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Lead pollution resulting from Roman gold extraction in northwestern Spain

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Abstract

Roman mining and metallurgy left a detectable signal of lead pollution throughout Europe, northern Africa, and the Middle East. Las Médulas, in Northwestern Iberia, was the largest Roman gold mine and fundamentally altered the local landscape. To document the environmental consequences of this activity, we present a 4000-year record of lake sediment geochemistry from Laguna Roya, 35 km south of Las Médulas. Using the concentrations of trace metals weakly bound to sediment including lead, antimony, bismuth, and arsenic, we find increased levels of these metals from 300 BC to AD 120, during the Roman Republic/Empire. We attribute these increases to the atmospheric deposition of heavy metals arising from the regional extraction, processing, and/or smelting of gold ores. Lead pollution at the peak of this activity (15 BC) is twice as high as modern-day concentrations, suggesting that the amount of pollution generated by pre-Industrial civilizations and the associated environmental impacts are much larger than previously estimated. We find additional increases in antimony and bismuth from AD 1500 to 1700, possibly associated with post-medieval mining activity. Concentrations of lead begin to increase again ~AD 1860 during the start of the Industrial Revolution and reach a peak in AD 1990. Declining modern-day levels of lead can be attributed to the phase out of leaded gasoline. This is one of only a handful of studies to document pre-industrial pollution levels substantially higher than present-day, adding to a growing body of evidence that anthropogenic environmental degradation has been taking place for several thousands of years.

Keywords

Las Médulas, late-Holocene, lead pollution, paleolimnology, Romans, Spain

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Introduction

Northwestern Iberia is rich in mineral resources, particularly economically extractable and relatively abundant gold deposits. These resources have been exploited for several millennia, most extensively during the Roman period from the 1st to 3rd centuries AD (UNESCO World Heritage Center, 2016). During the height of mineral resource exploitation, an estimated 600 million cubic meters of earth were moved (Pérez-García et al., 2000) and around 195 tons of gold were extracted (Gómez-Fernández et al., 2012). Most of this extraction was from alluvial gold deposits; however, mesothermal gold-bearing quartz veins are abundant in this region as well (Gómez-Fernández et al., 2012; Figure 1) and were also heavily exploited. Nearly 15% of all Roman gold exploitation took place at the mining area known as Las Médulas, a World Heritage Landscape Site since 1997. Las Médulas contains gold-bearing gravel, overlain by extensive alluvial fan deposits (Pérez-García et al., 2000). Extraction relied on a technique known as *ruina montium* where water was forced through large pits in the alluvial deposits to cause wholescale collapse and subsequent hydraulic sorting of the gold-bearing gravel (Ruiz del Árbol Moro et al., 2014). Additional extraction of ores from hard-rock deposits relied on the technique of fire-setting where fires were set against stone and rapidly quenched, causing the rock face to shatter (Weisgerber and Willies, 2000). This method was extensively practiced on the gold deposits of northwestern Spain (Pliny, 1952). All of these processes fundamentally transformed the landscape, and these transformations persist to present.

Ores that were mined were eventually purified by the cupellation method where impurities were driven off in a high temperature furnace (Healy, 1978). These impurities, such as lead, were volatized, transported atmospherically, and eventually deposited as wet and dry fallout over the landscape. Lead from Iberia has been detected in Greenland ice cores using lead isotopes as tracers (Hong et al., 1994). This lead deposition is so widespread and concurrent in European lakes and peat bogs that some have suggested it may be used as a chronological marker for the Roman Period (Renberg et al., 2001). However, some differences in the magnitude and timing of increases in lead are observed, demonstrating the unique regional histories of mineral resource extraction. For example, both Zoñar (Figure 1) (Martín-Puertas et al., 2010) and Río Seco (García-Alix et al., 2013) lakes in Southern Spain record increases in lead associated with Roman metallurgy as well as earlier and larger increases. Both the Phoenicians and Carthaginians exploited Río Tinto in southwestern Spain, an area rich in silver (Richardson, 1976). These mining activities left

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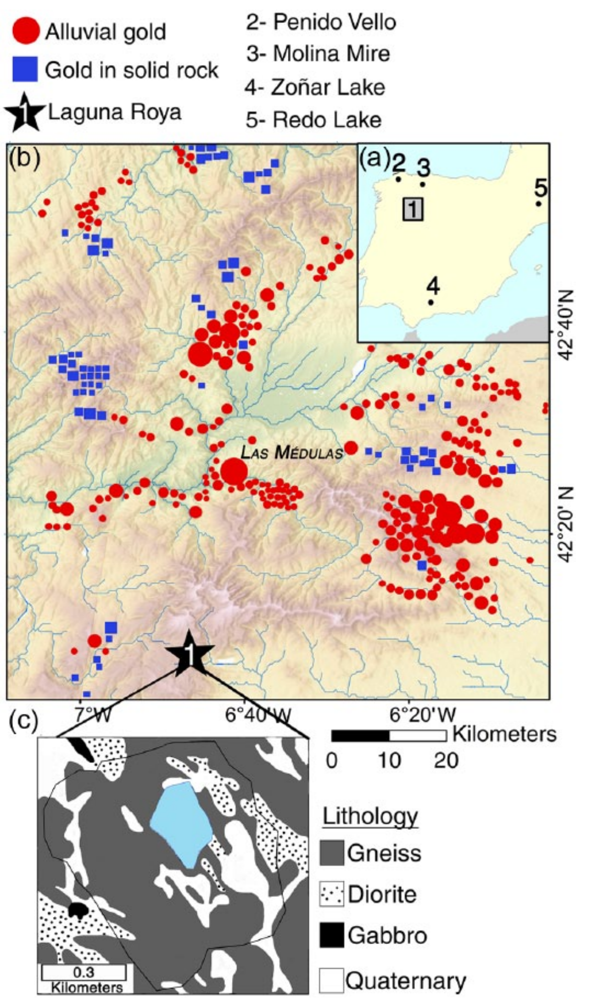

Figure 1. (a) 1: Laguna Roya; 2: Penido Vello; 3: Molina Mire; 4: Zoñar Lake; 5: Redo Lake. (b) Known Roman alluvial gold mines (red circles) and gold veins in solid rock (purple squares) adapted from Pérez-García et al. (2000). (c) Watershed of Laguna Roya with surficial geology adapted from Castro et al. (2003).

behind sediments contaminated in heavy metals (Leblanc et al., 2000) and the lead signature in the Greenland ice cores has been attributed, in part, to Carthaginian mines as well as Roman ones (Rosman et al., 1997). Most importantly for this study, the initiation of large-scale mineral resource exploitation at Las Médulas, by Roman and earlier cultures, remains uncertain (Lewis and Jones, 1970).

Most studies documenting Roman lead pollution have been focused on northern Europe (Brannvall et al., 1997; Mighall et al., 2009; Shotyk et al., 1998), though a few studies have looked at this disturbance in northern Spain (Figure 1). Molina mire in northwestern Spain found evidence of Roman metallurgy as well as 200 more years of additional mining activity after the decline of the Roman Empire (Martínez-Cortizas et al., 2013). The peak of metallurgical activity was accompanied by shifts in vegetation communities as well as changes in the hydrologic balance of the bog, likely because of human manipulation of water flow associated with ore washing (López-Merino et al., 2014). Another study of a more westerly peat bog, Penido Vello, also found increases in lead associated with Roman metallurgical activity (Martínez-Cortizas et al., 1997), and a follow-up study used lead isotopes and was able to source the Roman pollution to northwestern Spanish ores (Kylander et al., 2005), but did not find evidence for post-Roman extended metallurgical activity. An additional study of Penido Vello as well as several other peat bogs from this region (Borralleiras da Cal Grande and Pena da Cadela) examined nickel, zinc, arsenic, and cadmium and found concentration profiles similar to that of lead, peaking from AD 100 to 200 (Pontevedra-Pombal et al., 2013). In all of the aforementioned studies, pollution arising from Roman metallurgical activities was clearly detectable, but below that of modern-day levels.

Redo Lake (Figure 1) in the Pyrenees is unique in this regard. Pre-industrial lead concentrations in these sediments were at levels twice that of the last 50 years and 14 times higher than background concentration values at the peak in AD 650 (Camarero et al., 1998). Not only is the magnitude of these lead concentrations surprising, but the timing is later than would be expected. This suggests that either (1) Roman mining and metal-working activity did not leave a substantial signature in the lake and instead, this pollution was the result of medieval activities, or (2) the timing of this pollution was not properly dated. Therefore, the timing of the increase in lead remains uncertain, and the primary aim of this study is to clarify the magnitude and extent of Roman and post-Roman ore exploitation and mineral resource use not just in northern Spain, but throughout Europe (Tylecote, 1992).

From an environmental perspective, the long history of metallurgical activities contributed trace metal loadings to the landscape through wet and dry deposition of airborne pollution. A study of soils from the central Pyrenees found that the remobilization of sediments and soils contaminated by historical activities was a significant contributor to modern-day pollution accumulation (Bacardit et al., 2012). Therefore, a second aim of this study is to clarify metal distribution from this historical contamination that may be stored on the landscape of northwestern Spain, given that this area has experienced substantial metallurgical activity over several millennia.

To examine these questions, we present a 4000-year lake sediment record from Laguna Roya, a lake that has ideal characteristics for recording atmospheric pollution. Metals weakly sorbed to lake sediments have been used throughout Europe (Bindler et al., 2012; Brannvall et al., 2001), South America (Abbott and Wolfe, 2003; Cooke et al., 2007), North America (Pompeani et al., 2013), and Asia (Hillman et al., 2015; Lee et al., 2008) to infer metallurgical activities proximal to the lake as well as long-range atmospheric pollution and provide the conceptual basis for our own study. While we focus our attention on lead because it is relatively immobile once sorbed to lake sediments (Gallon et al., 2004) and insensitive to water chemistry changes such as oxidation or reduction potential (Hamilton-Taylor and Davison, 1978), we supplement our interpretation with other metals including antimony, bismuth, and arsenic.

Setting

Laguna Roya (42°13′N, 6°46′W, 1608 m a.s.l.) is a small glacial lake in northwest Spain with a maximum depth of 6.5 m and a surface area of 0.025 km^2. A survey of water quality observed a conductivity of 19 µS/cm, a pH of 7.3, and an alkalinity of 0.13 mEq/L (Aldasoro et al., 1996). The catchment area is small (0.150 km^2) and is primarily composed of augen gneiss with a few diorite intrusions (Castro et al., 2003), thinly developed soils (The European Soil Database Distribution v2.0, 2004), and low angled slopes. Vegetation is sparse and consists mainly of shrubs. There is limited hydrologic inflow and outflow, making it particularly sensitive to atmospheric processes. An average of 1.6 m of precipitation falls annually, primarily during the months of October–January (Global Network of Isotopes in Precipitation (GNIP), 2014), and the predominant wind direction is from the southwest. While many lakes in this region of Spain have been dammed, Roya has never been hydrologically modified because of its small size (Allen et al., 1996), and today, there is minimal human occupation of the watershed. Las Médulas, the largest Roman gold extraction operation, is 35 km north of Laguna Roya along with

Table 1. AMS radiocarbon dates.

UCI number	Composite core depth (cm)	Material	^{14}C age (BP)	Error ±	Median probability calibrated age (yr BP)	2σ calibrated age range (yr BP)
180956	26	Charcoal	725	15	675	665–685
164748	46	Wood	1125	30	1023	959–1172
164749	62	Charcoal	1460	30	1346	1302–1396
152027	89.5	Charcoal	2295	15	2336	2316–2349
180957	116.5	Charcoal	2875	45	2979	2874–3084
180958	132.5	Charcoal	3150	70	3359	3207–3512
152028	148.5	Moss	3470	15	3753	3651–3828
152029	209.5	Moss	3940	15	4415	4298–4438
152030	235.5	Moss	4260	20	4842	4829–4856
164750	336.5	Moss	5250	30	5996	5926–6177
164751	385.5	Wood	6460	250	7334	6756–7821
152031	427	Charcoal	7250	20	8062	8007–8159
152032	506.5	Leaf	8980	30	10,186	9941–10,232
152033	552	Leaf	9925	30	11,307	11,244–11,398
152034	587.5	Moss	10,350	30	12,207	12,034–12,388
152035	638.5	Moss	12,945	40	15,468	15,275–15,680

AMS: Accelerator Mass Spectrometer.

hundreds of other alluvial gold deposits as well as gold veins within solid rock (Figure 1).

Previous work on Laguna Roya focused on palynology (Allen et al., 1996). Approximately 8.2 m of sediment was collected and an age model was developed on the basis of Accelerator Mass Spectrometer (AMS) radiocarbon dates primarily on moss. Over 15,300 years, there were substantial changes in pollen reflecting temperature and moisture variations, but most importantly for our own study, indicators of human disturbance within the watershed were noted at a depth of around 184 cm, corresponding to 2700 yr BP or 750 BC. Anthropogenically driven vegetation changes around the watershed were inferred from the presence of disturbance taxa such as *Juglans* (walnut), *Castanea* (chestnut), *Cannabaceae* (hemp), and a variety of cultivation cereals. More recent work on Roya lake sediments focused on higher resolution palynological and diatom assemblages as well as chironomid-inferred July air temperatures only from the period of 15,500–11,200 yr BP (Muñoz Sobrino et al., 2013). In general, this work supported the findings of Allen et al. (1996), but did not focus on the time period relevant for our own study.

Methods

Field work

In 2014, a 1.24-m surface core with an intact sediment–water interface was collected using a light weight percussion coring system from the deepest part of the lake at a water depth of 6.6 m. The upper 15 cm was sliced in the field at 0.5-cm intervals and used for geochemical analysis and ^{210}Pb dating. The sediment was sampled using plastic instruments and divided into plastic bags, with little to no handling. Deeper sediment cores were collected from the same location using a steel barrel Livingston corer (Wright et al., 1984) for a total of 10 overlapping drives. Overlapping cores were correlated on the basis of field notes, visible sedimentology, and geochemical profiles to form a composite record of 6.96 m.

Water content, bulk density, and loss-on-ignition analysis

Water content, bulk density, and loss on ignition were measured at 2-cm intervals using 1-cm^3 samples. Samples were dried at 60°C for 48 h to remove water. Weight percent organic matter and carbonate content was determined by loss-on-ignition at 550°C and 1000°C, respectively (Dean, 1974).

Geochronology

Sixteen AMS radiocarbon ages were measured on wood, charcoal, and plant macrofossils (Table 1). These samples were pretreated using a standard acid, alkali, acid procedure (Abbott and Stafford, 1996), measured at the Keck Center for Accelerator Mass Spectrometry at the University of California Irvine, and calibrated using Calib 7.0 (Reimer et al., 2013). The upper 11 cm were dated using a constant rate of supply (CRS) ^{210}Pb age model (Appleby and Oldfield, 1983; Table 2). The resulting calibrated dates were used in the *BACON* code which uses Markov chain Monte Carlo statistics to create age–depth models and uses posterior probabilities to determine radiocarbon outliers (Blaauw and Christen, 2011) in the statistical software package 'R' (R Core Development Team, 2008).

Elemental analysis

Half-centimeter-thick slices were sampled at 1- to 3-cm intervals down the entire length of the core with higher resolution sampling in the upper sediment in order to validate the geochemical record against the historical record. Twenty-one replicate sediment samples were extracted from overlapping cores from a depth of 60.5 to 120.5 cm. Results were generally within 3 µg/g for Pb, 0.2 µg/g for As, 0.006 µg/g for Sb, and 0.004 µg/g for Bi. All samples were lyophilized and homogenized. Elements were extracted using 6 mL of 1 M HNO_3 overnight, a standard method for extracting weakly bound trace metals from sediments (Graney et al., 1995). Previous research has found that trace metals derived from atmospheric fallout are most frequently present as particulates, which are most commonly weakly adsorbed to clay surfaces and organic matter (Hilton et al., 1985). The supernatant was extracted and diluted before being measured on a Perkin Elmer NeXION 300X inductively coupled plasma mass spectrometer at the University of Pittsburgh. Duplicates were run every 20 samples and were generally within 10% of each other. Blanks were run every 20 samples to check for memory effects, and bleed-through was consistently below the detection limits of the instrument.

Results

Radiocarbon ages indicate continuous, relatively linear sedimentation from ~16,000 cal. yr BP to present-day (Table 1), but in this paper, we focus on the last 5000–4000 years of the record (Figure 2c) as the geochemical variations in this period

Table 2. Down-core ^{210}Pb activities, ^{214}Pb activities, cumulative weight, and CRS sediment ages.

Depth (cm)	^{210}Pb activity (Bq/g)	1σ error ^{210}Pb activity	^{214}Pb activity (Bq/g)	1σ error ^{214}Pb activity	Cumulative weight (g/cm)	CRS age (yr AD/BC)	1σ error age
Cores A-09							
0.0–0.5	0.5860	0.1615	0.1700	0.0560	0.0158	2014	1.16
1.0–1.5	0.8690	0.0970	0.0657	0.0146	0.0689	2010	1.23
2.0–2.5	0.8290	0.0905	0.0000	0.0000	0.1342	2005	1.35
3.0–3.5	0.8540	0.1005	0.0000	0.0000	0.1751	2001	1.42
4.0–4.5	0.8310	0.0895	0.0356	0.0080	0.2509	1994	1.67
5.0–5.5	0.7630	0.0815	0.0448	0.0090	0.3418	1983	2.06
6.0–6.5	0.5250	0.0580	0.0436	0.0069	0.4388	1972	2.37
7.0–7.5	0.4200	0.0487	0.0326	0.0075	0.5401	1958	2.98
8.0–8.5	0.3270	0.0406	0.0412	0.0069	0.6498	1941	4.15
9.0–9.5	0.2570	0.0345	0.0529	0.0077	0.7400	1923	5.50
10.0–10.5	0.2280	0.0318	0.0511	0.0079	0.8207	1896	10.63
11.0–11.5	0.1610	0.0296	0.0647	0.0076	0.8960	1843	46.66

CRS: constant rate of supply.

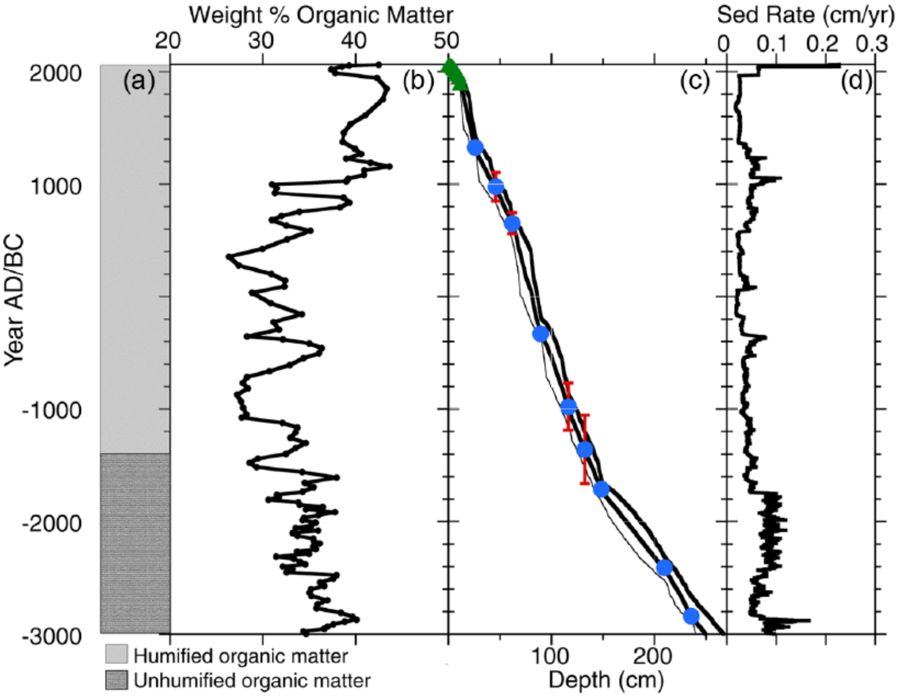

Figure 2. (a) Stratigraphic column, (b) weight percent organic matter estimated from LOI 550°C, (c) age–depth model with 95% confidence intervals and radiocarbon dates (blue circles) and 210Pb dates (green triangles) with 2σ error bars, and (d) sedimentation rate in cm/year.

encompass the most relevant archaeological and historical events. From 3000 to 1200 BC, sediments are composed of unhumified organic-rich sediment, which contains abundant discrete plant macrofossils such as moss (Figure 2a). From 1200 BC to present-day, sediments gradually transition to homogeneous humified organic-rich sediment, characterized by a lack of abundant macrofossils. Organic matter content is relatively high and ranges between 30% and 45% (Figure 2b). No carbonate material is present throughout the core.

Prior to 300 BC, concentrations of lead (Pb) and bismuth (Bi) are remarkably stable, averaging 11.19±1.56 µg/g for Pb and 0.01±0.003 µg/g for Bi (Figure 3). Antimony (Sb) and arsenic (As) are more variable, averaging 0.007±0.006 µg/g for Sb and 0.92±0.13 µg/g for As. The exception to this is a single sample where Sb concentrations increase to 0.05 µg/g at 510 BC. Henceforth, we will refer to the time prior to 300 BC as the 'background period' given the relative stability of the geochemistry. Beginning at 300 BC, metal concentrations begin to increase. They increase more substantially after 100 BC and peak at 15 BC, before declining to background values by 120 AD. Concentrations at 15 BC are 7× higher for Pb, 2× higher for Sb, 9× higher for Bi, and 1.5× higher for As than background values.

Lead concentrations remain stable up until AD 1860, but metals such as Sb and Bi show more variability beginning around AD 1500 and generally range between two and four times that of background values. Arsenic concentrations are also more variable, with a peak at AD 460 and then fluctuating between 0.9 and 1.4 µg/g from AD 1000 to present. By AD 1860, concentrations of Pb, Sb, and Bi markedly increase. Lead reaches a peak in AD 1990 of 39.0 µg/g and declines to 28.9 µg/g in the uppermost surface sediments of the core (Figure 4). In contrast, Bi and Sb concentrations continue to remain high up to the present-day at 0.075 µg/g and 0.15 µg/g, respectively. Arsenic concentrations only show an equivalent increase in the last 10 years.

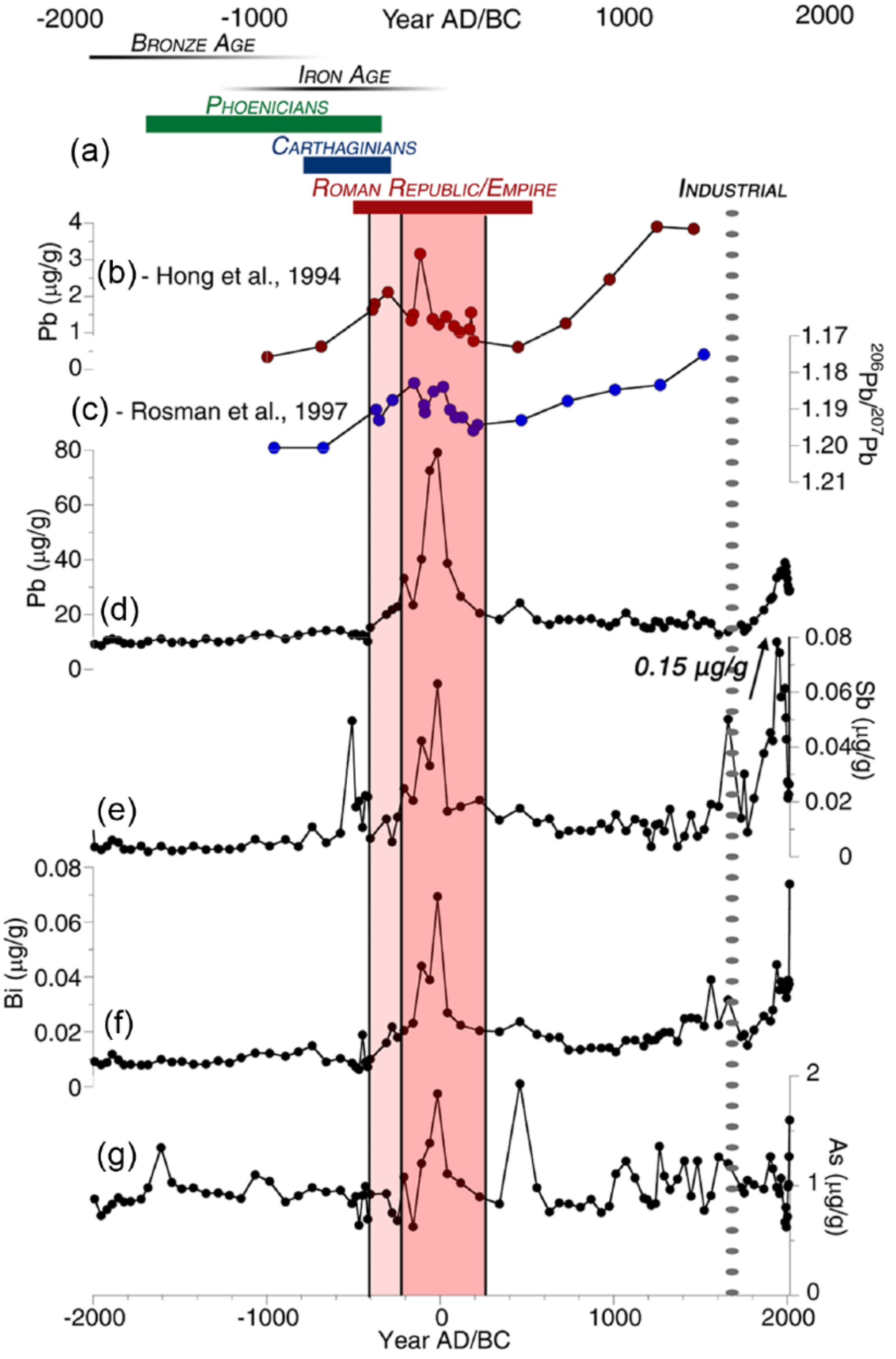

Figure 3. (a) Archaeological and cultural periods of the Mediterranean region; (b) concentrations of lead from the Greenland ice core (Hong et al., 1994); (c) 206Pb/207Pb ratio from the Greenland ice core (Rosman et al., 1997), note the flipped axis; (d) Roya lead (Pb) concentrations; (e) antimony (Sb); (f) bismuth (Bi); and (g) arsenic (As). The peak of metal concentrations at Roya is close in timing to that of the Greenland ice core.

Discussion

Natural airborne sources of Pb, Sb, Bi, and As include volcanoes, soil-derived dust, biogenic processes, and sea salt (Ferrari et al., 2000; Nriagu, 1989); however, anthropogenic sources now comprise the majority of emissions (Nriagu, 1989). The small changes in Pb, Sb, and Bi during the background period (pre-300 BC) are likely because of these natural processes, though variability is generally quite low. Known global-scale volcanic events, such as a large eruption from an unattributed location in 426 BC (Sigl et al., 2015), are not detectable in the Roya sediment core, suggesting that only variations in the local air-shed are responsible for the small background variability at Roya. The single point where Sb is high (0.05 µg/g at 510 BC) is possibly an anomalous data point given that it does not appear to be part of a larger trend in the dataset. Alternatively, it may reflect a natural source of antimony not derived from mining or human activity. Arsenic displays more variability during the background period which may be because in contrast to the other elements, it can be influenced by lake water pH, oxidation/reduction potential, and uptake by algae (Hamilton-Taylor and Davison, 1978). While the pH of Roya is neutral (Aldasoro et al., 1996), diagenetic effects do have the potential to affect the migration and diffusion of antimony and bismuth, although we suggest that this is not substantial, since trends in antimony and bismuth correlate well with trends in lead (0.58 and 0.82, $p < 0.01$, respectively).

Notable differences between this study and the previous study by Allen et al. (1996) are the age model. Equivalent depths in the Allen et al. (1996) study are ~1000–2000 years younger, but our work has more robust age control with more than twice as many radiocarbon dates. Allen et al. (1996) found an increased

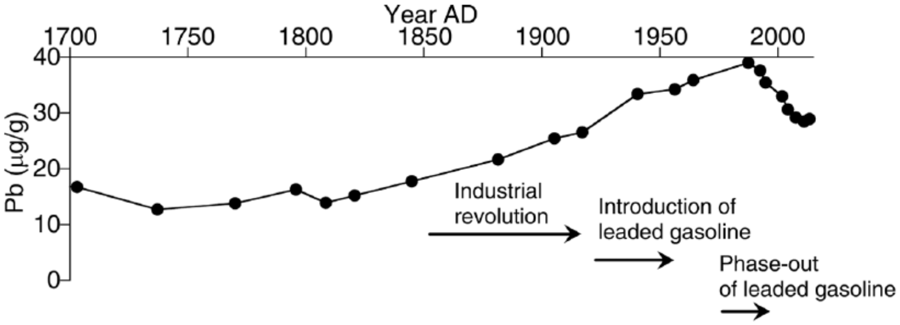

Figure 4. Lead concentrations over the last ~310 years showing a close correspondence between increases in concentration and historical events.

proportion of charcoal, as well as the presence of pollen from cultivated plants, indicating human-induced landscape and vegetation changes at 184 cm (750 BC) (Allen et al., 1996), which our age model would suggest is closer to an age of 2100 BC. Nonetheless, we do not observe any changes in our own geochemical record at either 750 or 2100 BC, suggesting that human occupation and subsequent landscape change of the Roya watershed is not a substantial driver of the geochemical signal.

The Roman period

The most prominent feature of the Roya metal record is the two-phase increase in metal concentration: phase 1 (300–110 BC) and phase 2 (110 BC–AD 120). This increase is very close to the peak in Pb concentrations (Hong et al., 1994) and decline in ^{206}Pb/^{207}Pb isotopes from the Greenland ice core (Rosman et al., 1997) that occurs from ~275 to 120 BC (Figure 3), though sampling resolution in the aforementioned studies is too coarse to pinpoint the exact timing of the change. These changes in the Greenland ice core were attributed to Roman lead smelting and are generally in agreement with numerous other geochemical records from Europe (Brannvall et al., 1997, 2001; Martínez-Cortizas et al., 2013; Renberg et al., 2001) that show widespread lead pollution during the Roman Republic/Empire.

We attribute the increases in metals at Roya, particularly Pb, to atmospheric processes. There are no surficial inflows to the lake and its catchment is relatively small. Additionally, the predominant bedrock in the catchment is gneiss (Castro et al., 2003), which is relatively resistant to erosion, and has led to the development of very thin soils (The European Soil Database Distribution v2.0, 2004) and low angled slopes. All these factors diminish the role that erosional processes play in influencing the geochemical signal. Moreover, other indicators of sediment flux that might explain the peak, such as changes in sedimentation rate (Figure 2d) or increases in lithogenic metals (Figure 5), are relatively stable through this period. Lead and other metals are commonly weakly sorbed to organic matter (Renberg, 1986); however, weight percent organic matter estimated from LOI at 550°C does not appreciably change in association with the peak (Figure 2b). We believe that it is more likely that atmospheric processes are primarily responsible for metal deposition at this site given the extremely high concentrations (7× that of background values for Pb), the abrupt increase during phase 2 that takes place over <100 years, the close correspondence to documented metallurgical activity in the region, and the unique setting of the lake. The prevailing wind direction is from the southwest while in winter the winds are predominantly from the northwest. The close proximity of Roya to Las Médulas (<35 km N) does not preclude the possibility of local, mesoscale atmospheric circulation being responsible for the deposition. Additionally, several smaller Roman mine sites occur nearby (El Teleno, Corporales, and Pozos).

While the Las Médulas alluvial gold deposits are the closest mining operation to Laguna Roya, approximately 70% of lead deposition in the Greenland ice core during Roman times was attributed to Río Tinto (Rosman et al., 1997) in Southern Spain, which was extensively mined for copper and silver (Tylecote, 1992). We do not know the potential transport range of metals to Roya, and it is possible that atmospheric transport occurred over ~550 km from Río Tinto, but the concurrent rise in Sb, Bi, and As in the Roya sediment cores (Figure 3) suggests it is related to the extraction and cupellation of gold. Following the extraction of alluvial gold deposits via hydraulic force, disturbed areas likely dried out, creating dust byproducts that were carried by the wind and deposited at Laguna Roya. However, the extraction of gold via fire-setting was an intensive process in this region as well and temperatures from these fires reached as high as 600−700°C (Weisgerber and Willies, 2000), likely producing a great deal of dust and smoke.

Hard-rock gold ores in this region are typically hosted in quartz veins that are rich in arsenopyrite (FeAsS), pyrite (FeS_2), galena (PbS), sphalerite ((ZnFe)S), and chalcopyrite ($CuFeS_2$) (Gómez-Fernández et al., 2012; Pérez-García et al., 2000), and further to the south in northern Portugal, bismuthinite (BiS_3) is also found (Noronha et al., 2000). Roman slag piles found elsewhere in Europe have high percentages of arsenic and antimony, indications that the Romans extracted trace amounts of gold from minerals such as arsenopyrite and stibnite (Sb_2S_3; Healy, 1978). Therefore, we suggest that the increase in metals at Roya is because of local extraction and processing of gold ores given (1) the prevalence of gold veins within solid rock in northwestern Iberia (Figure 1b), (2) the historical documentation of the widespread use of fire-setting in this region (Weisgerber and Willies, 2000), and (3) the geochemical signature in the Roya sediments that matches reasonably well with local ore geology.

These results contrast with the Lake Redo study which found a peak in Pb from ~AD 500 to AD 700 (Camarero et al., 1998; Figure 6), suggesting that the main depositional period was post-Roman–Medieval. The Lake Redo study was carried out nearly 18 years ago and relied on bulk sediment dating techniques. Bulk sediments may appear anomalously old because of the incorporation of ^{14}C depleted carbon from carbonate rocks in the watershed (Deevey et al., 1954). Such effects were noted and ages were corrected assuming a constant reservoir effect. However, reservoir effects may change through time because of lake level fluctuations and may vary with sediment type and composition (Geyh et al., 1998). Additionally, Redo Lake is surrounded by steep slopes, which are likely prone to rock slides and other material influx. Therefore, it is unclear if the peak in lead is because of atmospheric deposition or terrestrial sediment flux. The timing discrepancies between Redo and La Roya may also point to regional variability in the Iberian Peninsula and a strong role of local mining in atmospheric deposition.

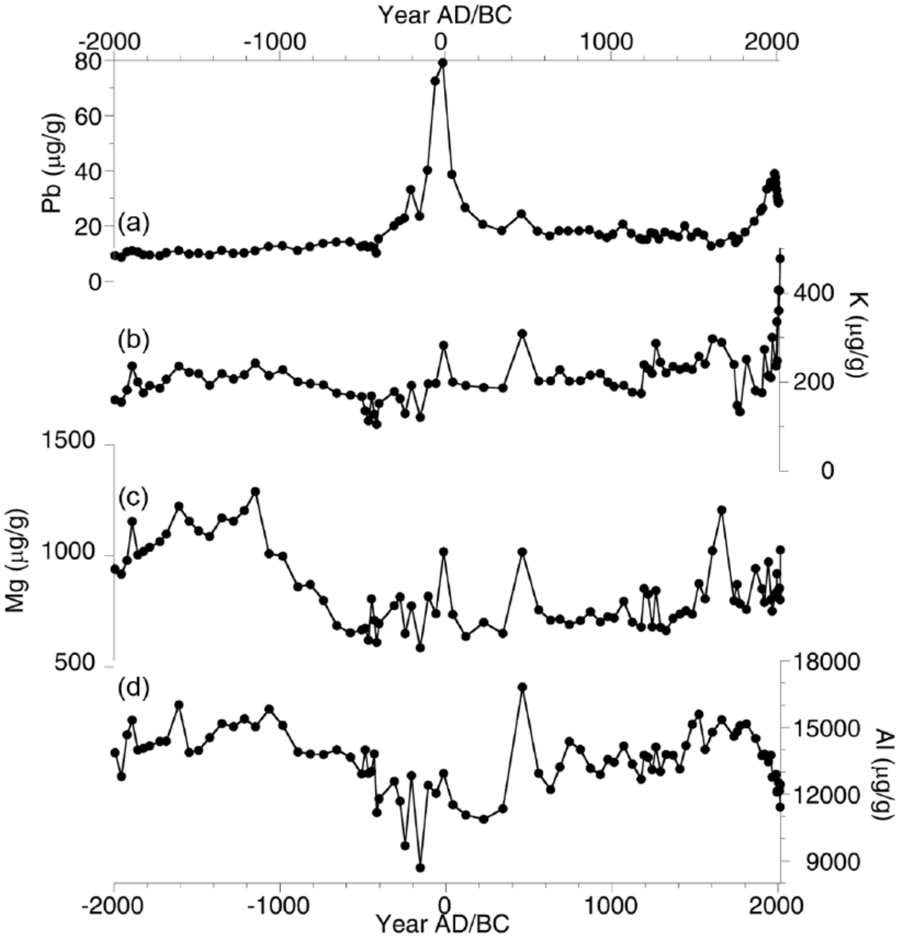

Figure 5. Comparison of lead concentrations (a) at Roya with those of lithogenic elements (b) potassium, (c) magnesium, and (d) aluminum over the last 4000 years. In general, the increases in lead concentration are not closely correlated to increases in lithogenic elements.

However, our results from Roya are broadly consistent with the timing of documented Roman lead deposition in other regional lake and peat bog studies, albeit with a slightly earlier increase by a few hundred years. Most studies find the peak of lead concentrations somewhere between 100 BC and AD 200. The peat bog studies that are closest to our own study site, particularly Penido Vello, observe Pb and other heavy metal deposition associated with Roman activities from ~AD 100 to AD 200 (Martínez-Cortizas et al., 1997; Figure 6). However, there are many important regional variations that are observed throughout Europe, reflecting unique histories. Given the proximity of many other known Roman mines to Penido Vello and Molina (Figure 1), spatial and temporal shifts in mining focus may be responsible for these differing geochemical increases.

It is unclear when Las Médulas was first exploited by the Romans. Archaeological finds suggest large-scale exploitation during the early imperial period (~25 BC–AD 197) (Lewis and Jones, 1970), but earlier use cannot be excluded because of the destructive nature of mining techniques (Edmonson, 1989). Therefore, the results of our study suggest that an earlier, small-scale, exploitation of Las Médulas beginning ~300 BC is possible. Interestingly, the study that most closely matches our own in terms of timing is from Zoñar Lake in southern Spain where pre-industrial Pb concentrations were highest from 500 to 100 BC (Martín-Puertas et al., 2010; Figure 6). In this study, the authors suggested that concentrations increased prior to the peak of the Roman Empire due to extensive mining on the southern and eastern areas of the Iberian Peninsula from Iberian societies influenced by Greek and Phoenician colonies. The increases in metals during phase 1 at Roya may partially be explained by Carthaginian mining activities, but the peak of concentrations during phase 2 is too late to be attributed to any civilization but the Romans.

Lead is a pollutant that may remain persistent in both terrestrial (Beyer et al., 1998) and aquatic (Hillman et al., 2015) environments. However, the Roya sediment Pb concentrations return relatively rapidly to within a few µg/g of background values. Heavy metals deposited on the landscape proximal to Laguna Roya are unlikely to be remobilized because of the resistant gneiss bedrock and the low potential for alluvial and colluvial storage locations. The spatial extent of this Pb deposition is difficult to quantify since only two other studies have been conducted in this region. However, the increased Pb deposition in northwestern Spain as a result of Roman activities appears to be clear; within this region, landscapes with greater potential for sediment remobilization may face contemporary contamination issues as a result of the remobilization of this Pb pollution.

The medieval and industrial periods

We do not observe any geochemical variations during the early medieval period that would suggest protracted post-Roman mining or metallurgical activity, contrary to what was inferred from other Spanish lake sediment studies (Camarero et al., 1998; Martínez-Cortizas et al., 2013). The spatial and temporal extent of post-Roman mineral resource exploitation is largely unquantified because the re-opening of abandoned mines within the last 50 years has destroyed previously occupied sites and focused only on hard-rock mines as opposed to alluvial deposits (Edmonson, 1989), such as Las Médulas. However, the Roya sediment record

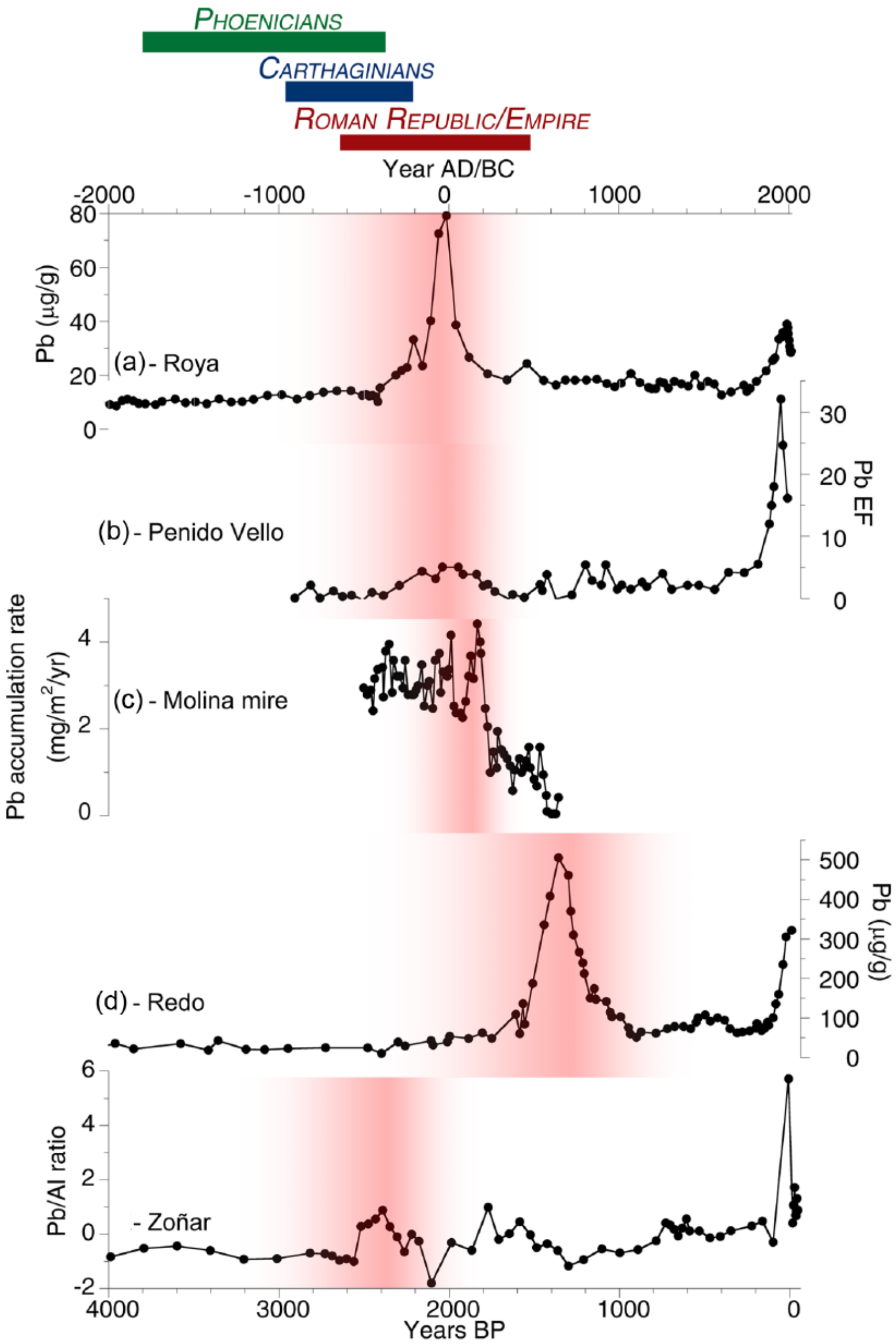

Figure 6. Comparison of lead pollution records from Spain (a) Laguna Roya lead concentrations; (b) Penido Vello lead enrichment factor (Martínez-Cortizas et al., 1997); (c) Molina mire lead enrichment factor (Martínez-Cortizas et al., 2013); (d) Redo Lake lead concentrations (Camarero et al., 1998); and (e) Zoñar Lake lead to aluminum ratio (Martín-Puertas et al., 2010).

does not show evidence of regional mineral extraction and processing after ~AD 120.

The increases in both Sb and Bi that take place between AD 1500 and AD 1700 may be the result of mining and smelting associated with the rise of the Spanish Empire. Neither Pb nor As show a contemporaneous increase, suggesting that a metallurgical process different than the Roman mode of exploitation is responsible for these increases. A study of several Swedish lakes found Pb concentration and isotopic changes beginning around AD 1400 that were attributed to new techniques of silver extraction from copper ores that required large amounts of lead (Brannvall et al., 2001). However, the increases in As and Bi at Roya occur without concomitant increases in Pb. It is difficult to attribute these increases to any particular process because little is known about late medieval Spanish metallurgy aside from the increasing skill and production of ferrous metal-working in northern Spain (Tylecote, 1992). However, concentrations of Ni, Zn, As, and Cd at Molina Mire increase beginning around AD 1300 (Pontevedra-Pombal et al., 2013), which points to a possible coherent period of regional mineral resource exploitation in northwestern Spain during this time period. The lowest Sb, Bi, and As concentrations occur around AD 1800, a period of political and economic crises in Spain (Barreiro-Lostres et al., 2015). Further investigation at Roya and other regional lakes would be needed to more definitively characterize the impacts of medieval and post-medieval metallurgy, and this is an area of potential future study for this region.

The changes in Pb concentrations at Roya over the past several hundred years closely correspond to known historical events (Figure 4). Concentrations begin to increase around the start of the Industrial Revolution and may be attributed to a variety of large-scale industrial processes that utilized lead as a flux material (Tylecote, 1992). Concentrations continue to increase with the advent of leaded gasoline in the 1920s, which resulted in the widespread atmospheric deposition of lead throughout Europe that peaked around AD 1970 (Renberg et al., 2001). Concentrations at Roya peak a bit later in AD 1990 (Figure 4). Many countries in Europe began phasing out leaded gasoline in the 1970s and 1980s, although Spain was given additional time to comply with such regulations, possibly explaining the slightly later peak in lead at Roya. The close correspondence between Pb concentrations and historical documentation further supports our supposition that Pb concentrations can be used to infer past anthropogenic changes in the metal cycle that occurred proximal to the lake. While present-day concentrations of As have remained relatively low compared to the historic period, concentrations of Sb and Bi are equal to or exceed the peak of Roman pollution. These modern-day increases are likely the result of industrial emissions which are estimated to be larger than natural emissions by as much as 100−200% (Nriagu, 1989).

In this paper, we have documented the contemporaneous environmental consequences of Roman mining activities taking place near the extensive Las Médulas gold mine. We find evidence for mineral resource exploitation beginning at ~300 BC, slightly earlier than was previously proposed for Roman activities in this region (Lewis and Jones, 1970). This regional metal pollution continued for 420 years and left a profound geochemical signature in the Laguna Roya sediments. The concentrations of Pb at Roya at the peak of Roman exploitation are double that of the last hundred years. These findings are somewhat unique as only a handful of studies have found pre-industrial pollution to be greater in magnitude than that of modern-day (Abbott and Wolfe, 2003; Hillman et al., 2015), including the study of Redo Lake in the Pyrenees (Camarero et al., 1998). This study adds to our understanding of large-scale Roman mineral resource exploitation and finds that the produced environmental consequences at this lake are substantial and exceed or rival that of today's lead pollution.

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