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ORIGINAL ARTICLE

Mineral deposits and Cu–Zn–As dispersion–contamination in stream sediments from the semiarid Coquimbo Region, Chile

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Abstract This paper presents Cu–Zn–As geochemical data from stream sediment surveys carried out in the three main watersheds of the Coquimbo Region of Chile. This mountainous semiarid realm occupies an area of 40,656 km^2 between 29° and 32°S. Given that the area has a long historical record of mining activities, important environmental disturbances were expected. However, despite the detection of three major geochemical anomalies for Cu, Zn, or As, only one can be unmistakably linked to the development of mining–metal recovery procedures (Andacollo–Panulcillo). An investigation of the other two anomalies (Elqui and Hurtado) reveals three major causes that fully or partially account for them: (1) the type of ore deposit and associated hydrothermal alteration; (2) the regional structural setting (intensity of fracturing); and (3) climate–landscape. Cu–Au–As epithermal deposits/prospects along the so-called El Indio belt are here regarded as the sources of both the Elqui and Hurtado anomalies. The strong advanced argillic alteration present in some of the epithermal deposits/prospects of the El Indio belt may have induced the loss of the buffering capacity of rocks, and therefore favoured metal dispersion during later oxidation–leaching of sulphides. This applies to the Elqui and Hurtado anomalies. Conversely, given that the potassic, propylitic and phyllic alterations do not affect the buffering capacity of rocks, only minor metal dispersion is observed in relation to the Los Pelambres porphyry copper deposit. Besides, the epithermal belt is located within a highly fractured Andean domain (3,000–4,000 m of altitude), which may have conditioned the fast unroofing of ore deposits, contributed to enhanced circulation of meteoric waters, and eventually, to strong oxidation, and leaching of metals. Metal dispersion is aggravated during rainy years in response to strong El Niño episodes.

Keywords Natural and industrial contamination · Watersheds · Stream sediments · Heavy metals · Mineral deposits · Northern Chile

Study area

An introduction to the problem

This paper presents integrated results from stream sediment surveys carried out successively in the three

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Fig. 1 The Coquimbo Region (Elqui, Limarí and Choapa watersheds). The figure shows sampling sites and location of major mining districts and hydrothermal alteration zones. Hydrothermal zones after Maksaev et al. (1984). Location of ESS and LIM samples after Oyarzun et al. (2004) and Oyarzun et al. (2006)

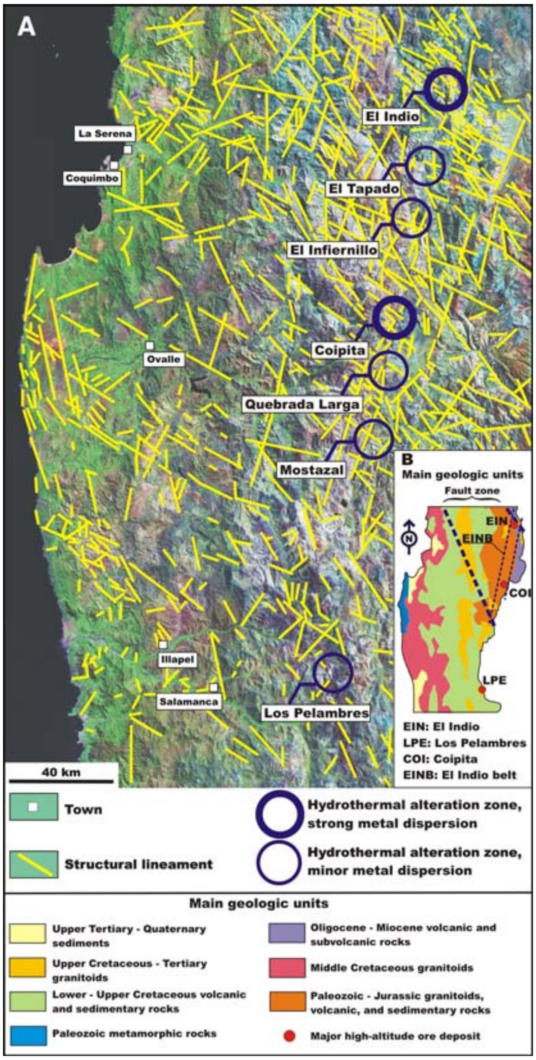

Fig. 2 **a** LANDSAT 7 image including approximate location of main alteration zones, prospects, epithermal ore deposits (*blue circles*), and major structural lineaments (*yellow lines*). **b** Simplified geologic map of the study area (after Maksaev et al. 1984; Frutos 1986; Oyarzun 1986)

main watersheds of the Coquimbo Region (Elqui, Limarí and Choapa) (Fig. 1) during 2002–2005 (Oyarzun et al. 2004; Oyarzun et al. 2006; this work). The Coquimbo Region has an area of 40,656 km^2 and is located in northern Chile, within the transition between the extremely dry Atacama desert and the Mediterranean central part of the country. The region is rich in mineral deposits and hydrothermal alteration zones of potential economic interest (Figs. 1, 2a). The region also sustains an important agricultural sector, oriented to both the domestic and international markets. From a physiographic point of view, the region is characterized by a mountainous landscape and a semiarid climate. This realm is dominated by a complex array of valleys (the so-called *Valles Transversales* system), having in common rivers that flow from the high altitude Andean domain to the coast in less than 150 km. As shown and discussed below, the geochemical surveys show contrasting results, revealing metal dispersion in relation to mining–metallurgical activities, but also as the direct consequence of geologic processes. Thus, the paper analyzes the Coquimbo Region case from a broader perspective, taking into account all the variables that may have played a role regarding metal dispersion. A pilot study (Oyarzún et al. 2003) showed that most metals in stream sediments from the Elqui basin (Pb, Hg, Ba, Co, Cr, Ni) displayed mean concentrations close to that of the Chilean igneous rocks (Oyarzún 1971; Oyarzún et al. 1993), whereas those of Cu, Zn and Cu, were very high compared to world baselines. Later studies in the region confirmed these results, indicating that these metals could be regarded as excellent pathfinders for mineral deposits and mining activities (Oyarzun et al. 2004; Oyarzun et al. 2006).

Geology and mineral deposits

The geology of the Coquimbo Region can be divided into two contrasted domains (Fig. 2b). A western zone comprising: (1) Palaeozoic metamorphic rocks and Miocene to Pliocene marine sediments that crop out along a narrow coastal belt (Le Roux et al. 2006); (2) Lower Cretaceous volcanic and sedimentary rocks (Aguirre and Egert 1965; Boric 1985; Rivano and Sepúlveda 1991). (3) Granitoids of Middle Cretaceous age. (4) Andesites and clastic sediments of Upper Cretaceous age and Lower Tertiary basaltic to rhyolitic rocks (Aguirre and Egert 1965). The high altitude (Andean) eastern domain is relatively more complex, comprising units that range in age from Palaeozoic to Miocene (Maksaev et al. 1984): (1) Palaeozoic rocks including Devonian–Carboniferous pelites and sandstones, Upper Palaeozoic rhyolites, breccias, tuffs, and andesites. Granitoids include those of the Elqui–Limari and Incaguas batholiths (Carboniferous). (2) Mesozoic rocks comprising Triassic andesites and sandstones, Lower Jurassic limestones, sandstones, and shales, Upper Jurassic–Cretaceous sandstones, tuffs, and rhyolites, and Upper Jurassic conglomerates, sandstones, andesites, breccias, and tuffs. (3) Oligocene–Miocene rocks including andesites, rhyolites, tuffs, ignimbrites, granites, granodiorites, monzodiorites, and andesite porphyries. The intrusive rocks are grouped into the so-called Infiernillo unit.

From a metallogenic point of view, two time spans are most relevant: (1) The Early to Middle Cretaceous transition, with stratabound and vein type Cu deposits, Ag vein type deposits, Cu–Hg–Au vein type deposits, and Mn stratabound deposits (Talcuna, Arqueros, Punitaqui, and Corral Quemado districts; Oyarzun et al. 1998; Higueras et al. 2004), epithermal gold and porphyry copper deposits (Andacollo district; Oyarzun et al. 1996), and Kiruna type iron deposits (El Romeral; Oyarzun et al. 2003) (Fig. 1). (2) The Late Miocene, with the El Indio Cu–Au–As epithermal belt (Maksaev et al. 1984) and the Los Pelambres porphyry copper deposit (Guzmán 1986; Reich et al. 2003), all of them along the high Andes (Fig. 3). The El Indio belt is NNE oriented, and comprises zones of alteration such as (Figs. 1, 2): El Indio (Fig. 3a), El Tapado, El Infiernillo, Coipita (Fig. 3b), Quebrada Larga, and Mostazal.

Fig. 3 High altitude Andean mineral deposits discussed in the text. **a** The El Indio Cu-Au–As epithermal deposit, **b** the Coipita Cu–Au prospect; **c** the Los Pelambres porphyry copper deposit. High intensity rains easily remove the metal-rich regolith to the local streams

Materials and methods

Stream sediments sampling in the Elqui, Limarí and Choapa watersheds was carried out during successive surveys starting from the north in the Elqui basin, and continuing southward with the Limarí and Choapa river systems. A total of 75 stream sediments samples were taken during the field work: 14 from the Elqui watershed (ESS samples), 33 from the Limarí watershed (LIM samples), and 28 from the Choapa watershed (CHO samples) (Fig. 1) (Table 1). Sampling procedures were the same for the three surveys. The sediment samples (~2 kg) were collected from the shores of the rivers, focusing on the silty fraction, and stored in plastic bags. The samples were dried at room temperature and sieved to <64 µm. The chemical analyses were done at the Geoanalítica Ltda (Chile)

Table 1 Mean values for Cu, Zn, As, and Cd in stream sediments from the Elqui, Limarí and Choapa watersheds (Coquimbo Region) and world baselines

	Cu ($\mu g\ g^{-1}$)	Zn ($\mu g\ g^{-1}$)	As ($\mu g\ g^{-1}$)	Reference
Elqui watershed				Oyarzun et al. (2004)
Elqui river	2,352	470	202	
Elqui Holocene lacustrine sediments	697	3,593	749	
Andacollo streams	417	161	7	Higueras et al. (2004)
Limarí watershed				Oyarzun et al. (2006)
All rivers	157	186	15	
River Hurtado	582	2117	52	
Choapa watareshed				
All rivers	139	98	13	
World averages (baselines)				
Stream sediments	39	132		Callender (2004)
Stream sediments			5	Smedley and Kinniburgh (2002)
Pre-industrial baseline lacustrine sediment	34	97		Callender (2004)

laboratories. The sample fraction was digested in hot aqua regia (3:1 HC1:HNO_3), followed by dissolution with HCl (25%), which leaves behind a silica-only residue, i.e. metals are completely leached and put into solution for the subsequent chemical analyses. Cu, Zn, and As were analyzed by atomic absorption. Detection limits for each set of samples are shown in Table 1. Quality control at the laboratory is done by analyzing duplicate samples to check precision, whereas accuracy was obtained by using certified standards. Blank samples were also analyzed to check procedures. The mineralogy of the sediments was studied by X-ray diffraction (XRD; instrument: Philips PW3040/00 X'Pert) and environmental scanning microscopy, with electron backscatter diffraction analysis and energy-dispersive X-ray capability (ESEM-EDX; instrument: Philips XL30; 25 kV) at the CAT facilities of the Rey Juan Carlos University (Madrid). In order to analyze the regional tendencies for element distribution, the results were treated with the Surfer 8 program, to assess the spatial continuity of data by point linear kriging.

Results

Mineralogy of the sediment fraction

The XRD study of the mineral phase (<64 μm fraction) reveals the presence of several types of mineral constituents in the studied sediments: (1) a silicate fraction, with quartz, plagioclase, and phyllosilicates, the latter comprising kaolinite, illite, bramallite (Na illite), sericite, smectite (saponite), and vermiculite. (2) A poorly XRD defined oxide fraction including goethite, thus suggesting a partially amorphous mineral phase. (3) Salts, with halite, gypsum, and bloedite ($Na_2Mg(SO_4)_2{\cdot}4H_2O$). Sulphates are relatively common minerals in the sediment fraction in rivers from the arid to semi arid environment of northern Chile (e.g. Romero et al. 2003; Oyarzun et al. 2004).

The metallic phase was studied by ESEM-EDX. A complex array of intermediate mineral phases is observed, showing the effects of partial oxidation of sulphide grains. The compositions suggest the presence of pyrite, together with Mn and Fe oxides (Cu–Zn bearing), native copper, and ilmenite. Zinc has been detected in grains with a complex composition, including Th–U or La–Ce–Pr–Nd–Sm–Gd, and P. This, together with the contents in Al and S in the grains indicates the presence of aluminum–phosphate–sulfate (APS) minerals. Minerals of this type are relatively common in the volcanic-epithermal environment (argillic alteration), and may accommodate in their crystal structures REE, Th, and metals such as Fe, Cu, or Zn (Dill 2003). As shown by the ESEM-EDX studies, there is a remarkable association between the iron oxide phase and arsenic (Oyarzun et al. 2004). For example, the analyses of the oxide mineral grains display contents of: As (1.53–2.35%), Cu (traces-0.89%), Zn (traces-0.44%), Fe (35.2–52.2%), with very low sulphur (1.45–4.36%), which suggests that the oxide phase derived from the almost total oxidation of sulphide minerals. The ESEM-EDX studies did not reveal the presence of arsenic in other mineral phases.

Geochemical anomalies in the stream sediments

Stream sediments sampling has proved to be a sound geochemical tool in the tropical, arid, and semiarid domains of the Andean chain to detect the presence of ore deposits (e.g. Cruzat 1984; Williams et al. 2000), to define baselines, and to constrain environmental disturbances (e.g. Williams et al. 2000; Higueras et al. 2004; Oyarzun et al. 2004, 2006). From the results of this study, a main conclusion emerges: compared to world baselines, the Elqui and Limarí (Hurtado river) stream sediments are highly enriched with Cu, Zn, and As, whereas those for the Choapa basin are generally closer to the baselines (Table 1). The latter hosts the giant Los Pelambres porphyry copper deposit (Figs. 1, 2a, b), which is currently being mined at an open-pit operation (Fig. 3c). Despite these facts, no extremely large geochemical anomalies were found in the Choapa watershed. The opposite is observed in relation to epithermal deposits (El Indio) or prospects (Coipita) from the Elqui and Limarí basins (Figs. 1, 2a) (Table 1). Thus, other factors must be analyzed to fully understand why a particular type of mineralization does not induce strong metal dispersion, whereas others contribute in excess. A description of the anomalies and a discussion on their origin follows.

Major geochemical anomalies: geological–industrial setting of the source

The kriging plots for Cu, Zn, and As (Fig. 4) show several important highs in the studied area. The Elqui and Hurtado systems in the NW corner of the area display the highest concentrations for Cu, Zn and As. Also, a large Cu high is provided by the Andacollo–Panulcillo anomaly. The latter receives a satisfactory explanation in terms of: (1) Long lasting mining activities in the Andacollo district (Fig. 1), which started in colonial time (sixteenth century), first for gold, and then in the early twentieth century for copper and gold (Higueras et al. 2004). (2) Continued metallurgical malpractice at the Cu recovery plant of Panulcillo (Fig. 1), a heap leaching operation adjacent to Ovalle inducing strong contamination along the El Ingenio stream. Metal concentrations in the sediments are in the range of Cu: 155–29,500 μg g^{-1}, Zn: 70–3,600 μg g^{-1} (Rojas 2004). Andacollo is a complex district, including porphyry Cu and strat-abound epithermal (sericite–adularia type) Au deposits (Oyarzun et al. 1996; Higueras et al. 2004). Hard-rock mining was introduced at Andacollo before the end of the sixteenth century, and the main technological innovation consisted in the introduction of the water powered "trapiches" (an old Spanish word for mill). An improved version (electricity-powered) of the old trapiches is used at present by the small-scale mining operations that still exist in the district. In 1996–1997, two mining companies started operations at Andacollo: Carmen de Andacollo (centred on the porphyry Cu deposit) and Compañia Minera Dayton (centred on the epithermal gold deposits). Both mines are of the open-pit type, leach piled ores, and operate under sound environmental regulations. However, the impact of the older and still present outdated trapiche metallurgical

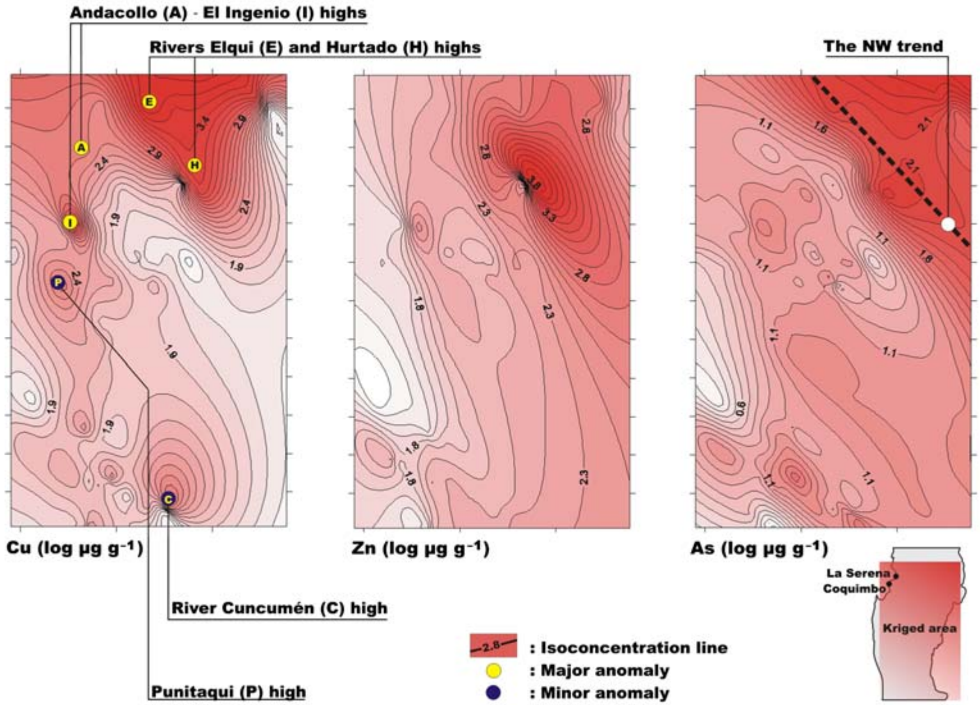

Fig. 4 Isoconcentration (log) maps for Cu, Zn and As in the Coquimbo Region. See *bottom right* corner for location of the kriged area

plants has left major environmental disturbances in the area (stream sediments: 75–2,200 μg g^{-1} Cu) (Higueras et al. 2004). Communities in this sector are underdeveloped, and decades of inefficient treatment of flotation tailings and waste rock stock-piles has resulted in significant contamination of the surrounding landscape. As a matter of fact, large piles of flotation tailings and mineral dumps can still be seen within the town of Andacollo and immediately outside the urban perimeter.

The Elqui and Hurtado anomalies are related to metal dispersion from the high-altitude El Indio epithermal belt (Fig. 2b). Many of the El Indio belt alteration zones comprise advanced argillic alteration mineral assemblages, with kaolinite, alunite, and silica jaspers. The Late Miocene history of hydrothermal processes in this realm is long and complex, although mineralization processes took place at the specific time span of 9.4–6.2 Ma (Bissig et al. 2002). Volcaniclastic facies of the Doña Ana Formation constitute the most typical altered rocks along the belt, although older units have been also affected by the hydrothermal processes.

The Elqui geochemical anomaly (405–6,789 μg g^{-1} Cu, 98–1,511 μg g^{-1} Zn, and 108–485 μg g^{-1} As) (Table 2) (Oyarzun et al. 2004) is related to the most conspicuous mineral deposit of the belt, that is, the world class El Indio (Maksaev et al. 1984; Araneda 1985; Siddeley and Araneda 1986). El Indio (Araneda 1985) is a vein type deposit bound by NNE–SSW faults defining a 500 m long, 100–150 m wide mineralized corridor. The deposit is hosted by rhyolitic to dacitic tuffs, and had (before mining started) two types of veins: gold–quartz (up to 6 m thick) and enargite-rich massive sulphide veins (up to 12 m thick). Alteration assemblages include those of the advanced argillic alteration (quartz–pyrophyllite, alunite), together with phyllic and propylitic mineral assemblages, and silicification. The mine was exploited both by open pit and underground works, and the mineral underwent cyanidation and flotation. The copper concentrate contained 20% Cu, 50 g t^{-1} Au, 300 g/t Ag, and 8% As, and was later treated in a roaster furnace to remove the arsenic (Lagos and Velasco 1998).

These mining and metallurgical procedures are likely to induce environmental disturbances involving strong Cu and As dispersion (Plumlee et al. 2004). However previous results (Oyarzun et al. 2004) show that these activities do not fully account for the high metal concentrations found along the Elqui river system (Table 2). In fact, a sequence of Early Holocene lacustrine sediments that occur as perched outcrops in the mountain slopes flanking the river Turbio (Fig. 1) proved to be extremely Cu- and As-rich (mean concentrations of 697 and 749 μg g^{-1}, respectively) (Oyarzun et al. 2004). Thus, metal dispersion in the Elqui watershed is a long-lasting geological process, which only became aggravated by the initiation of large-scale mining and metallurgical operations at El Indio in the late 1970s.

Although the source of the Elqui anomaly was easy to identify because only one major deposit (El Indio) is present in this sector, the Hurtado case (53–1,881 μg g^{-1} Cu, 64–6,585 μg g^{-1} Zn, and 6–186 μg g^{-1} As) (Table 3) proved to be more complex. In fact, not all the Late Miocene alteration zones seem to have equally contributed to metal dispersion. For example, the Coipita and Quebrada Larga alteration zones (Fig. 1) are drained by tributaries of the river Hurtado; however, the latter is also drained by the river Los Molles, and no important metallic contents are found in these samples. Thus, only one possibility is left, with a source originating in the Coipita alteration zone (Fig. 2a). Both the Coipita and Quebrada Larga zones are about 27 km^2 large, and their geological setting includes granitoids and rhyolitic lavas intruded by the Infiernillo unit.

Minor geochemical anomalies: geological–industrial setting of the source

The kriging plot for Cu allows recognition of two minor highs: Punitaqui and Los Pelambres (river Cuncumén) (Fig. 4). Compared to the epithermal belt, these constitute minor Cu highs, with metal concen-

Table 2 Cu, Zn, As geochemical data for stream sediments from the Elqui watershed (Oyarzun et al. 2004)

Elqui watershed														
Sample	ESS1a	ESS1b	ESS1c	ESS2a	ESS2b	ESS2c	ESS3a	ESS3b	ESS3c	ESS4	ESS5	ESS6	ESS7	ESS8
Element (μg g^{-1})														
Cu	550	405	638	4,293	1,281	660	3,832	6,129	6,789	2,949	4,973	365	30	36
Zn	98	129	129	558	331	1,511	491	647	1,166	460	609	139	165	140
As	327	485	150	231	122	347	138	168	447	108	146	39	55	59

Detection limits Cu = 1 μg g^{-1}, Zn = 1 μg g^{-1}, As = 2 μg g^{-1}

Table 3 Cu, Zn, As geochemical data for stream sediments from the Limarí watersheds (Oyarzun et al. 2006)

Limarí watershed (1)											
Sample	LIM-01	LIM-02	LIM-03	LIM-04	LIM-05	LIM-06	LIM-07	LIM-08	LIM-09	LIM-10	LIM-11
Element (μg g^{-1})											
Cu	864	730	153	70	124	76	46	47	59	27	51
Zn	3,399	2,481	598	142	133	97	83	134	216	163	92
As	48	14	6	19	13	12	10	13	13	5	6
Sample	LIM-12	LIM-13	LIM-14	LIM-15	LIM-16	LIM-17	LIM-18	LIM-19	LIM-20	LIM-21	LIM-22
Element (μg g^{-1})											
Cu	76	138	80	103	124	3,082	202	170	116	94	96
Zn	149	135	97	91	142	308	45	160	116	106	103
As	20	5	14	16	19	23	8	9	11	15	17
Sample	LIM-23	LIM-24	LIM-25	LIM-26	LIM-27	LIM-28	LIM-29	LIM-30	LIM-31	LIM-32	LIM-33
Element (μg g^{-1})											
Cu	155	143	196	491	228	60	94	53	1131	686	1,881
Zn	82	104	144	42	51	48	48	64	4,846	2,779	6,586
As	15	16	15	9	5	5	7	34	114	69	186

Detection limits Cu = 5 μg g^{-1}, Zn = 5 μg g^{-1}, As = 5 μg g^{-1}

trations in sediments of 228 and 491 μg g^{-1} in the Punitaqui river, and 563 and 575 μg g^{-1} Cu in the river Cuncumén (Los Pelambres) (Tables 3, 4). The Punitaqui district (Oyarzún et al. 2001; Higueras et al. 2004) has been intermittently mined since the eighteenth century, and corresponds to a complex case of shear-related, copper–gold and mercury mineralization of Cretaceous age. The copper–gold mineralization is emplaced along the Punitaqui shear zone, whereas the mercury deposits are located within associated fractures. Only the Cu–Au ores are presently mined in the district. The major cause of environmental concerns in the sector is the removal of mineral dumps during stormy episodes in the area (El Niño years), and the leaching of metals from the old tailings piles. Metal dispersion in the Punitaqui stream is not as strong as in the Andacollo district because flotation of sulphides has been generally performed with more efficient procedures, and therefore, the tailings are not as rich in Cu as those from Andacollo (Higueras et al. 2004). The open-pit operation and the tailings are regarded as the primary sources for Cu mobilization, although the stream sediments results indicate limited geochemical dispersion (Higueras et al. 2004).

Table 4 Cu, Zn, As geochemical data for stream sediments from the Choapa watershed

Choapa watershed (1)										
Sample	CHO-01	CHO-02	CH-O03	CHO-04	CHO-05	CHO-06	CHO-07	CHO-08	CHO-9a	CHO-9b
Element (μg g^{-1})										
Cu	95	242	75	78	72	61	573	565	42	47
Zn	80	35	86	80	88	69	137	129	180	199
As	9	11	10	15	12	8	9	9	21	24
Sample	CHO-10	CHO-11	CHO-12	CHO-13	CHO-14	CHO-15	CHO-16	CHO-17	CHO-18	CHO-19
Element (μg g^{-1})										
Cu	46	55	149	47	254	150	116	71	76	83
Zn	138	131	109	122	118	62	134	55	33	44
As	18	19	9	17	41	11	15	5	5	< 3
Sample	CHO-20	CHO-21	CHO-22	CHO-23	CHO-24	CHO-25	CHO-26	CHO-28	CHO-30	
Element (μg g^{-1})										
Cu	181	165	155	71	134	80	92	125	34	
Zn	95	70	78	132	105	148	146	111	20	
As	<3	<3	8	20	15	22	21	14	<3	

Detection limits Cu = 2 μg g^{-1}, Zn = 2 μg g^{-1}, As = 3 μg g^{-1}

The Los Pelambres porphyry copper mineralization (Guzmán 1986; Reich et al. 2003) is hosted by an intrusive complex emplaced within a sequence of andesitic rocks of the Los Pelambres Formation (Late Cretaceous). The intrusive complex consists of a main tonalite stock and porphyritic bodies, and a small number of post-mineralization andesite and aplite dikes. The rocks have been hydrothermally altered to potassic, propylitic, and phyllic mineral assemblages (biotite, sericite). Age dating of Los Pelambres porphyries yields an average of 9.9 ± 1 Ma. Magmatic/hydrothermal breccia pipes also occur within the deposit. Los Pelambres has reserves of 1.40 Gt at 0.74% Cu.

Origin of the Elqui and Hurtado anomalies: a discussion

Geological and mineralogical aspects

Key factors controlling the environmental behaviour of mineral deposits include ore and gangue mineralogy, host rock lithology, and wall-rock alteration, which influence the chemical response of mineral deposits (Plumlee et al. 1999; Plumlee and Nash 2004). The large Elqui and Hurtado, and minor Los Pelambres anomalies deserve a thorough analysis involving the many geological factors that may control metal dispersion. The El Indio (Elqui anomaly), Coipita (Hurtado anomaly), and Los Pelambres (Cuncumén anomaly) deposits share some geological and physiographic features but greatly differ in others. For example, the three are of Late Miocene age, are related to intermediate to felsic magmatic rocks, and are emplaced along the Andean chain at high altitude. However, the former two are of the epithermal type, whereas Los Pelambres is a porphyry copper deposit. As shown above, El Indio and Coipita have strong and extensive advanced argillic alteration zones. This has profound implications regarding metal dispersion, because this type of alteration greatly decreases the acid buffering capacity of host rocks (Plumlee 1999; Plumlee et al. 1999). The chemistry of these processes can be summarized in the following way. Enhanced hydrolysis during hydrothermal activity leads to the destruction of feldspars, through sequential formation of sericite (1), kaolinite (2), and even alunite (3) if H_2SO_4 is present in the system (Montoya and Hemley 1975):

$$KAlSi_3O_8 + 2\,H^+ \rightarrow KAl_3Si_3O_{10}(OH)_2 + K^+ \quad (1)$$

$$KAl_3Si_3O_{10}(OH)_2 + 6\,H_2O + 4\,H^+ \rightarrow 3\,Al_4Si_4O_{10}(OH)_8 + 4\,K^+ \quad (2)$$

$$KAl_3Si_3O_{10}(OH)_2 + 4\,H^+ + 2\,(SO_4)^{2-} \rightarrow KAl_3(SO_4)_2(OH)_6 + 6\,SiO_2 \quad (3)$$

This is particularly relevant to the case of high sulphidation epithermal deposits, which are rich in pyrite and other sulphides (Heald et al. 1987). Thus, when oxidation of pyrite begins in the weathering environment (4), no minerals (such as feldspars) are left to react with the acid:

$$4\,FeS_2 + 10\,H_2O + 15\,O_2 \rightarrow 4\,FeOOH + 16\,H^+ + 8\,(SO_4)^{2-} \quad (4)$$

This increases metal mobility during the leaching of Cu from chalcopyrite (5) or Cu and As from enargite (6):

$$CuFeS_2 + O_2 + 2\,H_2SO_4 \rightarrow CuSO_4 + FeSO_4 + 2\,H_2O + 2\,S \quad (5)$$

$$Cu_3AsS_4 + 2.75\,O_2 + 3\,H_2SO_4 \rightarrow 3\,CuSO_4 + 4\,S + H_3AsO_4 + 1.5\,H_2O \quad (6)$$

On the contrary, the Los Pelambres porphyry copper deposit has an entirely different array of alteration types, with potassic, phyllic and propilytic mineral assemblages (Guzmán 1986). Formation of either secondary biotite or K feldspar does not affect significantly the reactivity of the host rocks, whereas the propylitic alteration increases the buffering capacity of the rocks (Plumlee 1999). Furthermore, sericite from the phyllic alteration can be also a net consumer of H^+ (2) during supergene hydrolytic processes. Thus, compared to the El Indio belt deposits/prospects, the buffering capacity of the rocks at Los Pelambres remained important and therefore, metal leaching–dispersion must have been significantly reduced.

A final consideration regarding mineralogy in these deposits concerns the absence of any important signature of arsenic in the Choapa basin (Table 1). Different from the As-rich (enargite–tennatite) character of some of the El Indio belt epithermal deposits, the Los Pelambres porphyry copper is almost devoid of arsenical minerals, which explains why the large anomaly shown by the kriging plots is restricted to the northeastern domain of the study region (Fig. 4). However, can mineralogy alone explain the intensity and extension of the geochemical anomalies here discussed? Hardly, as discussed below, two crucial aspects remain to be analyzed: the fracturing pattern of the region, and climate–physiography.

Regional fracturing

Salfity (1985) was one of the first to recognize the importance of major NW–SE and NE–SW lineaments in northern Chile–Argentina. The visual inspection of a Landsat image of the region allows recognition of a NW–SE trending major zone of deformation with associated major NNE–SSW and NE–SW structures, in the north-eastern sector of the study area (Fig. 2a). Given the history of plate convergence between Nazca and South America, the fault zone may have been active during late Oligocene time. However, due to the clockwise rotation of the convergence vector of the Nazca–Farallon plate from Late Oligocene time onwards (from NNE to ENE directed) (Cande and Leslie 1986; Tebbens and Cande 1997), movement along the fault zone (Fig. 2b) must have gradually stopped. However, the NNE–SSW structures may have been reactivated during series of events in late Miocene time, involving the subduction of the Juan Fernández Ridge, the beginning of flat subduction, and crustal uplifting (Kay and Mpodozis 2002; Yáñez et al. 2002; Le Roux et al. 2006). Whatever the case, the sole presence of a structural domain at such a scale has enormous implications from the viewpoint of the unroofing of ore deposits and secondary metal dispersion. Highly fractured rock units facilitate erosion and movement of groundwater. Besides, the surface expulsion of groundwater from seismic activity is now a well-documented process (Kelley et al. 2006). This occurs by cyclical dilatancy pumping of groundwater held in fractures, which is expelled during and after earthquake events (Sibson 2001). Thus, deep groundwater surrounding mineral deposits has the potential to disperse metals away from the deposit during seismic events (Kelley et al. 2006).

The area hosting the El Indio epithermal belt is much more fractured than the southern realm hosting the Los Pelambres deposit (Fig. 2a), and conspicuously, metal dispersion is much stronger in the former (Fig. 4). Furthermore, element concentration distribution in the kriging plots shows a remarkable NW oriented anisotropy (Fig. 4), which matches the fault zone general orientation (Fig. 2b). Given that, it could be argued that this pattern is due to sampling bias (following NW-oriented directions), three facts must be stressed: (1) The trend is extremely consistent throughout the study area (Fig. 4). (2) Sampling was done along different orientations (Fig. 1). (3) The Hurtado and Elqui highs match almost perfectly the amplitude and orientation of the fault zone (Figs. 2a, b, 4).

Climate and physiography

As shown above, the Coquimbo Region is characterized by a mountainous landscape and a semi-arid climate, with highly variable precipitations. The average rain precipitation varies from 50 mm in the northern domain to 220 mm in the southern sector. Precipitation (rain + snow) in the high altitude Andean realm is of 180 mm (average of last 20 years), with a minimum of 27 mm in 1981 and a maximum of 740 mm in 1987. Average temperature in the coast is 14°C, which increases towards the interior to 16°C. The region is characterized by strong variations induced by the Westerly winds (Veit 1996), that correlate with El Niño years, which bring intense rains and subsequent flash-floods. For example, at least eight very important El Niño flood events have been observed during the last 50 years (Jenny et al. 2002). Increased influence of the Westerlies in this northern realm has been suggested for the following periods: prior to 7,300 years BP, 5,000–3,700 years BP, and 3,000–1,800 years BP (Veit 1996). These periods are only to be regarded as major wet cycles, which in turn comprise minor, however, numerous dry–wet series. A strong El Niño year usually has catastrophic consequences for the Coquimbo Region, such as those of 1997, when several roads and bridges were cut by huge debris flows, moving sediments and boulders, literally isolating the region from the rest of Chile.

Except for a discontinuous coastal narrow belt, the region is dominated by E–W oriented valleys, with rivers that flow from the Andean mountains to the coast. The main valleys, such as the Elqui, are flanked by mountain belts of about 50 km width and altitudes of 600 to 1,000 m above sea level. However, these are to be regarded as the 'low-lands', because the Andes, in an easternmost position, reach altitudes above 5,000 m. It is precisely within this high-altitude domain, where many of the potential sources for metal contamination are located. For example, some of the mining works at El Indio reach 4,400 m above sea level, and are only 125 km away from the coast, which creates a strong gradient of altitude. The high altitude fluvial system (e.g. Toro, Turbio, Hurtado rivers) (Fig. 1) is particularly relevant to the environmental setting of the Elqui and Limarí watersheds, because these rivers receive the waters from minor tributaries that cross-cut epithermal ore deposits/prospects. In

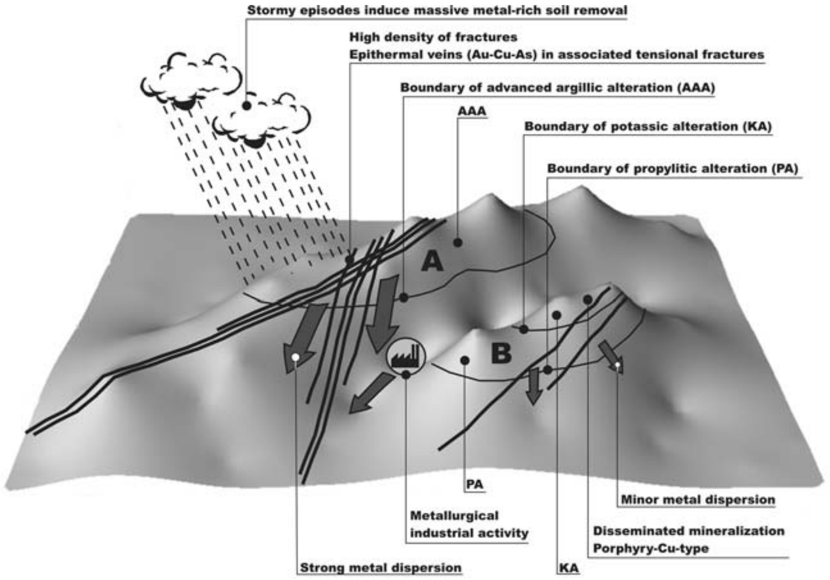

Fig. 5 Simplified scheme depicting the sources and intensity of metal dispersion in a mountainous semiarid, Andean type scenario. **a** (strong dispersion): epithermal Au–Cu–As type deposits with intensive and extensive zones of advanced argillic alteration and a high density of fractures. **b** (minor dispersion): porphyry copper type deposits with potassic and propylitic alteration within an area with low density of fractures

other words, this system drains a source area anomalously rich in Cu, Zn and As. Given the mountainous landscape, the high altitude of ore deposits (Fig. 3), and the periodic development of high-intensity rain storms, the metal rich regolith present in the alteration zones is easily eroded and washed down, transported, and incorporated to the sediment fraction of the fluvial system.

Conclusions

Metal dispersion in the Coquimbo Region is the direct response to a combination of industrial (anthropic), geologic, climatic and physiographic (natural) factors (Fig. 5). The latter include: (1) The type of ore deposit and associated hydrothermal alteration. Au–Cu–As epithermal deposits of the high sulphidation type in intermediate to felsic volcanic rocks develop extensive and intensive zones of advanced argillic alteration. Given that this type of alteration involves the strong, almost total hydrolysis of feldspars from the volcanic rocks, no minerals are left to react with the acid solutions derived from the oxidation of pyrite. These rocks lose the acid-buffering capacity and therefore, metals easily migrate from the deposit. On the contrary, the potassic and propylitic alterations associated to porphyry copper deposits (e.g. Los Pelambres) either do not modify the buffering capacity or even increase it. This would explain why metal dispersion is so strong in relation to El Indio deposit (Elqui anomaly) and mild in relation to the Los Pelambres deposit (Cuncumén anomaly). (2) The intensity of fracturing may also play a major role in the process. A high density of major fractures facilitates erosion and therefore, the unroofing of mineral deposits. Once the mineral deposit is in the surface or near surface environment, the fracturing will result in increased permeability, and therefore, in enhanced movement of oxygen-rich meteoric solutions throughout the ore bodies. This implies higher rates of oxidation and metal leaching. This is well exemplified by the El Indio and Los Pelambres deposits, which are emplaced in contrasted structural domains: the former within a highly fractured area, the latter within a much lesser fractured sector. (3) Last but not least, climate and physiography do play a major role in metal dispersion. Although the Coquimbo Region is located within a semiarid zone of the Chilean territory, the area is subjected to periodic, strong stormy (El Niño) episodes. The subsequent flash floods have a strong capacity to remove soils and sediments. If this occurs within a high altitude scenario hosting mineral deposits of the epithermal type discussed above, then massive transport of contaminated sediments and soils will go directly to the rivers, and from there, to the lowlands.

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