Economic Geology
Vol. 95, 2000, pp. 655–662

4,500-YEAR-OLD MINING POLLUTION IN SOUTHWESTERN SPAIN: LONG-TERM IMPLICATIONS FOR MODERN MINING POLLUTION

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Abstract

The Tinto river drains the Rio Tinto mining district, which comprises the world's largest known massive sulfide deposits; these orebodies have been mined from the third millenium BC to the present. The Tinto river is strongly acidic (pH, 1.5–2.5); during flood events, it transports a sandy material, including abundant detrital pyrite grains. A core drilled in the Holocene sediments of the Tinto estuary allows for investigation of recent and historical mining pollution. Two anomalous horizons have been recognized (0–1.3 m; 3–4 m). Both are characterized by very high metal content (100 times over the background) and by the presence of abundant clastic pyrite grains. The metal association (Pb, Ba, As, Cu, Zn, Sn, Tl, Cd, Ag, Hg, Au) is typical of that of the Rio Tinto pyritic ore. The upper horizon corresponds to the modern mining activity; the lower horizon has been dated at 2530 BC (^{14}C AMS calibrated age).

We show here that active mining occurred early (Copper Age) in the Rio Tinto area, resulting in a watershed-scale metal contamination. We also show that anthropogenic input of metals may be accumulated and immobilized during thousands of years in estuarine sediments.

Introduction

Mining activity is a major source of metal contamination by toxic metals released into surface waters. Renewed interest in the impact of mining followed the recent accident at Aznalcollar, Spain. On April 25, 1998, a tailings spill from the mine of Aznacollar, in the southern Iberian pyrite belt, released about 7×10^6 m^3 of sulfide sludge in a tributary of the Guadalquivir river (Van Geen and Chase, 1998), which drains the Donana national park, the most important wildlife reserve of UNESCO in Europa (Fig. 1). The sulfide sludge contained a mixture of acidic waters (pH, 2–3.5) and very fine sulfide material (<30 μm) dominated by pyrite, with about 2 percent Zn, 0.9 percent Pb, 0.6 percent As, 0.2 percent Cu (dry material) and abundant traces of other toxic metals such as Tl, Hg and Cd (Table 1). The flood wave was toxic for plankton, benthos, fish, and crab populations in the river. One week after the spill, extremely elevated Zn concentrations (0.6–1.2%) were found in the river sediments downstream from the mine over a distance of 40 km (Van Geen and Chase, 1998).

There is much archeological evidence of ancient mining in the Iberian pyrite belt; it is well known, for example, that the Rio Tinto orebodies have been mined at various times since the third millennium BC (Briard, 1976; Rothenberg and Blanco Freijero, 1980). The aim of this study was to investigate the impact of ancient mining, at a watershed-scale, and to compare ancient mining contamination with modern mining release. This should allow predictions of the long-term behavior of modern metal-contaminated sediments in this area.

The Rio Tinto Watershed

The southern Iberian pyrite belt, which belongs to the southern part of the Iberian Variscan orogenic belt, is the largest repository of volcanogenic massive sulfide deposits in the world. The pyrite belt includes more than 80 known deposits that are hosted in a Late Visean volcano-sedimentary sequence. These massive pyrite deposits contain (mined and reserves) about 32 Mt Zn, 13 Mt Cu and 11 Mt Pb (metal tonnages, Leistel et al., 1994).

The Rio Tinto massive sulfide district is the biggest in its class. The Rio Tinto district comprises more than 10^9 t of massive pyrite ore. These super-giant deposits have abundant base metal sulfides (Zn, Cu, Pb) and associated trace metals (Cd, As, Tl, Sn, Hg, Ag and Au; Table 1). The deposits have also had an extensive mining history. The Rio Tinto deposit has been mined since the Copper Age, then during Tartessian and Phoenician times (1200–500 BC), with greatest amount of activity taking place during the Roman period (Flores, 1981). Mining started again in the last part of the nineteenth century and has continued to the present. These successive mining activities, from the Copper Age until the present day, have exploited outcropping and near-surface pyritic orebodies, leaving wide volumes of pyrite-rich waste rocks and mining wastes.

Acid mine drainage resulting from the oxidation of pyrite is especially important in the Rio Tinto mining district. The headwaters of the Tinto river are in the area of intense mining, which includes wide stockpiles of pyrite-rich wastes and retention ponds of acid mine

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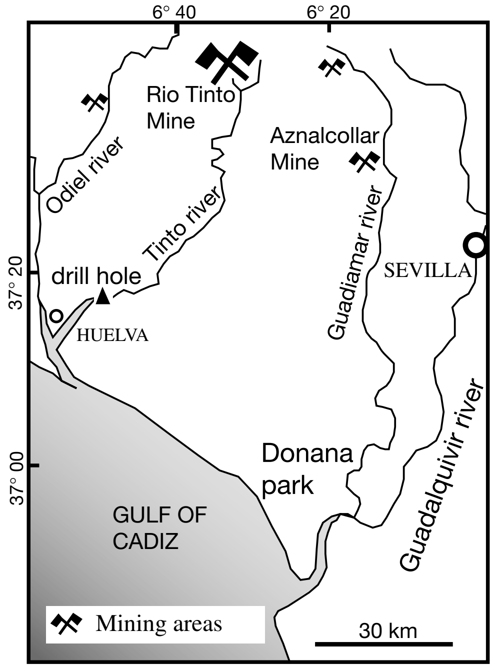

Fig. 1. Sketch map (southwest Spain) showing the location of the Rio Tinto and of the Aznalcollar mining areas and the location of the core drilled in the upper estuary of the Tinto river (Huelva ria).

drainage waters. The name of the Tinto river ("tinto " means "red wine" in Spanish) clearly refers to the uncommon brown-red color of its waters.

The Tinto river, which is 90 km long, remains strongly acidic (pH, 1.5–2.5) from its source zone, about 400 m elev, down to its estuary in the Ria of Huelva (Fig. 1). Its red-colored waters contain high sulfate and dissolved metal contents (Nelson and Lamothe, 1993; Elbaz-Poulichet et al., 1999). The mean discharge is relatively small—about 15 m^3/s, ranging from 1 to 100 m^3/s depending on seasonal variations, including dry periods and rainy periods with floods. The Tinto river sediments are gray sands, including quartz and slate elements and abundant detrital pyrite grains that are weakly weathered and slightly rounded.

Methods and Materials

A core was drilled (lat. 37°18'16", long. 6°48'10"), down to the bedrock, through the Holocene sediments of the upper part of the Rio Tinto estuary (Fig. 1). This zone corresponds today to a flood plain that is usually dry, being 1.15 m above the mean high-water level. The core, 7 cm diameter, is about 15 m in length. Core recovery was relatively good (92%) and the core material was only moderately disturbed and fragmented; consequently, there is no uncertainty in depth control. Core material was protected in a PVC sheath. It was sawed longitudinally in four parts for lithological, geochemical, and dating studies, and the last part was kept as reference. Lithology was studied both using optical microscopy and scanning electronic microscopy to investigate the sulfide phases. Twenty samples of core material (30–50 g dry material) were selected for major and trace elements analysis (Fig. 2).

Present sediments from the Tinto river were collected randomly within the uppermost 5 cm. They were dried before examination by SEM, then analyzed (30–50 g) for major and trace elements. The sulfide sludge from Aznalcollar was collected along the banks of the Guadiamar river one day after the spill.

The geochemical analyses for major (including S, CO_2,and organic C) and trace elements (including Cl and Hg) were done by X-RAL laboratories (Don Mills, Ontario, Canada) and at the Montpellier University, using XRF (X-ray fluorescence), NAA (neutron activation analysis), ICP-MS (inductively coupled plasma-mass spectrometry) and AA (Atomic Absorption) spectrophotometry.

The SEM investigations were performed with a Hitachi S-4500 instrument coupled with an energy-dispersive X-ray spectrometer (EDS); detection limits were about 0,1 percent, with a precision within 20 percent.

Activation mass spectrometry (AMS) radiocarbon dating was performed by Beta Analytic, Inc. (Miami). The analyzed sediment samples (35–75 g) contained enough organic carbon (0.5–1%) to ensure accurate analysis and all analytical steps went normally (graphitization and AMS radiocarbon counting); a charcoal fragment (4.3 g) was picked for complementary analysis. The conventional ^{14}C ages were calibrated to calendar years using the Pretoria Calibration Procedure based on tree-ring data as calibration curves (dendrocalibration); the calibrated ages are given BC ages with 95 percent probability.

The ^{210}Pb determinations were done on the uppermost 30 cm of the core in order to determine the chronology of pollu-

TABLE 1. Metal Contents of the Two Anomalous Horizons of the Core and Comparizon with the Normal Estuarian Sediments of the Core

	Zn	Cu	Pb	As	Cd	Sn	Ag	Tl	Hg	Au	Ba
Rio Tinto massive sulfide ore (avg)[1]	20,000	7,000	7,000	2,000	150	350	45	35	40	0.8	Unknown
Pyritic tailings of Aznalcollar (spill)	21,200	2,120	8,500	6,100	31	22	50	103	Unknown	0.06	70
Pyrite-rich sand from the Tinto river	3,200	950	1,200	3,900	57	20	14	24	12	0.07	2,900
Upper pyrite-rich sand horizon (core)	300	760	5,300	1,400	9	100	17	18	5.1	0.2	3,400
Lower pyrite-rich sand horizon (core)	240	400	2,500	900	6	45	10	12	3.0	0.1	1.600
Normal estuarian black mud (core)	67	24	7	12	<1	2	0.9	0.4	0.04	0.003	230

All values given in ppm

Metals concentrations in the sands from the upper part of the Tinto river, in Rio Tinto massive pyrite ore, and in pyrite sludge released from the Aznalcollar spill are given for comparizon with the anomalous horizons of the core

[1] Leistel et al, 1993

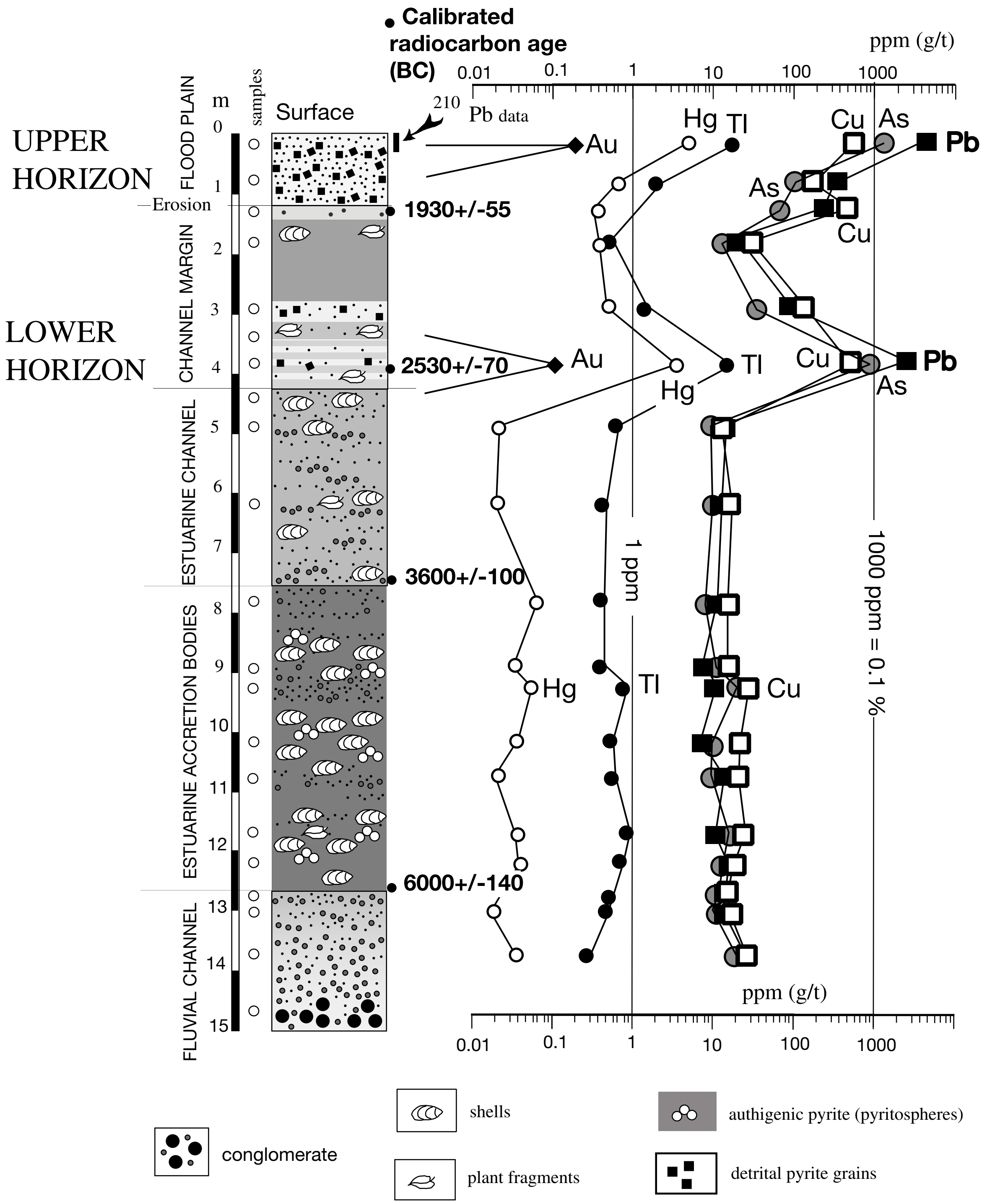

FIG. 2. Description, age dates and metal concentrations of the core. The lithostratigraphic sequence corresponds to an estuarine evolution, ending with an erosional hiatus (flood plain). The ^{14}C AMS radiocarbon dates (given as calibrated BC ages) agree with an Holocene transgressive cycle; the ^{210}Pb data from the uppermost part indicate present sediments. Two horizons show metal concentrations (ppm) that are two orders of magnitude over background. Both metal-contaminated horizons include abundant clastic pyrite grains.

tion associated with modern mining (Davis et al., in press); analyses were conducted at Florida State University by W. Burnett and associates.

Results

Lithostratigraphy

From bottom to top, the following materials are present in the core (Fig. 2): (1) coarse detrital sediments (fluvial channel and fluvial bar); (2) shelly and sandy black muds, including shell-rich horizons with authigenic pyritic nodules (estuarine accretion bodies); (3) muddy sands with shell fragments (estuarine channel); (4) alternating yellow sands and dark green muds (channel margins); and (5) yellow sands of the flood plain at the top of the core. This uppermost horizon results from flood deposits that may be strongly erosional, as suggested by the lithologic break and the sharp discontinuity with the underlying muddy horizon. Almost every year there is a major flood from the Tinto river, eroding and/or depositing up to 50 cm of sandy material on the flood plain.

Presence of metal-rich horizons

The trace metal contents in the Holocene estuarine sediments (Fig. 2, Table 1) are similar to averaged continental sediments (Taylor and McLennan, 1985). The highest contents are in organic carbon-rich sediments containing diagenetic pyrite (Fig. 3D) overgrowing plant debris or shell fragments. Against this normal geochemical background two remarkable horizons (0–1.3 m and 3–4 m) are characterized by metal concentrations that are two orders of magnitude higher than those of the other layers (Fig. 2). These horizons contain 2,500 to 5,300 ppm Pb and 900 to 1,400 ppm As, respectively. In both cases the same metal association is present, composed of high Pb, Ba, As-Cu, Zn-Sn, Tl-Cd, Ag, Hg-Au, in decreasing order of importance.

SEM observations (Fig. 3)

The two anomalous horizons are also remarkable for their mineralogic composition. They consist mainly of light yellow sands and silts, including abundant clastic pyrite grains (2–12 wt %). The pyrite grains are small and well sorted (20–50 μm); they correspond to angular fragments of subhedral pyrite grains (Fig. 3A2) that have been only slightly rounded, and which exhibit only rare dissolution pits and cracks. The only oxidized material consists of ochre fragments in the silt layers. EDS-SEM investigations suggest that galena is present as small accessory grains (1–5 μm), partly included in pyrite; rare gold inclusions (0.5 μm) are also present in pyrite. The high barium content is clearly explained by the presence of lamellar fragments of barite in the pyrite-rich sands. Cassiterite is present as small, perfectly euhedral crystals (10 μm), explaining the high Sn contents (40–100 ppm Sn).

The lower horizon (0.5–1.2% organic carbon) contains black plant fragments that often display woody cellular textures (Fig. 3C). These charcoal fragments are very small and well sorted (0.1–1.2 mm). A few small globules (30–500 μm) of vesicular glass, with smooth surfaces, are also present in this horizon (Fig. 3B). EDS-SEM analysis suggests they consist either of a Fe-Si glass, with traces of sulfur, or of a carbon-iron material with small contents of copper and sulfur (0.1–1%). These compositions, which differ from those of natural vesicular glasses, such as lavas, are similar to those of scorias and slags from metallurgical furnaces.

Dating results

The four ^{14}C calibrated ages (BC) obtained are consistent with the relative stratigraphic position of the analyzed samples (Fig. 2) : 6,000 ±140 yr for the base of the estuarine accretion bodies (12.5 m); 3,600 ±100 yr for the base of the estuarine channel (7.5 m); 2,530 ±70 yr for the lower metal-contaminated horizon (4 m) and 1,930 ±–55 yr for the floor of the uppermost metal-contaminated horizon (1.3 m).

The ^{210}Pb concentrations along the uppermost 30 cm of the core (Davis et al., in press) are strikingly constant and relatively high (8 ± –2 Bq/kg).

Discussion

Evolution of the Holocene depositional environment

The lithostratigraphic sequence and the ^{14}C ages correspond fairly well to the Holocene transgression that started in the Huelva area about 8,000 BC, filled up the estuary, and ended with a stabilization of the sea level about 3,000 BC (Borrego et al., 1999). The transgression is connected with a deglacial sea-level rise (Mannion, 1997). From ^{14}C radiodating, it appears the sedimentation rates of the estuarine sediments were between 1 and 7 mm/yr.

The two metal-contaminated horizons correspond to well-sorted sandy flood deposits. The lower horizon results from input of fluvial sands during a progradation stage in the estuarine system; the overlying muddy and shelly horizon corresponds to tidal sediments along channel margins. The upper horizon results from discontinuous input of fluvial sands over the surface of the flood plain—which is usually dry—during seasonal floods.

Geochemical and mineralogical evidence for metal contaminations from the Rio Tinto mineralization

The metals present in these two anomalous horizons reflect fairly well those of the Rio Tinto sulfide ore, including base and trace metals (Table 1). For example, the relatively high Au content of the pyritic horizons (0.1–0.2 ppm) is in agreement with the presence of gold in the Rio Tinto mineralization (0.5–1.5 ppm); SEM observations reveal that gold inclusions are present in the detrital pyrite grains. The abundance of barium, and the presence of barite detrital grains, may be explained by the fact that barite is a common gangue mineral of the sulfide ores. The relatively high Sn concentrations and the presence of cassiterite grains are in agreement with the presence of cassiterite in the Rio Tinto ore. The arsenic concentrations in detrital pyrite grains, which have been picked up from the core, range from 1 to 2 percent As, explaining the high arsenic contents of the pyrite-rich horizons.

However, the order of abundance is not exactly the same. For example, Zn and Cd concentrations are low compared to the other base metals (Pb, Cu) in the pyrite-rich sands. This may be explained either by the fact that Zn and Cd are relatively more easily soluble in surface waters or that sphalerite was not abundant in the transported pyritic material.

The pyrite grains from the two metal-contaminated hori-

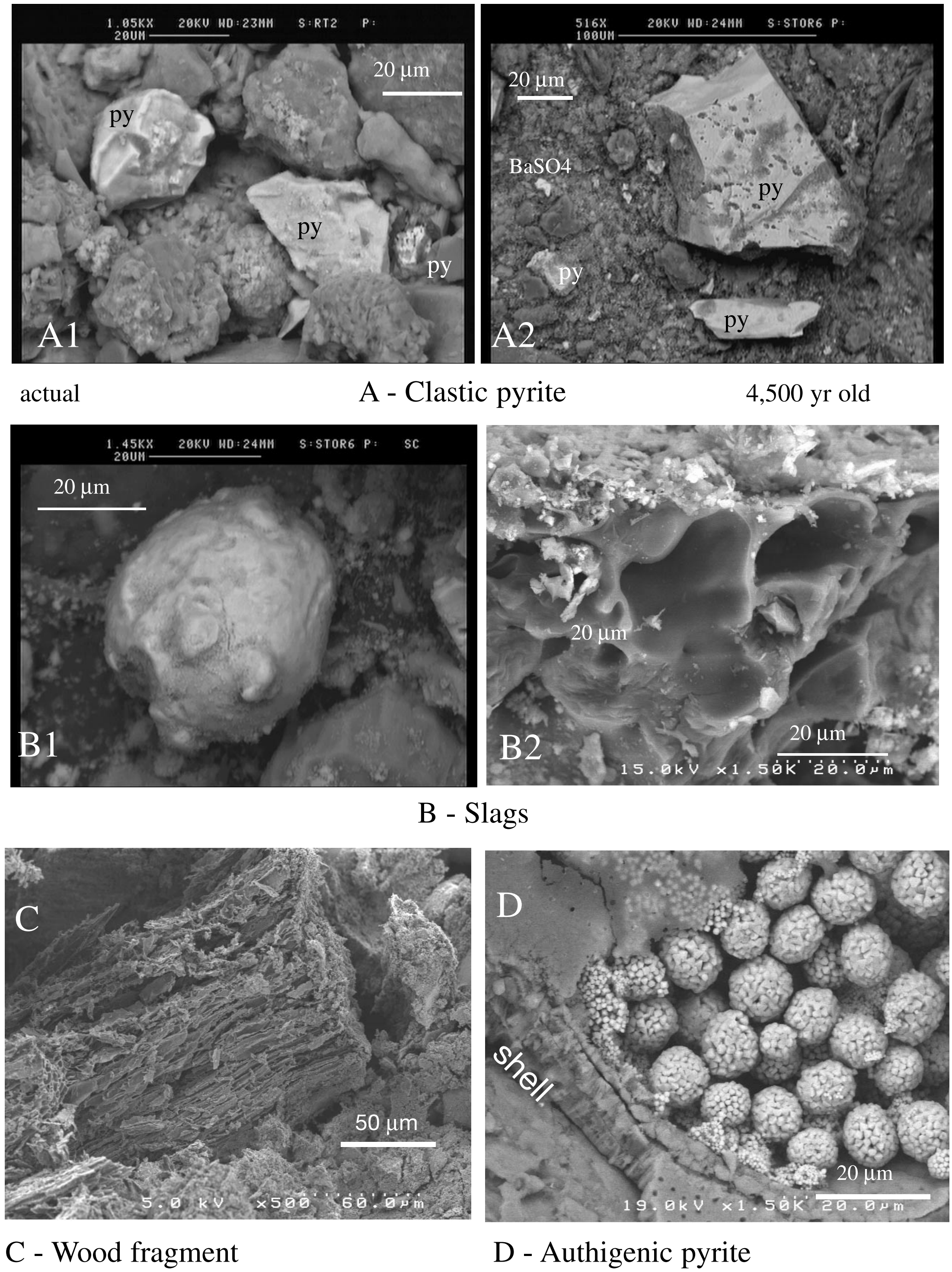

FIG. 3. Scanning electronic microscopic (SEM) images. A. (A1) Clastic pyrite grains, displaying subhedral to angular shapes, from the present sands of the Tinto river. (A2) Pyrite grains from the lower metal-contaminated horizon of the core (dated at 2530 ±70 BC) are similar in shape and size to the clastic pyrite grains from the present sands of the Tinto river (A1); note the presence of a barite fragment. B. (B1) Slag droplet from the lower metal-contaminated horizon; its composition is that of a Si-Fe glass with minor contents of sulfur (0.1–1% S). (B2) Vesiculated slag fragment, from the lower metal-contaminated horizon, showing a C-Fe-O composition with minor contents of copper, sulfur and silica (0.1–1%). The analytical data were performed using an energy-dispersive X-ray spectrometer (EDS). C. Wood fragments (charcoal) are relatively abundant (1%) in the lower metal-contaminated horizon (dated at 2530 ±70 BC) D. Authigenic pyrite crystallizing as agregates of pyritospheres in shell or plant fragments from the lower part of the core (black muddy estuarine sediments); note the difference in shape and size compared to the detrital pyrites (A1, A2).

zons are angular clastic pyrite grains (Fig. 3A2) that may be slightly rounded and corroded. They are clearly different in shape and size from the authigenic pyrite crystals and the spherulitic agregates of pyrite (Fig. 3D) that are present in the shelly black mud horizons of the core (Fig. 2). The only obvious source of pyrite in the catchment zone of the Tinto river is the Rio Tinto mining area. There are outcropping massive pyrite orebodies, with subhedral pyrite grains similar in shape and size to those of the anomalous horizons of the core, and huge stockpiles of pyrite-rich tailings and wastes from modern mining activity. The pyrite grains are very abundant in the present surface sands collected along the bed and the banks of of the Tinto river: in the immediate vicinity of the mine area, there are pyritic sands containing up to 60 wt percent pyrite, and downstream from the coring location, the estuarian sediments still contain 1 to 10 wt percent pyrite. The pyrite-rich sediments of the Tinto river display very high concentrations of toxic metals (0.5% As, 0.5% Pb, 0.3% Zn, 0.2% Cu; Table 1). These high metal contents can be ascribed to pyrite (this is the case for As) or to discrete Pb-Zn-Cu sulfide phases associated with or included in pyrite. The clastic pyrite grains from the surface sands along the Tinto river are similar in shape and size (Fig. 3A1) to those from the metal-contaminated horizons at depth in the core, providing evidence that pyrite grains may be transported by the Tinto river from the Rio Tinto mining zone to the estuarine zone. Considering the hydric flow during seasonal flood events and the average geometry of the Tinto river, the rate of sediment transport can be roughly calculated: the time for the transportation of the pyrite grains—from the source zone to the estuary—may be from 15 to 45 hours. Consequently, the pyrite grains may be deposited very quickly in the estuarine sediments without having suffered any weathering during their transportation. The same shape and size of pyrite grains characterize the pyritic sludge released within a few hours by the Aznalcollar tailings spill in the Donana national park, 40 km downsream (Fig. 1).

These geochemical and mineralogical observations are the first indication that the two anomalous horizons correspond to input of pyrite-bearing and metal-rich sands resulting from mining activity in the Rio Tinto source region.

Age of the upper metal-contaminated horizon

The impact of intensive modern mining activity that started 130 yr ago has been clearly recorded in shelf surface sediments of the Gulf of Cadiz (Van Geen et al., 1997). The upper metal-contaminated horizon of the core may correspond to this modern mining. The uppermost 30 cm of the core have high and constant ^{210}Pb concentrations; this means that the upper part of the upper contaminated horizon was deposited a short time ago, probably during recent flood events. However, considering the discontinuous sedimentary and/or erosional history of the flood plain of the upper estuary, we are not sure that this 1.3-m-thick pyrite-rich horizon corresponds in its entirety to the modern mining period. A ^{14}C AMS radiocarbon dating was performed on an ochre layer, just below the upper horizon (Fig. 2). The ochre has an age of 1930 ±50 BC (calibrated age). This is consistent with the chronostratigraphy of the core but indicates that the upper part of the Holocene sequence has been eroded before or during the deposition of the upper, metal-contaminated horizon.

Age of the lower metal-contaminated horizon

The lower horizon has been dated at 2530 ±70 BC (AMS ^{14}C calibrated age). The analyzed sample (pyrite-rich sand) contains 1 percent organic carbon. Tiny black fragments of charcoal are the only possible organic carbon source; there are no shell fragments or carbonate (<0.1%). Dating of a single charcoal material, picked up 10 cm below the first dated sample, has given a 500-yr older age (3015 ±70 yr BC), which could indicate derivation from a 500-yr-old tree (“old wood effect”) or material derived from an older layer. Although the ancients may have been burning old wood in their furnaces, this is unlikely to have significantly affected the observed ^{14}C stratigraphy of the core. The logical progression of ^{14}C dates down the core suggests that resedimentation processes in the estuary have not resulted in major disturbances in in the chronostrtigraphy.

These ages correspond to the Copper Age in the western Mediterranean area and confirm that active mining started early in the Rio Tinto district.

The presence of small droplets and fragments of likely slags (vesicular glasses with Fe-Si or C-Fe compositions and up to 0.5% copper and sulfur) in the lower horizon (Fig. 3B), is compelling evidence for contemporaneous metallurgical activity. In the same way, the presence of tiny and well-sorted charcoal fragments may reflect the common use of small charcoal fragments during metallurgical treatments.

Copper Age mining and metallurgy in the Rio Tinto area

The oldest findings indicate that metallurgical activities in the region date from 2700 BC (Rothenberg and Blanco Freijero, 1980). Except for a few metal tools in some graves and scarce traces of mining excavations and ovens, there has been little evidence of important Copper Age mining activity in the Rio Tinto district. However, the Almerian Copper Age civilization (3000–2200 BC) is well known in eastern Andalusia, Spain, for the important development of copper mining and metallurgy (i.e., in the fortified site of Los Millares, Almeria). Similar activity was likely taking place in western Andalusia, notably in the Rio Tinto area (Briard, 1976). Unfortunately, the subsequent mining periods probably erased most of the Chalcolitic mining and metallurgical works. The Romans started their mining activity from the Tartessian-Phoenician works, and active mining today recovers gold (1–1.5 ppm) from the Roman mining wastes.

Conclusions

1. We show here a new record of watershed-scale impact of early mining, over a distance of about 100 km. A 4,500-yr-old (2530 BC) metal contamination, caused by Copper Age mining, has existed in southern Spain. Notwithstanding the recent accident at Aznalcollar, it is possible that long-term release of metals from ancient mining operations that have not received the benefit of modern remediation may be a more serious problem than the impact of much larger, modern-day operations.

2. Anthropogenic input of metals may remain immobilized for millennia in estuarine sediments. Most metals can be locked as sulfides in estuarine sediments where anoxic condi-

tions (organic matter, fast sedimentation rates) can enhance the formation of authigenic sulfides and/or prevent the oxidation of detrital sulfides. Considering the recent spill of pyrite tailings at Aznalcollar, these findings may have implications for modern mining. Part of the sulfide-rich material recently discharged into the Guadiamar river (Fig. 1) might remain stored in the Guadalquivir estuarine sediments for millenia. Precautions must be taken to prevent any change in the estuarine system, particularly oxidation (by draining, dredging, or erosion) of these potentially highly toxic or deleterious materials.

3. Sulfide grains can be quickly transported far away from their source zone, during flood events, without having suffered weathering. This kind of metal transportation in surface waters, often neglected, can be of great importance, locally.

Acknowledgments

This work was funded by the European Commission (DGXII) under contract TOROS (Tinto Odiel Ocean River System), Environment and Climate Programme (ELOISE); for more information see the website <http://carpanta.ugr.es/toros/>.

We are grateful to Lex van Geen and to an anonymous member of the Editorial Board, who helped us considerably to improve this manuscript.

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