Strong arsenic enrichment in sediments from the Elqui watershed, Northern Chile: industrial (gold mining at El Indio–Tambo district) vs. geologic processes

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Abstract

Sediments from the Elqui watershed river system (9800 km^2; northern Chile) are highly enriched in arsenic. The river system initiates in the high altitude domain of the Andes (3500–4000 m) and drains important hydrothermal alteration zones and epithermal deposits, including the copper-, and arsenic-rich gold veins of the well-known El Indio–Tambo district. In order to study the extent, source, and age of contamination, we carried out a geochemical survey of stream sediments and older, Early Holocene lacustrine sediments. The results reveal very high contents of arsenic in both, the stream (55–485 ppm As) and lacustrine sediments (119–2344 ppm As). As shown by the ESEM-EDX study, arsenic is associated with the iron oxide mineral phase. Given that arsenic is enriched in both the stream sediments and the Early Holocene sequence, we suggest that contamination is not only industrial derived (mining operations), but also a major geological process, related to long-lived erosion of the As-rich epithermal ores and alteration zones. Erosion in this realm is particularly important during El Niño years, when increased activity of the Westerly winds brings intense rains, with catastrophic consequences in the Elqui watershed, including the massive removal of sediments in the form of large debris flows.

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Keywords: Arsenic; Chile; Elqui; Erosion; Contamination; Sediments; Gold mining; El Indio; El Niño

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1. Introduction

Arsenic is one of the most toxic elements found in nature, and constitutes one of the main concerns regarding human health. We present the results of a stream sediment geochemical survey carried out in the Coquimbo Region of Chile, that was aimed to study the extent, source, and age of arsenic contamination in the Elqui watershed (Fig. 1). The watershed covers an area of about 9800 km^2, and its main river (the Elqui) constitutes one of the few water resources of this hilly,

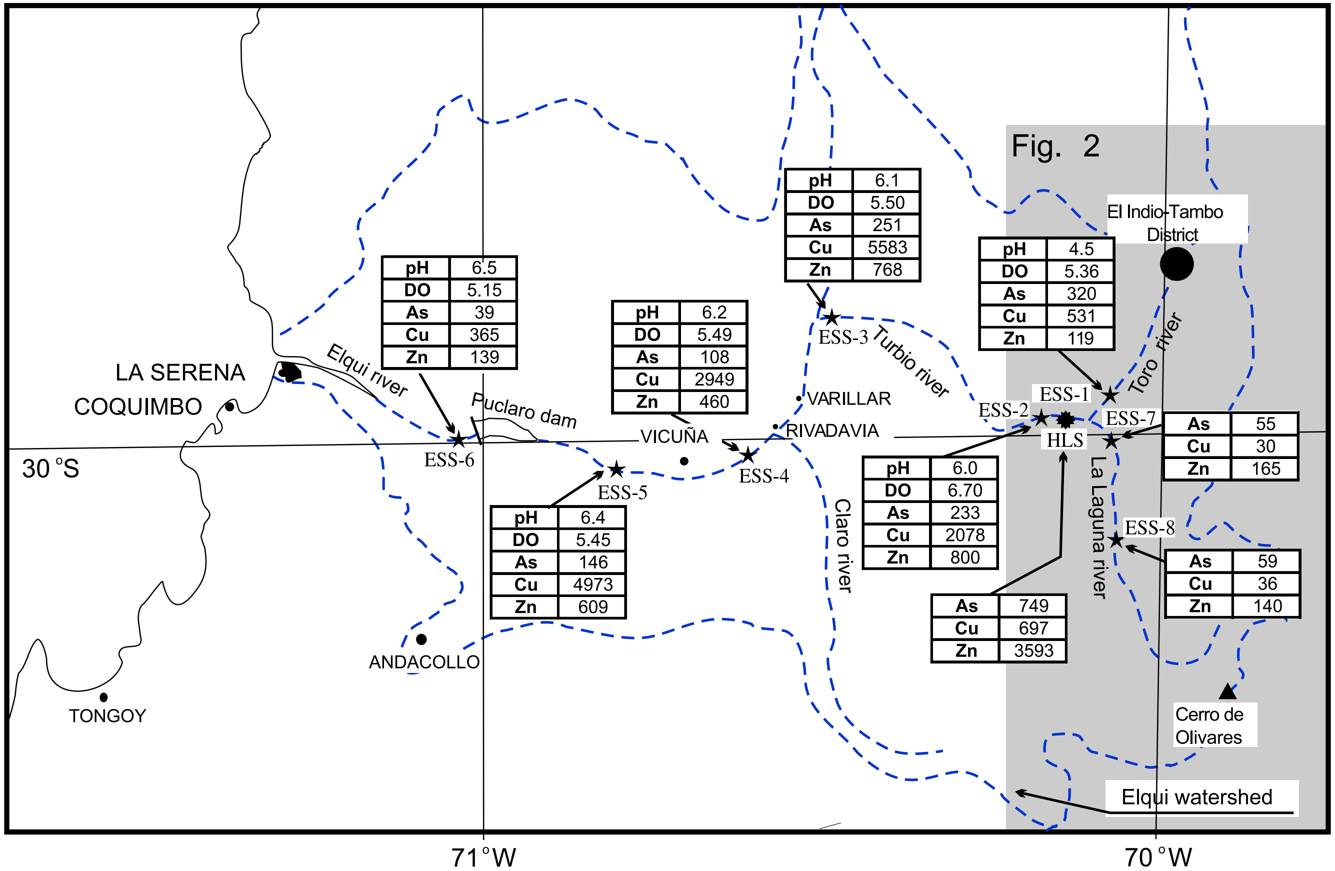

Fig. 1. The Elqui watershed and sampling stations ESS 1 – 8 (stream sediments), including location of HLS samples (Holocene lacustrine sequence). ESS and HLS boxes: mean values for As, Cu, and Zn (in ppm) and data for pH and dissolved oxygen (DO; in mg l^{-1}). The shaded sector on the right corresponds to the area depicted in Fig. 2.

semiarid region of Chile. The Elqui watershed has severe environmental problems regarding heavy metal and arsenic contents in the stream sediments and water (Maturana et al., 2001), but is not the only case of arsenic contamination in northern Chile. The Loa river, some 800 km to the north (Antofagasta Region), displays even worse contamination problems, which are enhanced by the extremely arid conditions of the deep Atacama desert (e.g., Smedley and Kinniburgh, 2002; Romero et al. 2003; among others). Arsenic contamination in the Elqui watershed, in both water and sediments, has been assumed to be related to the high-altitude mining operations of the El Indio–Tambo district. However, as observed in other mining districts (e.g., the mercury district of Almadén, Spain), contamination is usually a combination of both natural and anthropogenic processes (Higueras et al., 2003). In the case of the Elqui watershed, there are two probable sources of arsenic: (1) the mining activities developed upstream along the high-altitude tributaries (e.g., the Cu–As-rich gold ores from El Indio–Tambo district); and (2) a high-altitude, 20-km-wide N–S belt of hydrothermal alteration zones developed in volcanic rocks, that is eroded by the high altitude tributaries to the main river Elqui. The results of this study follow.

2. Physiography and climate

The El Indio deposits and alteration zones occur within a mountainous landscape in the heart of the Andes (Figs. 1, 2 and 3A), an area comprising peaks such as the Doña Ana (5690 m), or the Tórtolas (6330 m). Some of the mining works at El Indio reach 4400 m above sea level (Siddeley and Araneda, 1986), and are only 125 km away from the coast, which creates a strong gradient of altitude. Precipitation (rain + snow) in this high altitude Andean realm is of about 180 mm (average of last 20 years), with a minimum of 27 mm in 1981 and a maximum of 740 mm in 1987 (Maturana et al., 2001). However, from a geological time perspective, the whole region encompassing the so-called Norte Chico of Chile (27–33 °S) has been subjected to major climatic changes during the Holocene. In turn, these changes have been the result of the strong variability of the Westerly winds (Veit, 1996). Increased activity of the Westerlies, with more frontal activity during winter, is well correlated to El Niño years. 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 the Norte Chico has been suggested for the following periods: prior to 7300, 5000–3700, and 3000–1800 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 Elqui watershed, such as those of 1997, when roads and bridges were cut by huge debris flows, moving sediments and boulders, literally isolating the region from the rest of Chile.

The El Indio mine is crosscut by the river Malo (malo = bad) (Fig. 2) which is one of the easternmost tributaries of the Elqui watershed. The Malo is part of a high-altitude fluvial system (HAFS) of tributary rivers, comprising among others the Toro river, which together with the river La Laguna converge into the Turbio. The latter in turn is one of the main tributaries of the main river Elqui (Figs. 1 and 2). The HAFS is particularly relevant to the environmental setting of the Elqui watershed, because these rivers crosscut a Miocene hydrothermal alteration belt, and epithermal ore deposits/prospects such as El Indio, Tambo, or Vacas Heladas (Fig. 2). In other words, the HAFS drains a source area extremely rich in arsenic and heavy metals.

3. Geologic and metallogenic setting

The geology of the Elqui watershed includes a variety of rock units ranging in age from Paleozoic to Quaternary. At a more local scale, the high-altitude domain of the region comprises a series of volcanic sequences of Tertiary age, among which two are particularly important from a metallogenic point of view (Maksaev et al., 1984): the Doña Ana Formation (Upper Oligocene–Lower Miocene), with rhyolites, rhyolitic tuffs, andesites and basaltic andesites, and the so-called Infiernillo Unit (Lower Miocene) (Fig. 2). The latter unit intrudes the Doña Ana Formation, and consists of small bodies of granite, granodiorite, monzodiorite, and andesite porphyries. These intrusions triggered widespread hydrothermal processes leading to formation of precious metal epithermal

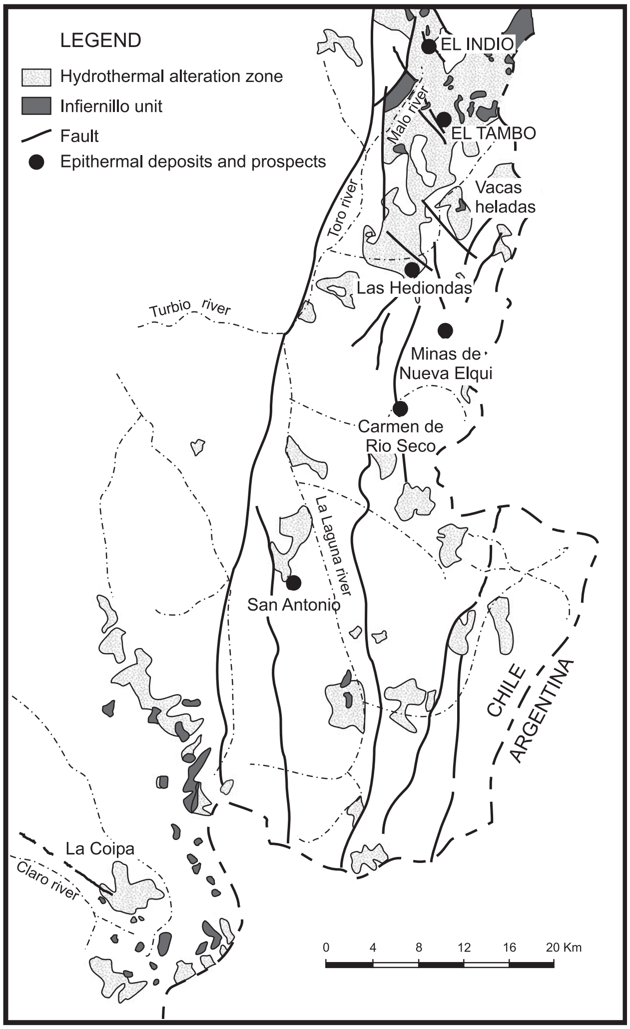

Fig. 2. Location of hydrothermal alteration zones, epithermal Au–Ag deposits, and prospects (after Maksaev et al., 1984).

deposits (e.g., El Indio–Tambo) (Figs. 2 and 3). More than 30 large alteration zones with spectacular colors (red, green, yellow) can be defined within a N–S belt of ~200 × 20 km, part of which is displayed in Fig. 2. Many of these zones comprise advanced argillic alteration mineral assemblages, with kaolinite, alunite, and silica jaspers. The Miocene history of hydrothermal processes in this realm is long and complex (Bissig et al., 2002a), including barren events spanning from about 20–10 Ma, and a main episode of mineralization at 9.4–6.2 Ma. The barren period include both high- and low-sulfidation episodes, whereas mineralization was accompanied by mostly high sulfidation episodes. Bissig et al. (2002a) indicate that the high-sulfidation, premineralization episodes in the main districts developed before incision of the pediment, whereas mineralization took place during formation of a major pediplain. Although the main hydrothermal episodes ended up by Late Miocene, magmatic activity continued until Late Pliocene (Bissig et al., 2002b). Another relevant feature in the study zone is a sequence of varved Early Holocene lacustrine sediments (HLS; 9640 ± 40 years BP, AMS radiocarbon date, Beta Analytic 175328; sample: HLS-17), which occur as perched outcrops in the mountain slopes, flanking the river Turbio for about

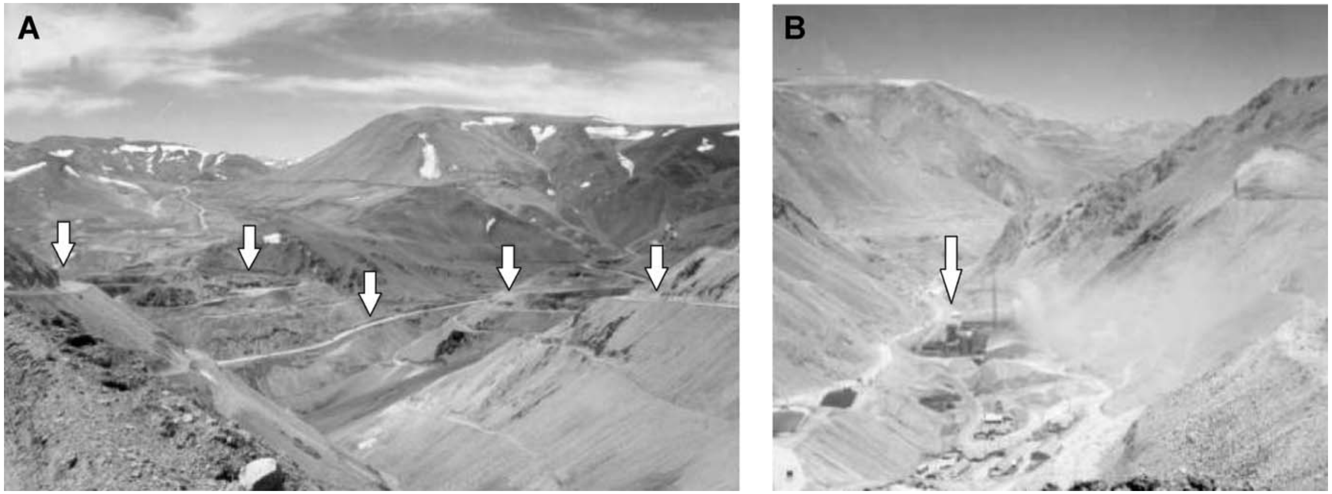

Fig. 3. The El Indio mining site. (A) General view of the works from the east; the arrows indicate earth movement works. (B) The El Indio roaster (view from the north).

3 km (Figs. 1 and 4). This +10-m-thick, As-rich sequence (up to 2344 ppm As) comprises varved, alternating light colored clay–gypsum beds and dark carbon- and gypsum-rich horizons, representing seasonal drier and wetter episodes. This unit represents the remnants of a small Early Holocene lake that most probably formed in response to extremely humid periods, associated landslides, and subsequent damming of the paleoriver system, a rather common process recorded in other sectors of the Andean realm (Trauth et al., 2000).

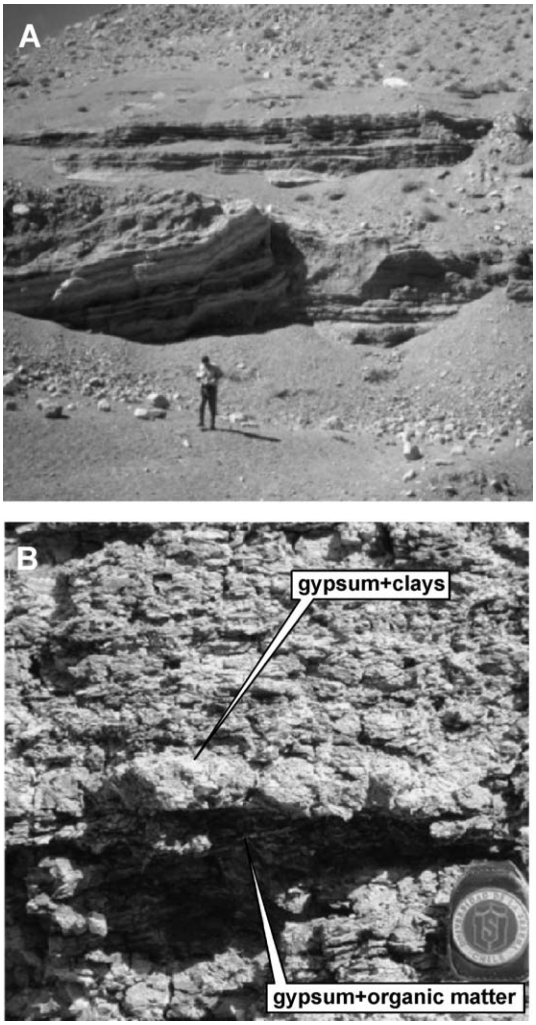

Fig. 4. The Early Holocene varved lacustrine sequence. (A) General view. (B) Detail view of the sediments.

4. Industrial setting

The El Indio–Tambo deposits (Figs. 1, 2 and 3A) have a mining history (Lagos and Velasco, 1998) that initiates during the 1960s. However, the early mining works were of small scale and no important mining took place until 1975 when the St. Joe Gold acquired the rights to the deposits. The deposits changed hands several times during the 1980s being first acquired by the Fluor (1981), then by the Alan Bond Group (1987), and finally by the Lac Minerals (now Barrick Gold). The El Indio mine (Lagos and Velasco, 1998) has been exploited both by open pit and underground works, whereas Tambo is an open-pit operation. Both mines are now closing. The extracted dry ore is sent to a plant with a capacity of 2600 t/day (1988). The mineral undergoes cyanidation and flotation. The copper concentrate (mainly from enargite flotation) contains 20% Cu, 50 g/t Au, 300 g/t Ag, and 8% As. The concentrate is later treated in a roaster furnace to remove the arsenic (Fig. 3B). The gas generated passes through two cyclones and is mixed with air to allow total oxidation of As and S. The gas eventually passes through an electrostatic precipitator and it is mixed with cool air, which leads to precipitation of arsenic trioxide (As_2O_3). The tailings of this first stage are then prepared for cyanidation to recover gold and silver.

5. The survey

Although the access to the Malo is not possible because the river is within the mining properties of El Indio, the Toro, Turbio, La Laguna, and Elqui rivers provide more than enough geochemical information regarding the high (HAFS) and low altitude realms of the Elqui watershed. We took 14 samples of stream sediments (ESS) and 14 from the Holocene lacustrine sediments (HLS) (Fig. 1). The ESS samples (~ 5 kg) were collected from the shores of the rivers, focusing on the silty fraction, and stored in plastic bags. Since previous studies (Maturana et al., 2001) had shown that chemical elements that might be of interest (e.g., Pb, Cd, Hg, Ba, Co, Cr, Ni) did not show significant variations in the watershed, and displayed normal values, we concentrated our efforts on As, Cu, and Zn, and Fe. Both vertical (different beds) and horizontal (along beds) sampling was carried out for the HLS samples. The samples (ESS and HLS) were dried and sieved at the University of La Serena (Chile). We selected the < 60 μm fraction after several preliminary tests, as it concentrated high contents of arsenic. The sediment samples were digested in hot aqua regia (3:1 HC1:HNO_3), followed by dissolution with HCl (25%), which leaves behind a silica-only residue. The elements were analyzed by Atomic Absorption at the Geoanalítica laboratories (Chile), with detection limits of 2 ppm for As, 1 ppm for Cu and Zn, and 0.01% for Fe. The mineralogy of the sediments was studied by XRD (instrument: Siemens Kristalloflex 810; 40 kV – 30 mA, $2\theta = 2°/40°$, time = 1, step: 0.03) at the Departamento de Cristalografía y Mineralogía (Universidad Complutense, Madrid), and ESEM-EDX (instrument: Philips XL30; 25 kV) at the CAT facilities of Universidad Rey Juan Carlos (Madrid). The field procedures for pH and dissolved oxygen determinations were equivalent; water was collected from the river, filtered, and placed in a clean plastic bottle (500 cc). To measure dissolved oxygen in the waters, we used a HACH instrument, model SensION-6. We calibrated the probe and meter using the fresh water–air calibration method, and we also calibrated for temperature and altitude. To measure pH, we used a HACH, model SensION-1 portable instrument, which was rinsed before the analyses with deionized water. In addition, the meter was systematically recalibrated using appropriate solution standards.

6. Results and discussion

6.1. The sediments: mineralogical characterization and trace elements

We observe three types of mineral constituents in the studied sediments: (1) a silicate fraction, with quartz, plagioclase, and phyllosilicates, the latter comprising smectitic clays (montmorillonite), kaolinite, and muscovite in a proportion of ~ 2:2:1 (relative intensity of peaks); (2) a poorly XRD defined oxide fraction comprising goethite, thus suggesting a partially amorphous mineral phase; and (3) salts, with halite, gypsum, and bloedite [$Na_2Mg(SO_4)_2 \cdot 4H_2O$]. Halite and sulfates precipitate because of the strong evaporation generated by the generally arid climate. Gypsum is particularly important in the Holocene lacustrine sequence (Fig. 4), where it can be found in both the carbon- (Fig. 5A), and silicate-rich beds.

As shown by the ESEM-EDX studies, there is a remarkable association between the iron oxide phase and arsenic (Fig. 5B and C). For example, the analyses of the oxide mineral grains in the HLS samples display contents of As (1.53–2.35%), Cu (traces – 0.89%), Zn (traces – 0.44%), Fe (35.2–52.2%), with very low sulfur (1.45–4.36%), which suggests that the oxide phase derived from the almost total oxidation of sulfide minerals. The ESEM-EDX studies did not reveal the presence of arsenic in other mineral phases.

Arsenic, copper and zinc are enriched or extremely enriched in the studied sediments. Copper and zinc are enriched up to factor of 119 and 184 compared to normal sediments (clay + slates; Rösler and Lange, 1972). Both arsenic and zinc are particularly enriched in the lacustrine sediments, whereas the higher values of copper are found in the stream sediments. Compared to reference values of arsenic (EF1–EF2; Table 1) the Elqui samples are enriched by a factor of 1.4–89.4 (stream sediments) and 4.2–468.8 (lacustrine sediments). This reveals the importance of contamination in the sediments of the watershed, and calls the attention upon the perched lacustrine sequence, that is to be regarded as a natural secondary deposit of As, which should be closely examined in any future risk assessment studies in the Elqui watershed.

Although we did not analyze arsenic in water, data for the year 1995 indicate values of 1.514 mg l^{-1} at the river Toro, 0.227 mg l^{-1} at Varillar, and 0.008 mg l^{-1} at La Serena (see Fig. 1 for location), showing a remarkable downstream decrease in As concentrations (Guevara, 2003).

6.2. Geochemical behavior of arsenic: potential sources and transport

The geochemical behavior of arsenic in natural waters differs from that of cations (Smedley and Kinniburgh, 2002). For example, arsenic is mobile under a wide range of pH and Eh, as either oxyanions of arsenite (As^{3+}) or arsenate (As^{5+}). If conditions are oxidizing, arsenate species (e.g., $HAsO_4^{2-}$) dominate over those of arsenite (e.g., $H_2AsO_3^-$). The source areas

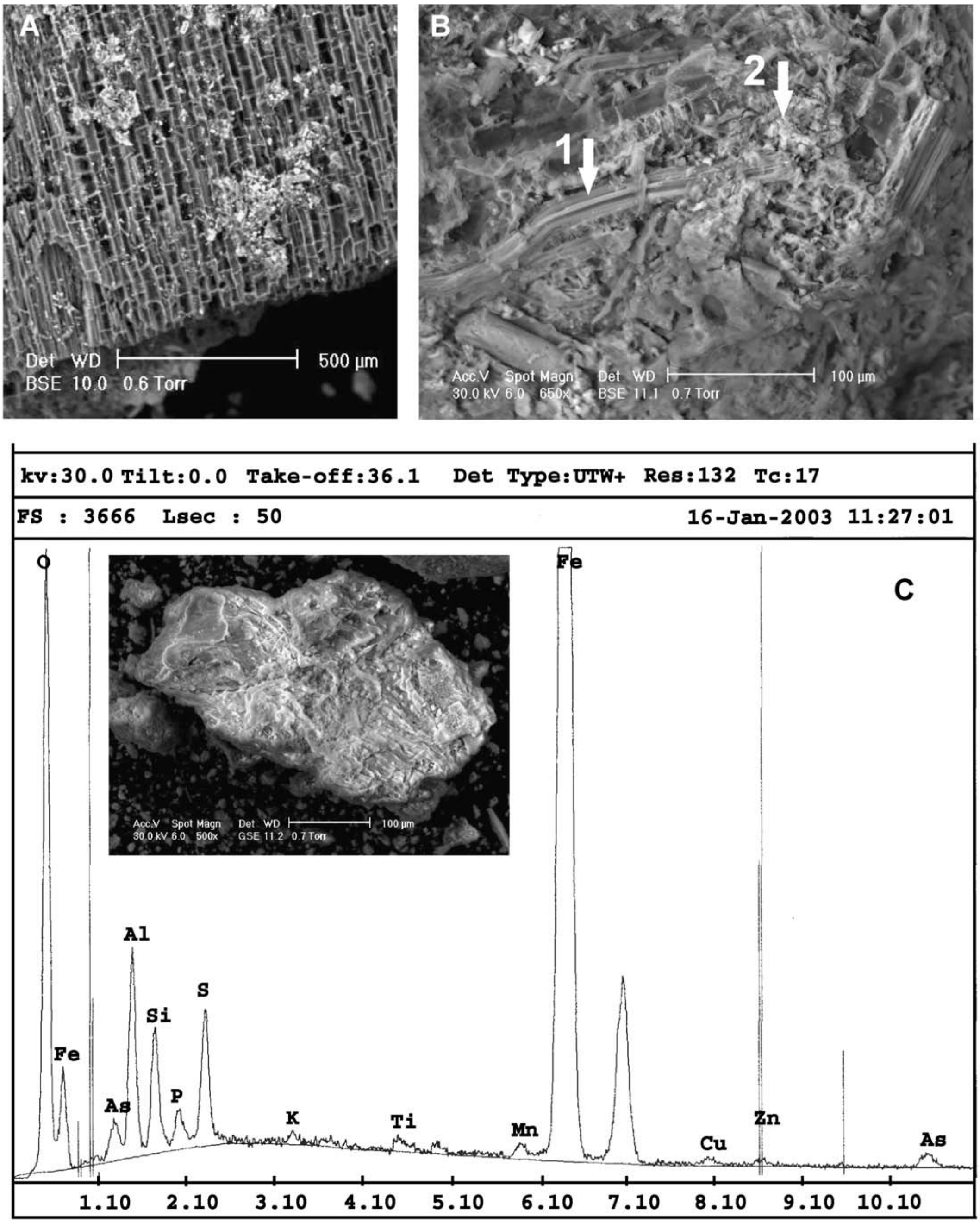

Fig. 5. ESEM images and EDX spectrum. (A) BSE image of a vegetal cell wall from sample HLS-17. (B) BSE image of fibrous gypsum (1), and As-goethite grains (2) (brighter spots), sample HLS-17. (C) EDX spectrum and GSE image of sample HLS-11 (As-goethite grain). Instrument: Philips XL30 ESEM; 25 kV (CAT, Universidad Rey Juan Carlos, Madrid).

Table 1

Results for samples Elqui stream sediments (ESS) and Holocene lacustrine sediments (HLS)

Sample	As (ppm)	As (EF1)	As (EF2)	Cu (ppm)	Zn (ppm)	Fe 1(%)
ESS-1(a)	327	11.5	65.4	550	98	4.5
ESS-1(b)	485	17.1	97.0	405	129	9.4
ESS-1(d)	150	5.3	30.0	638	129	4.9
ESS-2(a)	231	8.1	46.2	4293	558	4.8
ESS-2(b)	122	4.3	24.4	1281	331	4.0
ESS-2(c)	347	12.2	69.4	660	1511	5.4
ESS-3(a)	138	4.9	27.6	3832	491	3.6
ESS-3(b)	168	5.9	33.6	6129	647	4.7
ESS-3(c)	447	15.7	89.4	6789	1166	4.8
ESS-4(a)	108	3.8	21.6	2949	460	2.9
ESS-5	146	5.1	29.2	4973	609	3.4
ESS-6	39	1.4	7.8	365	139	4.7
ESS-7(ll)	55	1.9	11.0	30	165	6.5
ESS-8(ll)	59	2.1	11.8	36	140	4.9
Mean	202	7.1	40.3	2352	470	4.9
S.D.	145	5.1	28.9	2415	423	1.6
HLS-1(25)	647	22.8	129.4	524	1770	4.2
HLS-4	354	12.5	70.8	253	728	3.8
HLS-5	909	32.0	181.8	599	1427	4.9
HLS-7	1122	39.5	224.4	1390	4066	9.1
HLS-9	455	16.0	91.0	312	951	3.9
HLS-10	119	4.2	23.8	111	518	3.1
HLS-11	2344	82.5	468.8	685	1810	11.0
HLS-12	487	17.1	97.4	583	8143	6.7
HLS-13	557	19.6	111.4	889	3868	1.1
HLS-14	577	20.3	115.4	1590	14765	4.8
HLS-15	302	10.6	60.4	401	2285	4.0
HLS-16	597	21.0	119.4	742	8907	4.6
HLS-16(a)	629	22.1	125.8	214	650	6.2
HLS-17	1393	49.0	278.6	1462	412	5.5
Mean	749	26.4	149.9	697	3593	5.2
S.D.	544	19.9	112.9	460	4056	2.4

Enrichment factor for As (EF) = sample/reference value; EF1: 28.4 ppm As, North American Shale Composite (NASC) (Gromet et al., 1984); EF2: 5 ppm As, world average river sediments (Smedley and Kinniburgh, 2002). Standard deviation (S.D.). The EF1 and EF2 reference values are composite data that include a number of different analytical procedures, applied to relatively different types of samples having in common to be fine grained.

of arsenic are varied, although the main ones are related to geothermal fields and mineral deposits (natural sources) and mining operations (anthropogenic sources). Not only arsenic minerals such as arsenopyrite (FeAsS), enargite (Cu_3AsS_4), or tennantite [$(Cu,Fe)_{12}As_4S_{13}$], are to be regarded as potential sources of arsenic, because pyrite (FeS_2) can be also extremely rich in this element (up to 7.7%) (Smedley and Kinniburgh, 2002). Although the igneous rocks are generally poor in arsenic, the volcanic ash deposits (tuffs) may be implied in the generation of high-As waters (Smedley et al., 2002). These features are particularly relevant to the Elqui watershed case, because of the important units of Miocene pyroclastic (ash type) deposits. Additionally, the whole high-altitude belt of alteration zones (Fig. 2) was the result of large-scale, time-persistent geothermal activity during the Miocene (Bissig et al., 2002a). Furthermore, arsenic is a typical element associated with epithermal processes of the acid-sulfate type (high-sulfidation systems), and occurs in mineral assemblages of the type enargite–pyrite (Heald et al., 1987). This is particularly relevant to the case of El Indio, which hosts two types of veins (Siddeley and Araneda, 1986): (1) massive sulfides (enargite–pyrite) and (2) quartz–gold. The massive sulfide veins (before mining) were up to 200 m long and 0.5–12 m thick, and had grades of 6–12% Cu, 4–10 g/t Au, 60–120 g/t Ag. The quartz–gold veins (before mining) were up to 200 m long and 0.5–6 m thick. These veins were extremely rich in gold, including an early exploration assay yielding 3500 g t^{-1} Au, which actually gave name to one of the lodes (the 3500 vein). However, the latter veins were not devoid of arsenic and sulfur, which reached mean values of 1.7% As and 7.4% S (Siddeley and Araneda, 1986).

Oxidation and leaching of arsenic ores in the superficial environment of pyrite–enargite veins lead to formation of H_3AsO_4 (e.g., Escobar et al., 1997):

$$\begin{aligned}&Cu_3AsS_4 + 5.5Fe_2(SO_4)_3 + 4H_2O \rightarrow 3CuSO_4\\&\quad + 11FeSO_4 + 4S + H_3AsO_4 + 2.5H_2SO_4\end{aligned}$$

However, as pH increases, H_3AsO_4 becomes unstable, and the dominant arsenic species is $H_2AsO_4^-$ (pH>2; Smedley and Kinniburgh, 2002). On the other hand, the oxidation process of pyrite is a net producer of goethite:

$$\begin{aligned}&4FeS_2 + 10H_2O + 15O_2 \rightarrow 4FeO(OH)\\&\quad + 16H^+ + 8SO_4^{-2}\end{aligned}$$

Colloidal goethite has a net positive charge (e.g., Seaman et al., 1997) in acid media, which binds arsenic complex ions by adsorption. However, these complex ions may remain strongly bound to goethite up to higher pH values of 8.0–8.5 (Smith, 1999; Smedley and Kinniburgh, 2002). Desorption of arsenic from goethite may occur by competition between negative charges for the positive colloid, a reduction of the iron oxide mineral phase (Meng et al., 2002), or high pH values (>8.5). Given the Eh–pH conditions of the superficial environment of the supergene alteration zones (As source area), we may rule out the second and third possibility. Those As complex ions which are not adsorbed by goethite will migrate in solution either as $H_2AsO_4^-$ at pH 2–7 or as $HAsO_4^{2-}$ at pH ≥ 7 (Smedley and Kinniburgh, 2002). Since the observed pH in our field stations 1–6 varies from 4.5 to 6.5 (Fig. 1), we may infer that the dominant aqueous As species is $H_2AsO_4^-$.

Given the mountainous landscape, the high-altitude character of the tributary rivers of the study region, and the periodic development of high-intensity El Niño rain storms (once every 2–7 years; average: 3–4 years), we may assume that the As-, goethite-rich regolith in the alteration zones is easily washed down to the rivers, and transported as particles of different sizes. On top of these natural mechanisms of arsenic leaching-transport in the study area, we have to add those triggered by the mining operations at the El Indio–Tambo district for the last 25 years, including open-pit works, road construction, and others of similar characteristics involving earth moving (e.g., Lagos and Velasco, 1998) (Fig. 3A). Thus, we may infer at least two main mechanisms of arsenic input into the river system in the study area: (1) as unbound complex ions of the type $H_2AsO_4^-$; and (2) as adsorbed As species to iron oxides removed from the mountain slopes by erosion and mining works.

While reducing environments lead to desorption of arsenic from iron oxide minerals (Smedley and Kinniburgh, 2002), the Elqui watershed provides oxidizing conditions (5.15–6.70 mg l^{-1} of dissolved O_2; Toro, Turbio, and Elqui rivers; stations 1–6) (Fig. 1) allowing the existence of goethite phases that bind the arsenic species. In turn, this mineral phase is rapidly incorporated to the sediments, thus removing part of the arsenic dissolved in the waters. This assumption is supported by the high As contents present in the sampled stream sediments. Station 6 (immediately after the Puclaro dam) (Fig. 1) records the lowest value of As, which may be the result of sedimentation of the silt fraction and iron oxides in the bottom of the water reservoir.

6.3. *Industrial vs. geologic process*

This survey may provide some useful insights into the problem of evaluating the actual risk derived from mining operations. Given the nature of the mining works at El Indio–Tambo district, it is relatively easy at first sight, to find a ‘clear culprit’ regarding the ultimate source of As contamination in the Elqui watershed. However, we must take into account that once erosion starts, the unroofing of a mineral deposit (a process enhanced in the high-altitude environment) may lead to the massive and sustained leaching of metals, and therefore, to long-lived ‘natural contamination’ of rivers. The longer the process, the greater the effect. As shown by the arsenic contents of the Early Holocene sequence, we believe that the Elqui watershed proves this rule to be true. Does this mean that the mining operations at El Indio–Tambo have nothing to do with the arsenic contamination in the Elqui watershed? Hardly, it would be unreasonable to think that preparation of the mining areas (involving important road construction works), and the development of open pit mining and metallurgical operations (Fig. 3) did not contribute with some arsenic to the river system.

7. Conclusions

In the absence of the Holocene sequence of lacustrine sediments, it would have been difficult to study the relative importance of industrial and natural process. However, the high levels of arsenic displayed by these Early Holocene sediments, together with their high position respect to the river, suggest that contamination in the Elqui watershed (both water and sediments) is a well-established geological phenomenon, predating human activities in the area. Furthermore, the sediment samples from La Laguna river (samples ESS-7–8) (Fig. 1) show that the El Indio–Tambo sector is not the only source of arsenic in this realm.

Taking into account the ^{14}C age (9640 years BP) of the lacustrine sequence, we may infer that sedimentation started right after the sudden ending (10,000

C^{14} years BP) of the Younger Dryas (global arid and cold period), which in turn coincides with the onset of the milder and wetter conditions that led to the so-called Holocene Optimum. Under these new global climatic conditions, the rain and temperatures increased, and the ice sheets began to melt. In the case of the Elqui area, this period also coincides with an increased influence of the Westerly winds (Veit, 1996), which bring most of the winter rain to central and southern Chile (e.g., Jenny et al., 2002). This climatic scenario may explain the sudden appearance of the As-rich lacustrine facies in the 'paleo Elqui' system. Intense rain (and snowfall), coupled to rapid snowmelts, and earthquakes (the region is very seismically active; Pardo et al., 2002) would explain two major points: (1) increased erosion of the higher mountains, and therefore, important transport of arsenic from the hydrothermally altered zones; and (2) damming phenomena during the Holocene in the river system and storage of the sediments in lacustrine sediments.

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