonate is determined by that of *in situ* soil waters, which reflect the O isotope composition of local meteoric precipitation (Cerling, 1984; Cerling and Quade, 1993). The relationship between the O isotope composition of soil carbonates and meteoric water can be described by the following equation (Cerling, 1984):

$$\delta^{18}\text{O}_{\text{VPDB}}(\text{soil carbonate}) = 1.015 \cdot \delta^{18}\text{O}_{\text{VSMOW}}(\text{meteoric water}) + 1.15 (R^2 = 0.969) \quad (1)$$

The isotopic composition of $\delta^{13}\text{C}$ in soil carbonate is primarily governed by the local proportions of C_3 and C_4 plants and the respiration rates of CO_2 in the soils (Cerling and Quade, 1993; Quade et al., 2007). Most soils have plants and bacteria that release CO_2 more depleted in ^{13}C than atmospheric CO_2 . Cerling (1984) showed that atmospheric CO_2 is only significant in controlling the $\delta^{13}\text{C}$ value of soil carbonate at depths < 10 cm or where soil respiration rates are low. For the Atacama Desert locations described here that have no vegetation, we suggest that the effects of plant respiration can be neglected, so that the dominant source of CO_2 in the soil carbonates is atmospheric CO_2 . Modern, pre-industrial CO_2 , based on ice core measurements in Antarctica, has a $\delta^{13}\text{C}$ of -6.5‰ and this is assumed to have been relatively constant throughout the last 100 Ma (Ekart et al., 1999). The isotopic fractionation between $\text{CO}_{2(\text{g})}$ and carbonate is -10.4‰ $\delta^{13}\text{C}$ at 25°C (Bottinga, 1969). Thus, modern soil carbonate formed at 25°C in equilibrium with atmospheric CO_2 has a value for $\delta^{13}\text{C}$ of ca. 3.9‰ . A recent study of hypolithic (cyanobacteria) communities on surface pebbles along a rainfall gradient transect of the Atacama Desert found that in its hyperarid core, the Atacama Desert is essentially devoid of significant life (Warren-Rhodes et al., 2006).

For Spence deposit soils, Ca was extracted using ammonium acetate, which specifically dissolves carbonate. Two types of carbonate have been identified at the Spence deposit; 'Type A' carbonates have a lower range of Ca contents (Fig. 4) that we suggest represents carbonate precipitated by "normal" soil-forming processes for the hyperarid Atacama Desert. In this case, the weathering of clastic silicate minerals releases Ca^{2+} , which combines with carbonate species formed by the dissolution of atmospheric CO_2 in percolating rainwater with subsequent evaporation driving soil waters towards supersaturation and precipitation of calcite. Additional CaCO_3 that occurs over the fracture zones ('Type B'

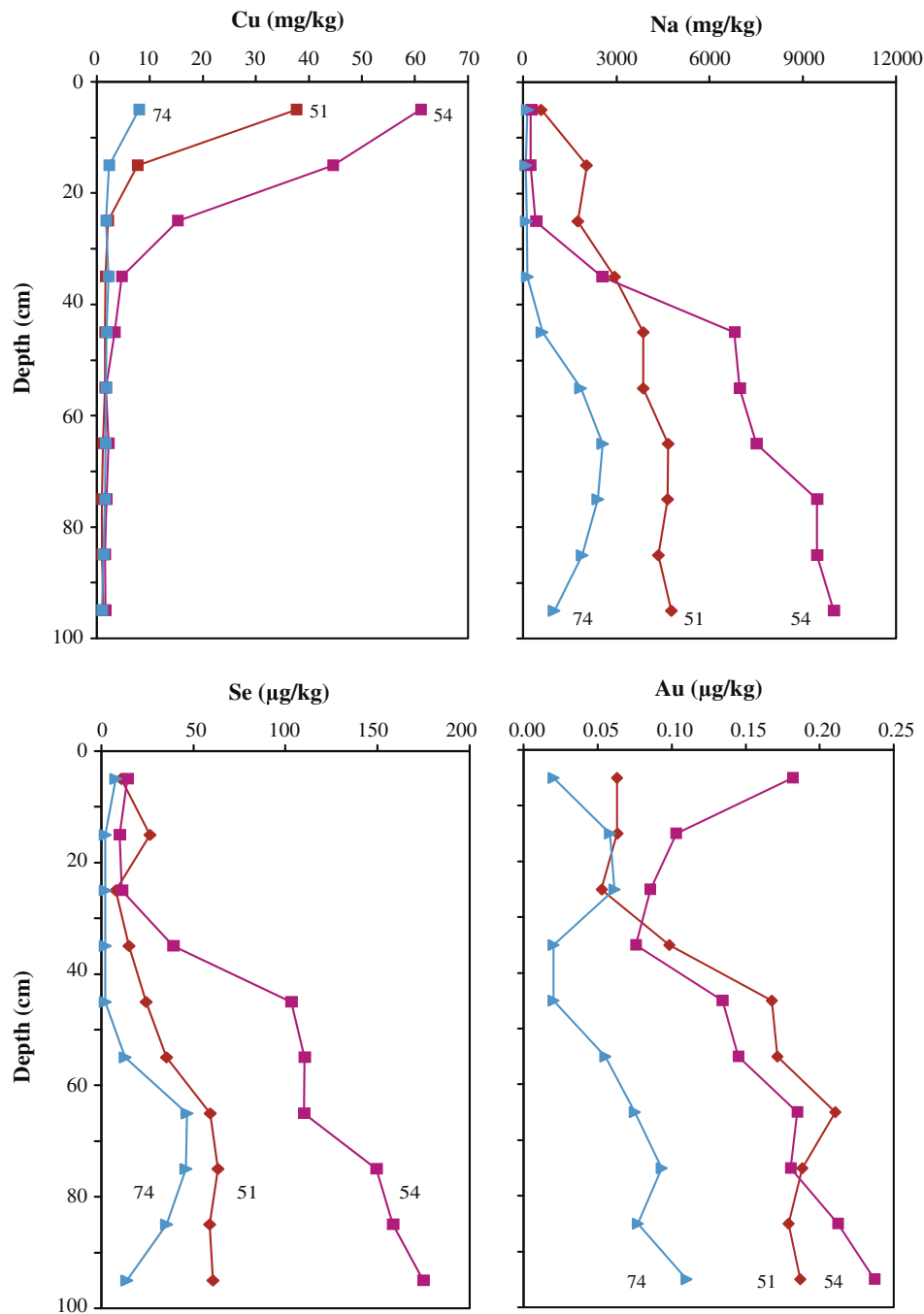


Fig. 7. Profiles of Cu, Na, Se and Au with depth from three trenches across the Spence deposit. Line 74 represents a background (distal from mineralization) site, line 54 is from directly over mineralization, and line 51 is from the eastern margin of mineralization. Species fixed to oxides (Cu, Au) remain elevated near the surface, whereas more labile species (Se, Na) are displaced down the profile by infrequent rains.

carbonate) is interpreted as partially coming from groundwater that was pumped to the surface during earthquakes (see below).

The average $\delta^{13}\text{C}$ value of Spence deposit soil calcite is 3.2‰, which is close to the value (3.9‰) expected for carbonate that has equilibrated with atmospheric CO_2 in a modern, pre-industrial atmosphere with $\delta^{13}\text{C}$ of -6.5‰. Dissolved inorganic C (DIC; i.e., HCO_3^-) in groundwaters from the Spence deposit shows a wide range of $\delta^{13}\text{C}$, ranging from -15‰ to +9.4‰ (Fig. 6; note one sample at -28‰) (Leybourne and Cameron, 2006a). In part, this wide range likely reflects the oxidation of sulfide minerals serving as an energy source for bacteria, which fractionate DIC. Some groundwater samples are saturated in $\text{CO}_{2(g)}$ compared to the atmosphere.

If CO_2 has degassed from Spence deposit groundwaters, rising through the fracture zone in the gravels, this gas could have been incorporated into carbonate (Type B) in the soils directly above the deposit, giving type B carbonate a different C isotope composition from that which had equilibrated with atmospheric CO_2 (i.e., Type A carbonate). Fig. 6A shows a field containing the range of $\delta^{13}\text{C}$ values for the soil carbonates within Spence deposit soils projected onto a plot of Spence deposit groundwaters. The majority of the Spence deposit groundwaters have pH values above 6.4, the pH at which HCO_3^- becomes the dominant component of DIC. This dominance of HCO_3^- permits a direct comparison of $\delta^{13}\text{C}$ values between the groundwater and the soil carbonates. If CO_2 had

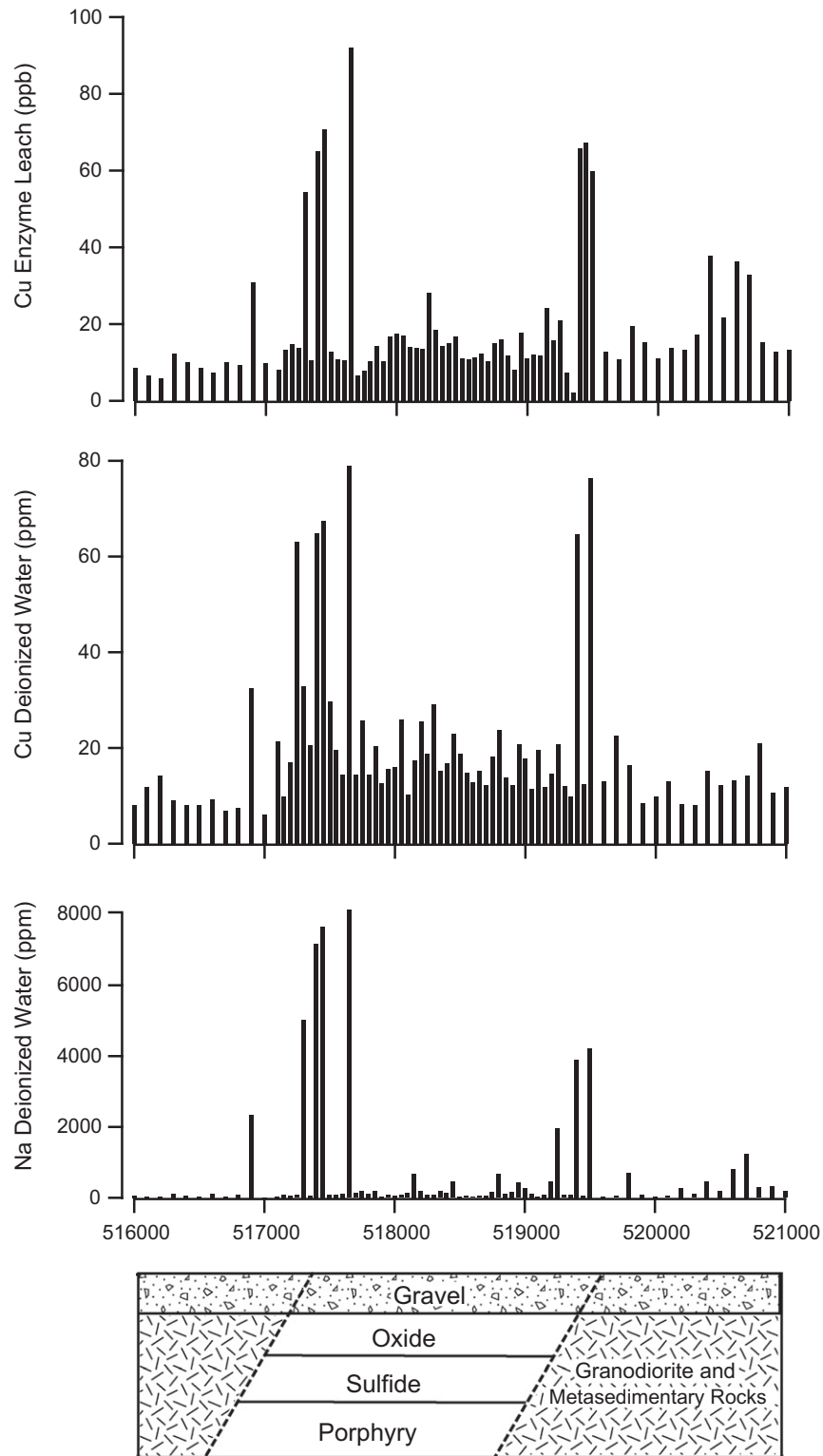


Fig. 8. Sodium, after dissolution by deionized water and Cu after dissolution by Enzyme Leach and deionized water, in soils along an east–west traverse across the Gaby Sur deposit.

degassed from the groundwaters, the CO_2 would have been lighter in ^{13}C by about 10‰ relative to the principal HCO_3^- component of dissolved inorganic C. The narrow range of $\delta^{13}\text{C}_{\text{VPDB}}$ for the soil carbonates, relative to that in groundwater, and the lack of differentiation between soil carbonates over the fracture zones and those elsewhere along the traverse, indicate that CO_2 degassed from groundwater is unlikely to have been involved in the formation

of the soil carbonates. Therefore, data strongly suggest that C in soil carbonate is derived from atmospheric CO_2 .

Soil carbonates normally derive their O isotope composition from that of local precipitation (Cerling, 1984; Cerling and Quade, 1993). Values of $\delta^{18}\text{O}_{\text{VSMOW}}$ for precipitation tend to become more negative with altitude (Fig. 6B) (Dansgaard, 1964; Aravena et al., 1999). The Spence deposit occurs at an altitude of 1700–1770 m

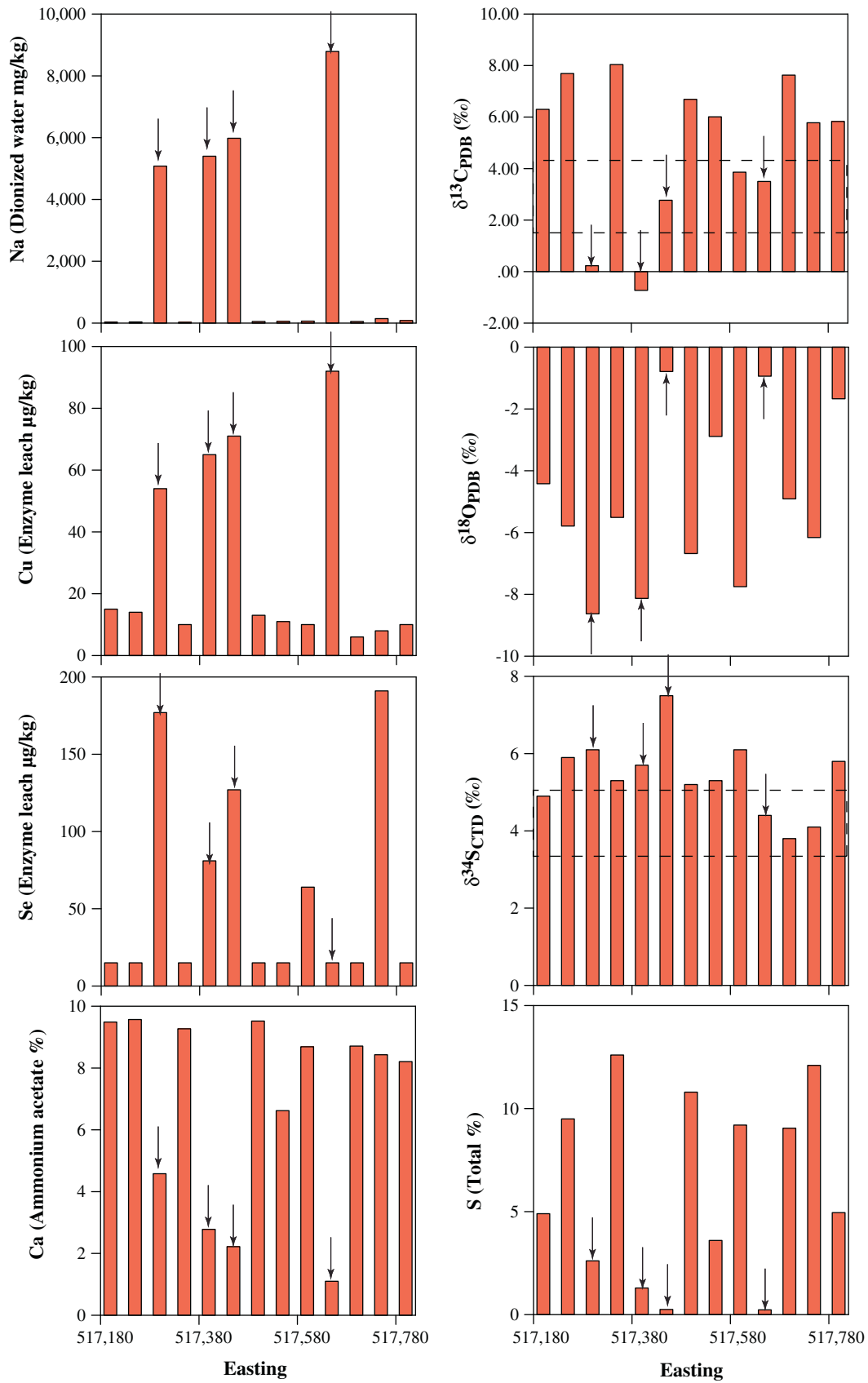


Fig. 9. Plots of Na, Ca, S, Cu, Se and $\delta^{34}\text{S}$ for sulfate, and $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ for carbonates in soils at Gaby Sur from 517200E to 517800. Arrows point to samples with high salt contents, which are interpreted to be areas where mineralized groundwater has reached the surface during earthquakes. Box on plots for $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$ indicates limits for similar data from the Spence deposit.

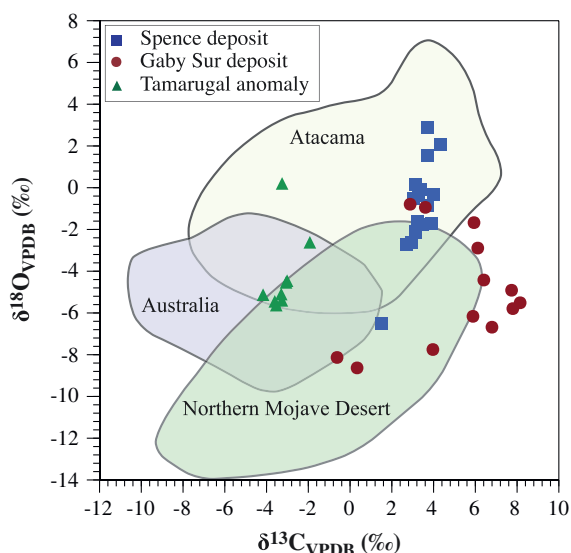


Fig. 10. Comparison between soils analyzed in this study from the core of the Atacama Desert (Spence, Gaby Sur, Tamarugal) with data from other parts of the Atacama Desert, Australia and the northern Mojave Desert (modified from Quade et al., 2007).

above sea level. After conversion to $\delta^{18}\text{O}_{\text{VSMOW}}$, the data for the soil carbonates not associated with fractures (Type A) at the Spence deposit are reasonably consistent with the data of Aravena et al. (1999) (Fig. 6B). The lowest altitude that these authors sampled was 2380 m, because of the difficulty in collecting precipitation over the hyperarid core of the Atacama Desert. It is possible that the difference in O isotope values between the type A and B carbonates is due to those above the fracture zones having equilibrated or partly equilibrated with saline groundwater, rather than with rainwater, consistent with the fact that the fractures are interpreted to serve as conduits for more saline fluids, with heavier $\delta^{18}\text{O}_{\text{VSMOW}}$ values than meteoric waters, propagated from depth through the deposit during seismic events (Cameron et al., 2002; Cameron and Leybourne, 2005).

Based on the present data, the $\delta^{18}\text{O}_{\text{VPDB}}$ values of soil carbonate at the Spence deposit can be interpreted as reflecting a mixture between meteoric fluids, saline fluids expelled at or near the surface during seismic events, and infiltration from rare local rainfall. This interpretation is consistent with elevated Na and Cl associated with the fractures (Fig. 2). Alternatively, Quade et al. (2007) suggested that evaporation of local meteoric fluids was likely the dominant control on the O isotopic composition of pedogenic calcite in the Atacama Desert, and further noted that in arid and hyperarid climates, evaporation would hinder the use of calcite $\delta^{18}\text{O}$ in paleoelevation reconstruction. It is noted that the samples with the heaviest $\delta^{18}\text{O}$ values at the Spence deposit occur directly over the fracture zone (Fig. 4). If the variation in calcite $\delta^{18}\text{O}$ values were dominantly controlled by evaporation, it is unclear why the soils would be heaviest over the fracture zones. However, if movement of saline fluids does influence soil carbonate isotopic compositions, it would add a further complication to paleoelevation reconstructions. Note also that the isotopic composition of the meteoric waters at the Spence deposit is primarily controlled by recharge in the high Andes, not by local precipitation (Cameron and Leybourne, 2005; Leybourne and Cameron, 2006a).

It is also possible that groundwater DIC is incorporated into pedogenic calcite over the fracture zones at the Spence deposit. Many of the groundwaters sampled from within the deposit at Spence have $\delta^{13}\text{C}$ values of around 0.0‰ (although ranging from -10‰ to +10‰; Fig. 6A). There is only a small C isotopic fraction-

ation between water and calcite (-0.9‰ at 25 °C; Mook et al., 1974) so the calcite that would form during evaporation of saline fluids would have a $\delta^{13}\text{C}_{\text{VPDB}}$ not much lighter than the saline fluids, assuming no fractionation of ^{12}C during evaporation and CO_2 degassing.

At the Gaby Sur deposit, it is doubtful that all the soil carbonates formed in equilibrium with atmospheric CO_2 . Two of the samples with elevated salt contents have low values for $\delta^{13}\text{C}$, which may derive from groundwater at the Gaby Sur deposit. Data for $\delta^{18}\text{O}_{\text{VSMOW}}$ also have a wider range in the soils at the Gaby Sur deposit than at the Spence deposit (Figs. 5 and 6). As a group, soils at the Gaby Sur deposit have isotopically heavier $\delta^{13}\text{C}$ compared to $\delta^{18}\text{O}$ than the soils at the Spence deposit (Fig. 5).

The Tamarugal anomaly soil carbonates are also interpreted to have derived part of their C from groundwater. Two groundwater samples from Tamarugal have $\delta^{13}\text{C}$ values of -10.6‰ and -12.2‰ for DIC (Leybourne and Cameron, 2006b). This is in the lower part of the range found for the Spence deposit groundwaters (Fig. 6A) and compares with values of -2.0‰ to -4.3‰ for Tamarugal anomaly soil carbonate and +1.4‰ to +4.2‰ for Spence deposit soil carbonate. The Tamarugal anomaly carbonates are, therefore, interpreted to be a mixture of DIC from groundwater and carbonate that has equilibrated with atmospheric CO_2 . Calculated values of $\delta^{18}\text{O}_{\text{VSMOW}}$ for Tamarugal anomaly carbonates overlap those for the local groundwaters (Fig. 6).

Taking the three locations together, the primary influences on the C and O isotopic composition of soil carbonate above Cu ore deposits and geochemical Cu anomalies of the Atacama Desert appears to be dominated by atmospheric CO_2 , with minor to significant influence from local groundwaters, depending on location and presence/absence of fractures and faults. Biologically respired, soil zone CO_2 appears to have little impact on the $\delta^{13}\text{C}$ values of the soil carbonates owing, in large part, to the lack of surface vegetation and minimal to non-existent soil development (see also Rissmann, 2003; Quade et al., 2007).

It is also possible that the shift to significantly heavier C isotopic values for calcite in soils at the Spence and Gaby Sur deposits may have resulted from evaporative enrichment (Stiller et al., 1985; Potter et al., 2004). As discussed by Cerling (1984), precipitation of carbonate in soils is considered to result from evaporation, evapotranspiration, and lowering of P_{CO_2} (degassing). For soil calcite formation in most environments, evaporation will not be a significant contributor because the presence of vegetation results in evapotranspiration being predominant (Cerling, 1984). However, in the hyperarid core of the Atacama desert, evaporation has the potential to affect both the $\delta^{18}\text{O}$ values (Cerling, 1984) and the $\delta^{13}\text{C}$ values (Stiller et al., 1985; Potter et al., 2004). Rech et al. (2003a) has documented Atacama Desert soil carbonate isotopic compositions near the coast (<1000 m elevation) and at higher elevations in the Andes (2500–4000 m elevation). Values for $\delta^{13}\text{C}$ ranged from -8.2‰ to +7.9‰ and for $\delta^{18}\text{O}_{\text{VPDB}}$ from -6.0‰ to +7.0‰ (Rech et al., 2003a). Rech et al. (2003a) suggested that evaporation may have influenced the C and O isotopic composition of the isotopically heavier carbonates. Although difficult to quantify owing to the lack of good estimates of the fractionation factors for ^{13}C during evaporation and loss of CO_2 , the $\Delta^{18}\text{O}_{\text{VPDB}}/\Delta^{13}\text{C}_{\text{VPDB}}$ value for the soil carbonates studied by Rech et al. (2003a) is ~ 1 , similar to values expected under normal pedogenic calcite formation (Cerling, 1984). In contrast, the $\Delta^{18}\text{O}_{\text{VPDB}}/\Delta^{13}\text{C}_{\text{VPDB}}$ for Spence deposit soils is ~ 3 , suggesting greater fractionation of O.

5.2. Origin of soil gypsum

Rech et al. (2003b) reported S and Sr isotopic compositions of soil gypsum and calcite collected along three transects from the coast towards the Andes in the Atacama Desert. They interpreted

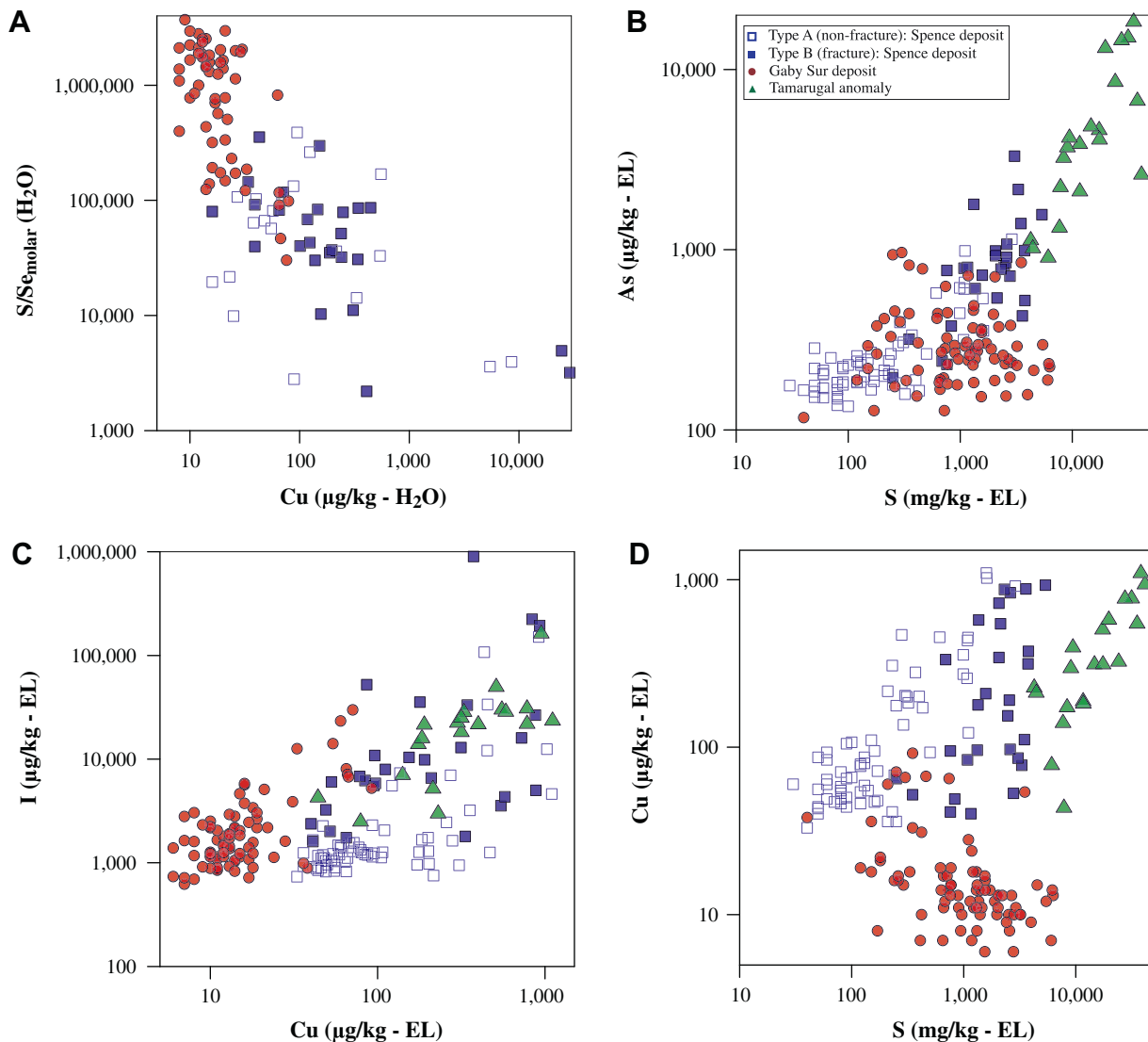


Fig. 11. Plots of (A) S/Se vs. Cu, (B) As vs. S, (C) I vs. Cu, and (D) Cu vs. S for weak partial leaches for soils associated with the Spence and Gaby Sur deposits and the Tamarugal anomaly. Soils at the Spence deposit are elevated in Cu, Se and I from earthquake-induced movement of groundwaters to surface and have elevated Cu/S values relative to the Tamarugal anomaly owing to more proximal porphyry Cu source. The Tamarugal anomaly has elevated S, As, I and Cu owing to long periods of evaporation of groundwater. Most of the soils at the Gaby Sur deposit have low I, Cu and As and elevated S/Se because they are dominated by atmospheric deposition over groundwater addition.

soils with $\delta^{34}\text{S}$ values $>14\text{‰}$ (i.e., values approaching modern sea-water with $\delta^{34}\text{S} = 20.9\text{‰}$; Rees et al., 1978; Claypool et al., 1980), as having been dominantly influenced by marine aerosols (primarily by coastal fog). In contrast, soil gypsum with $\delta^{34}\text{S}_{\text{CDT}}$ values between $+5\text{‰}$ and $+8\text{‰}$ is interpreted to represent dust redistributed from salars. Salars and rare streams in the Atacama Desert have average $\delta^{34}\text{S}_{\text{CDT}}$ values of $5.4 \pm 2\text{‰}$, with a range of $2.9\text{--}8.7\text{‰}$ (Rech et al., 2003b) and waters and sulfates from the Salar de Atacama exhibit a similar range, i.e., $5.9 \leq \delta^{34}\text{S} \leq 9.0\text{‰}$ (Carmona et al., 2000). Likewise, groundwaters from in and around the Salar de Punta Negra, near Mina Escondida, have $\delta^{34}\text{S}$ values ranging from $+3.0\text{‰}$ to $+8.3\text{‰}$ (Rissmann, 2003). In addition, the Central Depression (Fig. 1) hosts remnants of the Hilaricos and Soledad formations (Upper Miocene and Pliocene continental evaporites) that have $\delta^{34}\text{S}$ values between $+4.5\text{‰}$ and $+9\text{‰}$, consistent with an origin dominantly from volcanic influence (Pueyo et al., 2001). The characteristically positive and relatively homogenous isotopic values for dissolved SO_4 and gypsum/anhydrite in groundwaters and salars of the Atacama Desert have also been attributed to the isotopic enrichment of SO_4 during the oxidation of S in shallow epi-

thermal systems related to local volcanic activity (Pueyo et al., 2001).

Leybourne and Cameron (2006a) have previously interpreted the S isotopic composition of Spence deposit groundwaters as resulting from mixing between the dilute regional groundwaters flowing into the deposit from the east, with $\delta^{34}\text{S}$ typical of the interior of the Atacama Desert and recharge in the high Andes ($+4.5\text{‰}$ to $+9\text{‰}$), and lighter S derived from (a) more saline (formation) waters; and (b) dissolution of hypogene and/or supergene sulfides in the deposit, with the latter likely dominating this end member. There are no data on the isotopic composition of hypogene sulfides or supergene sulfides and sulfates at the Spence deposit, although data are available for similar deposits in northern and central Chile. Hypogene sulfides at the Mantos Blancos, El Teniente, Río Blanco-Los Bronces and El Salvador Cu deposits, for example, have average $\delta^{34}\text{S}_{\text{CDT}}$ values of -1.4‰ , -1.0‰ , -1.1‰ , and -3.0‰ , respectively (Field and Gustafson, 1976; Dold and Spangenberg, 2002; Ramirez et al., 2006). The same authors report that supergene sulfates at El Salvador had $\delta^{34}\text{S}$ values of -0.7‰ , whereas averages of hypogene sulfates at the three deposits ranged from 10.2‰ to 11.9‰ .

In Spence deposit groundwaters, there is a good correlation between $\delta^{18}\text{O}_{\text{VSMOW}}$ and $\delta^{34}\text{S}$ (Fig. 6C). The soils above both fracture zones, when plotted in terms of these isotope ratios, fall within the array, which is consistent with the derivation of the SO_4 from local groundwater. As discussed above, this interpretation does not appear to be supported by the C isotope composition of the soil carbonate. However, groundwater migrated to the surface during seismic events will have, in terms of mass balance, much higher S and O relative to atmosphere compared to dissolved C. DIC in the Spence deposit groundwaters is commonly lower relative to atmospheric sources (Leybourne and Cameron, 2006a); although it is the latter that are most likely to dominate the isotopic signature of soil carbonate minerals. Soil samples were also collected from a salar SW of Spence into which the groundwaters for the region discharge. These salar samples were analyzed for S by Enzyme Leach and for S isotope ratios, and have a mean $\delta^{34}\text{S}$ value of 3.6‰ (Table 1). The salar samples have $\delta^{34}\text{S}$ values similar to the mean value for the soils at the Spence deposit (4.4‰). Hartley and May (1998) suggested that gypcrete in the Atacama Desert that is present beneath a 9.5 Ma ignimbrite is Miocene; after 9.5 Ma, the Atacama Desert was hyperarid, which they suggest impedes the formation of gypcrete. However, they do not take into account the possibility of earthquake-induced groundwater migration to the surface (Section 5.3 below). Furthermore, the present isotopic and geochemical data for soil carbonate and gypsum (Fig. 5) and groundwaters from the Tamarugal anomaly (Leybourne and Cameron, 2006b) are consistent with long term accumulation of salts from groundwater, coupled with gradual lowering of the water table as the Rio Loa incised. Young, on-going supergene mineralization is also suggested by groundwater data at Spence and dating of atacamite (Cameron et al., 2007; Leybourne and Cameron, 2008; Reich et al., 2008, 2009).

The $\delta^{34}\text{S}$ values for the Gaby Sur deposit soils (3.8–6.1‰) may suggest ore-associated input. The implications of the data are that it is not possible to distinguish between the sources of S in gypsum from S of local porphyry origin. Rech et al. (2003b) reported an isotopic study of soil gypsum from the Atacama Desert, with samples collected along a traverse from the coast inland. Near the coast more than half of the S is of marine origin with $\delta^{34}\text{S}$ values >14‰, i.e., similar to the Namibian gypcrettes (Eckardt and Spiro, 1999). Inland, $\delta^{34}\text{S}$ values ranged from 5.0‰ to 8.0‰, which are similar to the values obtained from soils at the Gaby Sur deposit. These values also resemble those obtained from the salars, $\delta^{34}\text{S}$ values of $5.4 \pm 2\%$, suggesting that the gypsum is the result of aeolian redistribution of salts from the salars. However, aeolian features, such as dunes, are rare in the Atacama Desert and the even distribution of gypsum over wide areas and its occurrence on the slopes and tops of hills argue against this interpretation. There is also a wider range in $\delta^{34}\text{S}$ values for SO_4 at the Gaby Sur deposit compared to the Spence deposit (Fig. 5), but these do not discriminate between SO_4 present in gypsum from that which may be derived from the oxidation of igneous sulfide and brought to the surface in mineralized groundwater.

The gypsum at the Gaby Sur deposit is interpreted to be of atmospheric origin derived from the SO_4 -rich fog. On hill slopes in this region, the amount of gypsum increases with height until thin soils over decomposed bedrock are commonly largely comprised of massive gypsum overlain by a pebble and sand carapace. The fog condensates are essentially a weak solution of H_2SO_4 , with pH as low as 3.5 (Schemenauer and Cereceda, 1992). The weak acid can attack soil minerals, decomposing silicates and carbonates to release Ca, which reacts with SO_4 to produce gypsum. Gypcrettes also occur in the hyper-arid Namib Desert of Namibia, located inland from the Atlantic Ocean and the cold Benguela Current, analogous to the Atacama Desert, the climate of which is influenced by the cold, north-moving Humboldt Current (Hartley and Chong,

2002). The Namibia gypcrettes have distinctive $\delta^{34}\text{S}$ values in the range 13.0–18.8‰, taken to indicate derivation from marine dimethyl sulfide (DMS), which has been incorporated into fog generated over the cold ocean water (Eckardt and Spiro, 1999). Atmospheric condensate collected by these authors on the Atlantic shore had a $\delta^{34}\text{S}$ value of 15.9‰. The Namibian gypcrettes also have an excess of ^{17}O (Bao et al., 2001a,b), which is interpreted to be due to the oxidation of reduced S in the atmosphere by O_3 and/or H_2O_2 , both of which also have excess ^{17}O .

The $\delta^{34}\text{S}$ values of the soils at the Tamarugal anomaly are isotopically lighter than the corresponding groundwaters (Fig. 6). Gypsum of atmospheric origin is well developed in the Tamarugal area, suggesting that part of the material analyzed for S isotopes was derived from the atmosphere (Rech et al., 2003b). But, like those at the Gaby Sur deposit, there is no distinct “marine” dimethyl sulfide isotopic signature in the range 13–19‰ that characterizes gypsum close to the Pacific coast (Rech et al., 2003b). The S isotopic composition of the soils in the Tamarugal anomaly may, therefore, reflect distal sulfide mineralization, consistent with the interpretations based on the porphyry deposit associated metal contents and Se/S values of the soils (Leybourne and Cameron, 2006b).

5.3. Earthquake-induced groundwater flow and application of soil isotopes to mineral exploration

Soil anomalies over the Spence deposit and the eastern fracture zone suggest that mineralized groundwaters have reached the surface along fracture zones in the gravel above basement faults (e.g., see Cameron et al., 2002; Leybourne and Cameron, 2008; Reich et al., 2008). The anomalously elevated contents of saline and porphyry-associated elements in the anomalous soil zones is similar to that of local groundwater and is inconsistent with interpretations other than physical movement of groundwater to the surface (Cameron et al., 2008, 2002; Cameron and Leybourne, 2005; Palacios et al., 2005). The abundance of Na and Cl, which are not volatile species, associated with the fractures indicates that vapor transport was not the cause. The theoretical basis for earthquake-induced groundwater flow was developed by Sibson (Sibson et al., 1975; Sibson, 1981) and empirical evidence is provided by increased permeability and flooding of the surface along fault lines for weeks and months following earthquakes, including desert areas (Nur, 1974; Montgomery and Manga, 2003; Elkhoury et al., 2006). The model has been refined most recently by Cameron (in press). At the Spence deposit, earthquake-induced flow of saline water was initiated along basement faults at depths of several kilometers. As the saline water rose, it mixed with groundwaters in contact with the deposit and with less saline groundwaters in the overlying gravel aquifers. Upon discharge of these mixed groundwaters at the surface along the fracture zones (Fig. 2), it was evaporated, and the major salts and trace elements were subsequently selectively redistributed during rare, periodic rains (Fig. 7). Gravel exposed in the trenches above the deposit show two sets of vertical fractures at ~1 m intervals; east to west and north to south. Furthermore, within trenches constructed in a background area, where earthquake-induced groundwater flow has not occurred, only one north–south fracture has been identified, underscoring the importance of these fractures in bringing deep groundwater to the surface. The clear association of ore-related metals and metalloids with these fractures indicates that the fractures are not surface polygonal fractures or Neptunian dykes. The latter represent top down processes, whereas it can be shown that at the Spence deposit, the dominant process is bottom up, albeit with some redistribution by infrequent rains. The relationship between Cu deposits, groundwater and soil geochemical anomalies is also demonstrated by the variation in soil chemistry at the three study areas (Fig. 11). Thus, soils overlying the

Spence Deposit show direct evidence of the underlying deposit; low S/Se, elevated Cu contents, elevated I and As (high Cu/S, I/Cu and As/S values) (Fig. 11). By contrast, soils overlying the Gaby Sur deposit only show anomalous Cu in fractures; most of the soils have S/Se and Cu, As and I contents more consistent with atmospheric deposition, as also suggested by the soil isotope values. Finally, the soils at the Tamarugal anomaly show evidence for long periods of accumulation (elevated S, Ca, Na, Cl; Figs. 5 and 11), but also the clear signature of distal mineralization (elevated Cu, I and As; Fig. 11).

Soils above the Spence Deposit exhibit poor correlation between Na and Cu, despite the presumed groundwater source of both Na and Cu in these soils (Fig. 7A and B). Copper is concentrated in the upper 20 cm of the gravel soils, as a result of adsorption onto Fe oxyhydroxides and other soil materials (e.g., clay minerals), whereas the constituents of the groundwater that are less easily adsorbed, e.g., Na, B, Se and As are concentrated at depths of 50 cm and below. The differences in behavior between species that are adsorbed and retained higher in the soil profile compared to more labile species is also observed in filtered vs. unfiltered samples of groundwater (Cameron and Leybourne, 2005; Leybourne and Cameron, 2008).

There is a broad spatial correlation between fracturing of the gravels and the presence of groundwater-derived constituents. But small-scale correlation is limited: at site 51 over the deposit there is a correlation between Na and fracturing, with the highest concentrations in soils where an east–west and north–south fracture intersect and the lowest concentration in an unfractured profile. However, at site 54 over the deposit, there is no such correlation and there is no correlation between Cu and fracturing at either site.

If some portions of the soil calcite or gypsum that form in and over fractures that intersect porphyry Cu mineralization are influenced by earthquake-induced deep groundwater flow, it was originally postulated that this might be detected in the isotopic composition of these authigenic soil minerals, thereby providing a new mineral exploration tool. However, as has been shown above, although the isotopic data for soil calcite and gypsum can be interpreted as including at least some component of a groundwater isotopic signature, there appear to be no obviously systematic differences in the isotopic compositions of soil carbonate or sulfate associated with fractures that cross-cut mineralization compared to barren fractures and unfractured soils. Groundwater transported to surface from depth has not previously been considered as a source of dissolved solutes for soils in the Atacama Desert (e.g., Rech et al., 2003b; Bao et al., 2004; Quade et al., 2007; Ewing et al., 2008).

5.4. Implications for paleoclimate research

Current models that use the C isotopic composition of pedogenic carbonate to interpret paleoclimate are limited by a number of constraints. One of the largest problems is that the soil zone P_{CO_2} is a major influence on these calculations and this value is difficult to quantify (Ekart et al., 1999; Robinson et al., 2002), although estimates in wet soils have been made using the C isotopic composition of carbonate substituted into goethite (Tabor et al., 2004). Much of the hyperarid core of the Atacama Desert is devoid of any vegetation (and in the driest parts, even hypolithic bacteria are essentially absent e.g., Warren-Rhodes et al., 2006), so that the P_{CO_2} of the soil zone will essentially be largely controlled by diffusion from the atmosphere. Another unknown in these calculations is the $\delta^{13}C$ value of the atmosphere through time. In using pedogenic carbonate as a paleobarometer, the C isotopic ratio of the atmosphere is typically either assumed to be the same as the modern pre-industrial value, or assumed to be controlled by the

fractionation factor between marine carbonate and atmospheric CO_2 (Ekart et al., 1999). However, by looking in hyperarid climate regions, a more direct proxy for atmospheric $\delta^{13}C$ values may be recorded in soil calcite. Thus, the assumptions regarding the $\delta^{13}C$ values of past atmospheres could be tested by investigation of pedogenic calcite in regions with a hyperarid climate such as the Atacama Desert, in particular where carbonate can be related to ash beds that can be isotopically dated, or where other independent ages can be determined. For example, studies on the groundwaters and soils at the Spence deposit have suggested that the Cu mineral atacamite may not be related to the main supergene oxidation events in the Miocene, but might be very young, associated with earthquake-induced groundwater migration (Cameron et al., 2007; Leybourne and Cameron, 2008). Subsequent work has shown, based on ^{36}Cl dating of atacamite and U-series disequilibrium dating of gypsum intergrown with atacamite, that atacamite at many of the porphyry Cu deposits is relatively young, with ages ranging from 240 to 80 ka (Reich et al., 2008, 2009).

6. Conclusions

Soils overlying the Spence and Gaby Sur porphyry Cu deposits and the Pampa del Tamarugal, Atacama Desert, northern Chile display variable evidence in the isotopic values of stable isotopes of carbonate and sulfate for the influence of saline groundwaters. Pedogenic calcite is present in all soils at the Spence deposit, but increases volumetrically above fracture zones that cut the Miocene gravels overlying the deposit. The C isotope values of carbonate from the soils overlying the fracture zones is indistinguishable from pedogenic carbonate elsewhere at the Spence deposit and formed in equilibrium with atmospheric CO_2 . However, $\delta^{18}O$ values for carbonate over both fracture zones are statistically different from carbonate elsewhere, consistent with involvement of groundwater in their formation. The Spence deposit is characterized by soils that have elevated contents of saline and porphyry-associated elements only above the fracture zones over the deposit and to the east, with isotopic values (3.7–4.9‰ $\delta^{34}S$) near the middle of the range for SO_4 in groundwater at the Spence deposit (0.9–7.3‰). At the Spence deposit, the original soil profile, including surface gypsum and NO_3 that can be found nearby, has been removed by “recent” erosional events. There has been insufficient time since then to develop much of a true soil profile, except for some limited calcrete over the fracture zones, particularly in the eastern fracture zone. Thus, the effects of earthquake-induced movement of groundwaters are most evident in the major and trace element chemistry of the soils, and the O and S isotopic composition of the carbonate and sulfate, respectively, associated with the fractures.

The composition of soils at the Tamarugal anomaly has been most strongly affected by earthquake-related surface flooding and evaporation of groundwater with long-term accumulation; $\delta^{13}C$ values (−4.3‰ to −2.0‰) are interpreted to be a mixture of dissolved inorganic C (DIC) from groundwater and atmospheric CO_2 . Sulfur in soils at the Gaby Sur deposit ($\delta^{34}S$ values = 3.8–6.1‰) is dominated by gypsum, which primarily occurs on the flanks and tops of hills, suggesting deposition from SO_4 -rich fog. The SO_4 in Gaby Sur deposit gypsum is possibly derived by condensation of airborne SO_4 derived from SO_2 of volcanic origin from the nearby Andes.

Soil carbonate from soils across the Spence deposit has O and C isotopic values similar to those recorded for other studies in the Atacama Desert. By contrast, those from the Gaby Sur deposit are amongst the heaviest isotopically for C, with lighter O isotope values than previously recorded in the Atacama Desert. Finally, although the soils from the Tamarugal anomaly fall within the

range for Atacama Desert soils, they are much lighter in C isotope values than soils at either of the two porphyry Cu deposits. The accumulation of salts at all three sites has different histories and display variable influence of groundwater, which is interpreted to have been forced to surface during recurrent seismic events in the Atacama region. The clear accumulation of salts associated with fractures at the Spence deposit, and shifts in the isotopic composition of carbonate and sulfate in the fractures despite clear evidence of relatively recent removal of salts indicates that transfer from groundwater is an ongoing process. The interpretation that groundwaters can influence the isotopic composition of soil calcite and gypsum has important implications not only for exploration of covered Cu deposits but also for paleoenvironmental reconstructions in the hyperarid Atacama Desert.

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References

- Alpers, C.N., Brimhall, G.H., 1988. Middle Miocene climatic change in the Atacama Desert, northern Chile: evidence from supergene mineralization at La Escondida. *Geol. Soc. Am. Bull.* 100, 1640–1656.
- Alpers, C.N., Brimhall, G.H., 1989. Paleohydrologic evolution and geochemical dynamics of cumulative supergene metal enrichment at La Escondida, Atacama Desert, Northern Chile. *Econ. Geol.* 84, 229–255.
- Arancibia, G., Matthews, S.J., De Arce, C.P., 2006. K–Ar and Ar-40/Ar-39 geochronology of supergene processes in the Atacama Desert, Northern Chile: tectonic and climatic relations. *J. Geol. Soc. London* 163, 107–118.
- Aravena, R., Suzuki, O., Pena, H., Pollastri, A., Fuenzalida, H., Grilli, A., 1999. Isotopic composition and origin of the precipitation in northern Chile. *Appl. Geochem.* 14, 411–422.
- Bao, H.M., Michalski, G.M., Thiemens, M.H., 2001a. Sulfate oxygen-17 anomalies in desert varnishes. *Geochim. Cosmochim. Acta* 65, 2029–2036.
- Bao, H.M., Thiemens, M.H., Heine, K., 2001b. Oxygen-17 excesses of the Central Namib gypcretes: spatial distribution. *Earth Planet. Sci. Lett.* 192, 125–135.
- Bao, H., Jenkins, K.A., Khachatryan, M., Chong Diaz, G., 2004. Different sulfate sources and their post-depositional migration in Atacama soils. *Earth Planet. Sci. Lett.* 224, 577–587.
- Bottinga, Y., 1969. Calculated fractionation factors for carbon and hydrogen isotopic exchange in the system calcite–carbon dioxide–graphite, methane–hydrogen–water vapor. *Geochim. Cosmochim. Acta* 33, 49–64.
- Breecker, D.O., Sharp, Z.D., McFadden, L.D., 2009. Seasonal bias in the formation and stable isotopic composition of pedogenic carbonate in modern soils from central New Mexico, USA. *Geol. Soc. Am. Bull.* 121, 630–640.
- Cameron, E.M., in press. From Chile to Nevada to the Athabasca Basin: Earthquake-induced geochemical anomalies from near-field to far-field. *Geochem. Explor. Environ. Anal.*
- Cameron, E.M., Leybourne, M.I., 2005. Relationship between groundwater chemistry and soil geochemical anomalies at the Spence copper porphyry deposit, Chile. *Geochem. Explor. Environ. Anal.* 5, 135–145.
- Cameron, E.M., Hall, G.E.M., Veizer, J., Krouse, H.R., 1995. Isotopic and elemental hydrogeochemistry of a major river system: Fraser River, British Columbia. *Chem. Geol.* 122, 149–169.
- Cameron, E.M., Leybourne, M.I., Kelley, D.L., 2002. Exploring for deeply covered mineral deposits: formation of geochemical anomalies in northern Chile by earthquake-induced surface flooding of mineralized groundwaters. *Geology* 30, 1007–1010.
- Cameron, E.M., Hamilton, S.M., Leybourne, M.I., Hall, G.E.M., McClenaghan, B., 2004. Finding deeply-buried deposits using geochemistry. *Geochem. Explor. Environ. Anal.* 4, 7–32.
- Cameron, E.M., Leybourne, M.I., Palacios, C., 2007. Atacamite in the oxide zone of copper deposits in northern Chile: involvement of deep formation waters? *Miner. Depos.* 42, 205–218.
- Cameron, E.M., Leybourne, M.I., Reich, M., Palacios, C., 2008. Economic geology models 1. Geochemical exploration and metallogenic studies, Northern Chile. *Geosci. Canada* 35, 97–105.
- Carmona, V., Pueyo, J.J., Taberner, C., Chong, G., Thirlwall, M., 2000. Solute inputs in the Salar de Atacama (N. Chile). *J. Geochem. Explor.* 69 (70), 449–452.
- Cerling, T.E., 1984. The stable isotopic composition of modern soil carbonate and its relationship to climate. *Earth Planet. Sci. Lett.* 71, 229–240.
- Cerling, T.E., 1991. Carbon dioxide in the atmosphere: evidence from Cenozoic and Mesozoic paleosols. *Am. J. Sci.* 291, 377–400.
- Cerling, T.E., Quade, J., 1993. Stable carbon and oxygen isotopes in soil carbonates. In: Swart, P.K., Lohmann, K.C., McKenzie, J., Savin, S. (Eds.), *Climate Change in Continental Isotopic Records*, Washington, DC, pp. 217–231.
- Clarke, J.D.A., 2006. Antiquity of aridity in the Chilean Atacama Desert. *Geomorphology* 73, 101–114.
- Claypool, G.E., Hosler, W.T., Kaplan, I.R., Sakai, H., Zak, I., 1980. The age curves of sulfur and oxygen isotopes in marine sulfate and their mutual interpretation. *Chem. Geol.* 28, 199–260.
- Dansgaard, W., 1964. Stable isotopes in precipitation. *Tellus* 16, 436–468.
- Dold, B., Spangenberg, J.E., 2002. Study of water-soluble sulfates in tailings profiles from porphyry copper deposits by sulfur and oxygen isotopes. In: 12th Ann. Goldschmidt Conference, Davos, Switzerland, August 18–23, p. 189.
- Dunai, T.J., Lopez, G.A.G., Juez-Larre, J., 2005. Oligocene–Miocene age of aridity in the Atacama Desert revealed by exposure dating of erosion-sensitive landforms. *Geology* 33, 321–324.
- Eckardt, F.D., Spiro, B., 1999. The origin of sulphur in gypsum and dissolved sulphate in the Central Namib Desert, Namibia. *Sed. Geol.* 123, 255–273.
- Ekart, D.D., Cerling, T.E., Montanez, I.P., Tabor, N.J., 1999. A 400 million year carbon isotope record of pedogenic carbonate: implications for paleoatmospheric carbon dioxide. *Am. J. Sci.* 299, 805–827.
- Elkhoury, J.E., Brodsky, E.E., Agnew, D.C., 2006. Seismic waves increase permeability. *Nature* 441, 1135–1138.
- Ewing, S.A., Sutter, B., Owen, J., Nishiizumi, K., Sharp, W., Cliff, S.S., et al., 2006. A threshold in soil formation at Earth's arid-hyperarid transition. *Geochim. Cosmochim. Acta* 70, 5293–5322.
- Ewing, S.A., Michalski, G., Thiemens, M., Quinn, R.C., Macalady, J.L., Kohl, S., Wankel, S.D., Kendall, C., McKay, C.P., Amundson, R., 2007. Rainfall limit of the N cycle on Earth. *Global Biogeochem. Cycles* 21.
- Ewing, S.A., Yang, W., DePaolo, D.J., Michalski, G., Kendall, C., Stewart, B.W., et al., 2008. Non-biological fractionation of stable Ca isotopes in soils of the Atacama Desert, Chile. *Geochim. Cosmochim. Acta* 72, 1096–1110.
- Field, C.W., Gustafson, L.B., 1976. Sulfur isotopes in the porphyry copper deposit at El Salvador. *Econ. Geol.* 71, 1533–1548.
- Friedman, I., O'Neil, J.R., 1977. Compilation of stable isotope fractionation factors of geochemical interest. U.S. Geol. Surv. Profess. Paper 440-KK.
- Garzzone, C.N., Molnar, P., Libarkin, J.C., MacFadden, B.J., 2006. Rapid late Miocene rise of the Bolivian Altiplano: evidence for removal of mantle lithosphere. *Earth Planet. Sci. Lett.* 241, 543–556.
- Ghosh, P., Garzzone, C.N., Eiler, J.M., 2006. Rapid uplift of the Altiplano revealed through C-13–O-18 bonds in paleosol carbonates. *Science* 311, 511–515.
- Hall, G.E.M., 1998. Analytical perspective on trace element species of interest in exploration. *J. Geochem. Explor.* 61, 1–19.
- Hartley, A.J., Chong, G., 2002. Late Pliocene age for the Atacama Desert: implications for the desertification of western South America. *Geology* 30, 43–46.
- Hartley, A.J., May, G., 1998. Miocene Gypcretes from the Calama Basin, northern Chile. *Sedimentology* 45, 351–364.
- Hartley, A.J., Chong, G., Houston, J., Mather, A.E., 2005. 150 million years of climatic stability: evidence from the Atacama Desert, northern Chile. *J. Geol. Soc. London* 162, 421–424.
- Houston, J., Hartley, A.J., 2003. The central andean west-slope rainshadow and its potential contribution to the origin of HYPER-ARIDITY in the Atacama desert. *Int. J. Climatol.* 23, 1453–1464.
- Kaakinen, A., Sonninen, E., Lunkka, J.P., 2006. Stable isotope record in paleosol carbonates from the Chinese Loess Plateau: implications for late Neogene paleoclimate and paleovegetation. *Palaeogeog. Palaeoecol.* 237, 359–369.
- Leybourne, M.I., Cameron, E.M., 2006a. Composition of groundwaters associated with porphyry-Cu deposits, Atacama Desert, Chile: elemental and isotopic constraints on water sources and water–rock reactions. *Geochim. Cosmochim. Acta* 70, 1616–1635.
- Leybourne, M.I., Cameron, E.M., 2006b. Composition of soils and groundwaters at the Pampa del Tamarugal, Chile: anatomy of a fossil geochemical anomaly derived from a distant porphyry copper deposit. *Econ. Geol.* 101, 1569–1581.
- Leybourne, M.I., Cameron, E.M., 2008. Source, transport, and fate of rhenium, selenium, molybdenum, arsenic, and copper in groundwater associated with porphyry-Cu deposits, Atacama Desert, Chile. *Chem. Geol.* 247, 208–228.
- Michalski, G., Böhlke, J.K., Thiemens, M., 2004. Long term atmospheric deposition as the source of nitrate and other salts in the Atacama Desert, Chile: new evidence from mass-independent oxygen isotopic compositions. *Geochim. Cosmochim. Acta* 68, 4023–4038.
- Montgomery, D.R., Manga, M., 2003. Streamflow and water well responses to earthquakes. *Science* 300, 2047–2049.

- Mook, W.G., Bommerson, J.C., Staverman, W.H., 1974. Carbon isotope fractionation between dissolved bicarbonate and gaseous carbon dioxide. *Earth Planet. Sci. Lett.* 22, 169–176.
- Nur, A., 1974. Matsushiro, Japan, earthquake swarm: confirmation of dilatancy–fluid diffusion model. *Geology* 2, 217–221.
- Palacios, C., Guerra, N., Townley, B., Lahsen, A., Parada, M.A., 2005. Copper geochemistry in salt from evaporite soils, Coastal Range of the Atacama Desert, northern Chile: an exploration tool for blind copper deposits. *Geochem.: Explor. Environ., Anal.* 5, 371–378.
- Potter, J., Siemann, M.G., Tsypukov, M., 2004. Large-scale carbon isotope fractionation in evaporites and the generation of extremely ^{13}C -enriched methane. *Geology* 32, 533–536.
- Pueyo, J.J., Chong, G., Jensen, A., 2001. Neogene evaporites in desert volcanic environments: Atacama Desert, northern Chile. *Sedimentology* 48, 1411–1431.
- Quade, J., Cerling, T.E., Bowman, J.R., 1989. Systematic variations in the carbon and oxygen isotopic composition of pedogenic carbonate along elevation transects in the southern Great Basin, United States. *Geol. Soc. Am. Bull.* 101, 464–475.
- Quade, J., Rech, J.A., Latorre, C., Betancourt, J.L., Gleeson, E., Kalin, M.T.K., 2007. Soils at the hyperarid margin: the isotopic composition of soil carbonate from the Atacama Desert, Northern Chile. *Geochim. Cosmochim. Acta* 71, 3772–3795.
- Ramirez, L.E., Palacios, C., Townley, B., Parada, M.A., Sial, A.N., Fernandez-Turiel, J.L., et al., 2006. The Mantos Blancos copper deposit; an Upper Jurassic breccia-style hydrothermal system in the Coastal Range of northern Chile. *Miner. Depos.* 41, 246–258.
- Rech, J.A., Quade, J., Betancourt, J.L., 2003a. Controls on the isotopic composition of soil carbonate in a hyperarid environment; a case study from the Atacama Desert, Chile. *Geol. Soc. Am.*, 2003 Ann. Meeting, Abstracts with Programs 35, No. 6., 408.
- Rech, J.A., Quade, J., Hart, W.S., 2003b. Isotopic evidence for the source of Ca and S in soil gypsum, anhydrite and calcite in the Atacama Desert, Chile. *Geochim. Cosmochim. Acta* 67, 575–586.
- Rech, J.A., Currie, B.S., Michalski, G., Cowan, A.M., 2006. Neogene climate change and uplift in the Atacama Desert, Chile. *Geology* 34, 761–764.
- Rees, C.E., Jenkins, W.J., Monster, J., 1978. The sulfur isotopic composition of ocean water sulfate. *Geochim. Cosmochim. Acta* 42, 377–382.
- Reich, M., Palacios, C., Parada, M.A., Fehn, U., Cameron, E.M., Leybourne, M.I., et al., 2008. Atacamite formation by deep saline waters in copper deposits from the Atacama Desert, Chile: evidence from fluid inclusions, groundwater geochemistry, TEM, and ^{36}Cl data. *Miner. Depos.* 43, 663–675.
- Reich, M., Palacios, C., Vargas, G., Luo, S., Cameron, E.M., Leybourne, M.I., et al., 2009. Supergene enrichment of copper deposits since the onset of modern hyperaridity in the Atacama Desert, Chile. *Miner. Depos.* 44, 497–504.
- Rissmann, C.F.W., 2003. Dilute Hydrothermal Fluids within the Groundwaters of the Monturaqui Basin, Northern Chile: The Role of Volcano Socompa. Geosciences Department, Univ. Texas at Dallas.
- Rissmann, C.F.W., Leybourne, M.I., Christenson, B., Benn, C., in preparation. Volcanic-Hydrothermal Solutes within a High Andean Aquifer: The role of Volcano Socompa, Northern Chile. *Geochim. Cosmochim. Acta*.
- Robinson, S.A., Andrews, J.E., Hesselbo, S.P., Radley, J.D., Denni, P.F., Harding, I.C., et al., 2002. Atmospheric pCO_2 and depositional environment from stable-isotope geochemistry of calcrite nodules (Barremian, Lower Cretaceous, Wealden Beds, England). *J. Geol. Soc. London* 159, 215–224.
- Schemenauer, R.S., Cereceda, P., 1992. The quality of fog water collected for domestic and agricultural use in Chile. *J. Appl. Meteorol.* 31, 275–290.
- Sibson, R.H., 1981. Fluid flow accompanying faulting: field evidence and models. In: Simpson, D.W., Richards, P.G. (Eds.), *Earthquake Prediction: An International Review*, pp. 593–603.
- Sibson, R.H., Moore, J.M., Rankin, A.H., 1975. Seismic pumping – a hydrothermal fluid transport mechanism. *J. Geol. Soc. London* 131, 653–659.
- Sillitoe, R., McKee, E., 1996. Age of supergene oxidation and enrichment in the Chilean Porphyry Copper Province. *Econ. Geol.* 91, 164–179.
- Stiller, M., Rounick, J.S., Shasha, S., 1985. Extreme carbon-isotope enrichments in evaporating brines. *Nature* 316, 434–435.
- Tabor, N.J., Yapp, C.J., Montanez, I.P., 2004. Goethite, calcite, and organic matter from Permian and Triassic soils: Carbon isotopes and CO_2 concentrations. *Geochim. Cosmochim. Acta* 68, 1503–1517.
- Warren-Rhodes, K.A., Rhodes, K.L., Pointing, S.B., Ewing, S.A., Lacap, D.C., Gomez-Silva, B., et al., 2006. Hypolithic cyanobacteria, dry limit of photosynthesis, and microbial ecology in the hyperarid Atacama Desert. *Microb. Ecol.* 52, 389–398.