



Early atmospheric metal pollution provides evidence for Chalcolithic/Bronze Age mining and metallurgy in Southwestern Europe



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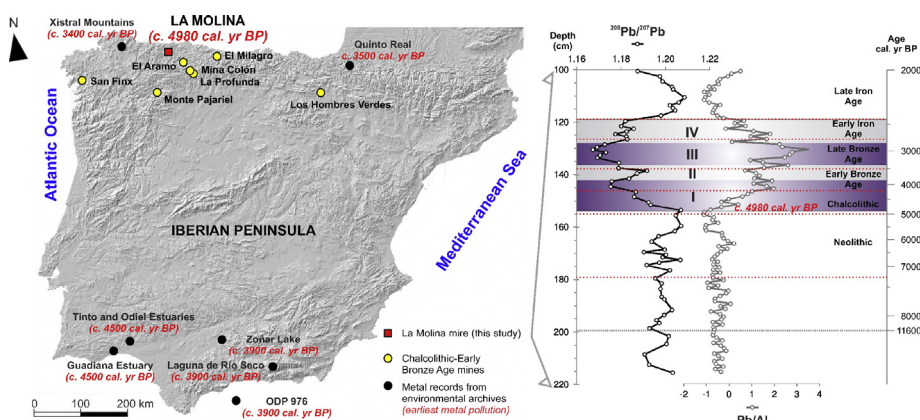
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GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 10 October 2015

Received in revised form 14 December 2015

Accepted 17 December 2015

Available online xxxx

Editor: D. Barcelo

Keywords:

Chalcolithic

Ancient metal pollution

Pb isotopes

Peat records

Iberian Peninsula

ABSTRACT

Although archaeological research suggests that mining/metallurgy already started in the Chalcolithic (3rd millennium BC), the earliest atmospheric metal pollution in SW Europe has thus far been dated to ~3500–3200 cal. yr. BP in paleo-environmental archives. A low intensity, non-extensive mining/metallurgy and the lack of appropriately located archives may be responsible for this mismatch. We have analysed the older section (>2100 cal. yr. BP) of a peat record from La Molina (Asturias, Spain), a mire located in the proximity (35–100 km) of mines which were exploited in the Chalcolithic/Bronze Age, with the aim of assessing evidence of this early mining/metallurgy. Analyses included the determination of C as a proxy for organic matter content, lithogenic elements (Si, Al, Ti) as markers of mineral matter, and trace metals (Cr, Cu, Zn, Pb) and stable Pb isotopes as tracers of atmospheric metal pollution.

From ~8000 to ~4980 cal. yr. BP the Pb composition is similar to that of the underlying sediments ($Pb_{15} \pm 4 \mu g g^{-1}$; $^{206}Pb/^{207}Pb$ 1.204 \pm 0.002). A sustained period of low $^{206}Pb/^{207}Pb$ ratios occurred from ~4980 to ~2470 cal. yr. BP, which can be divided into four phases: Chalcolithic (~4980–3700 cal. yr. BP), $^{206}Pb/^{207}Pb$ ratios decline to 1.175 and Pb/Al ratios increase; Early Bronze Age (~3700–3500 cal. yr. BP), $^{206}Pb/^{207}Pb$ increase to

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1.192 and metal/Al ratios remain stable; Late Bronze Age (~3500–2800 cal. yr. BP), $^{206}\text{Pb}/^{207}\text{Pb}$ decline to their lowest values (1.167) while Pb/Al and Zn/Al increase; and Early Iron Age (~2800–2470 cal. yr. BP), $^{206}\text{Pb}/^{207}\text{Pb}$ increase to 1.186, most metal/Al ratios decrease but Zn/Al shows a peak. At the beginning of the Late Iron Age, $^{206}\text{Pb}/^{207}\text{Pb}$ ratios and metal enrichments show a rapid return to pre-anthropogenic values. These results provide evidence of regional/local atmospheric metal pollution triggered by the earliest phases of mining/metallurgy in the area, and reconcile paleo-environmental and archaeological records.

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1. Introduction

Metal mining and metallurgy have played a fundamental role in world history (Killick and Fenn, 2012). The use of native copper in the late ninth millennium BC in Anatolia (Stech, 1999) may represent the earliest known use of metals by humans. Other metals were progressively exploited thereafter, from the late sixth millennium to the early second millennium BC: lead and smelted copper in the late sixth millennium BC; native and smelted silver in the mid-sixth millennium BC; native gold, arsenic (as Cu–As alloys) and antimony (as Cu–Sb alloys) in the fifth millennium BC; tin (as Cu–Sn alloys) in the fourth millennium BC; zinc (as Cu–Zn alloys) in the third millennium BC; and iron in the early second millennium BC (Killick and Fenn, 2012).

The smelting of ores probably began around 7000 years ago in Iran and Serbia (Radiwojevic et al., 2010; Frame, 2012), which in turn resulted in an enhanced release of metals to the environment (atmosphere, waters and soils), leading to local pollution as metallurgy was more widely adopted and practised. In the Faynan Orefield in Jordan, Grattan et al. (2011) found that metal pollution first appeared in the Late Neolithic and substantially increased in the Early Bronze Age, as a consequence of copper smelting and mining. Even in North America, Pompeani et al. (2011) found lead enrichments in lake sediments (Lake Manganese and Copper Falls Lake) dating back to 8000 years ago, which were interpreted as the result of the exploitation of the Keweenaw Peninsula (Michigan, USA) copper deposits.

In Europe, many reconstructions of past metal pollution have been made using environmental archives, such as lake, river and estuarine sediments, coastal marshes, complex soils, mussel shells, and peat (Martínez Cortizas et al., 2013 and references therein). These investigations show that atmospheric metal pollution started in the Bronze Age, both on the continent (Görres and Frenzel, 1997; Leblanc et al., 2000; Brännvall et al., 2001; Martínez Cortizas et al., 2002; Renberg et al., 2002; Monna et al., 2004; Kylander et al., 2005) and in the British Isles (West et al., 1997; Mighall et al., 2002, 2009).

The Iberian Peninsula has a long history of metal mining and metallurgy. It was one of the main source areas for metals in the Bronze Age (Stos-Gale et al., 1995; Hunt-Ortiz, 2003) and during the Roman Empire (Nriagu, 1980). Hunt-Ortiz et al. (2011) suggest that cinnabar (mercury sulphide) was already being mined in the Neolithic, from the late sixth millennium BC, and this activity subsequently expanded in the Chalcolithic. The southernmost regions, and in particular the Iberian Pyrite Belt (S Portugal – SW Spain), are considered to be the areas where mining first took place. Holocene sediments from the Tinto and Odiel estuaries (Fig. 1) have high metal (Cu, As, Pb, Au, Hg) concentrations in layers dated to 2530 BC (Leblanc et al., 2000; Nocete et al., 2005). Additionally, in a study of the sedimentary infill of the Guadiana Estuary (Fig. 1), Delgado et al. (2012) determined that anthropogenic sources of metal (indicated by enrichments in Pb, Co, Ni, Mn, and Cu) prevailed over natural sources at the same time (c. 4500 cal. yr. BP). Nocete et al. (2005) suggest that inland mining activities at the beginning of the third millennium BC were of such magnitude that they resulted in an increased flux of metals into the river network and contaminated the estuarine sediments. In contrast, García-Alix et al. (2013) proposed that clear evidence for metallurgically-derived pollution commenced around c. 3900 cal. yr. BP (c. 1900 BC), based on lake sediments from Laguna de Río Seco and from Zoñar Lake as well as the ODP 976 Mediterranean marine core (Martín-Puertas et al., 2010) (Fig. 1). They

attribute these regional differences to the local, small-scale character of early mining activities.

In northern Iberia, mining is known to have started in the Chalcolithic–Early Bronze Age (de Blas, 1996), about 4500 years ago, as attested by radiocarbon dating of animal and human bone remains found in El Aramo, El Milagro, and La Profunda copper mines (Fig. 1) (de Blas, 2005, 2011; de Blas and Suárez Fernández, 2009). Despite this archaeological information, analyses of environmental archives have not yet detected any evidence of regional atmospheric pollution prior to 3400–3200 cal. yr. BP (Martínez Cortizas et al., 1997, 2002; Monna et al., 2004; Kylander et al., 2005; Pontevedra-Pombal et al., 2013). The oldest date proposed by Pontevedra-Pombal et al. (2013), c. 3400 cal. yr. BP, is based on nickel enrichments in peat cores from mountain mires in NW Spain (Xistral Mountains, Fig. 1). This date was questioned by García-Alix et al. (2013) due to nickel being a redox-sensitive, and therefore, potentially mobile, element. Although this date has to be taken with caution in the absence of further evidence, it is unlikely that redox processes produced an apparent enrichment in nickel in peat layers of the same age from three different bogs at varying depths.

The absence of evidence for earlier metal pollution in northern Iberia paleo-environmental archives could be explained by two facts. First, that mining/metallurgy was non-extensive and of too low intensity to generate significant levels of pollution. Second, that appropriately located environmental archives have yet to be studied. To address this, we present an early Holocene to Iron Age record of metal deposition obtained from a peat core collected in La Molina mire (Asturias, N Spain, Fig. 1). This area was extensively mined during Roman times and the history of atmospheric pollution and related landscape changes from the Late Iron Age, and especially during Roman times, has been previously investigated (López-Merino et al., 2011, 2014; Martínez Cortizas et al., 2013). Here, we combine radiocarbon dating, geochemical (biophile, lithogenic and metal elements), and isotopic (Pb) composition together with metal/Al ratios to reconstruct the chronology of ancient atmospheric pollution linked to prehistoric mining and/or metallurgy in N Iberia.

2. Material and methods

2.1. Location

La Molina is a mire located at 650 m a.s.l. on the hilltop of the Alto de La Espina Range (Concejo de Salas, Asturias; Fig. 1). Current peatland vegetation is composed mainly of *Sphagnum* mosses, together with *Scirpus* sp., *Festuca* sp., *Polygonum amphibium*, *Menyanthes trifoliata*, *Molina caerulea*, *Potentilla* sp., *Dactylorhiza maculata*, *Digitalis purpurea*, *Mentha rotundifolia* and dwarf shrub species (*Erica tetralix*, *Erica mackaiana* and *Calluna vulgaris*). Some remnants of the original deciduous forest, once composed of oak (*Quercus robur*), beech (*Fagus sylvatica*), birch (*Betula alba*), and sweet chestnut (*Castanea sativa*), still exist. Today, the landscape is dominated by recently afforested areas with pine and eucalyptus, cereal fields, and pastureland. Geologically, the area belongs to the Narcea Antiform that was raised in the Tertiary and later modified by differential erosion, leading to a system of ridges of moderate elevation (600–800 m a.s.l.). The local lithology is comprised of quartzite and slates.

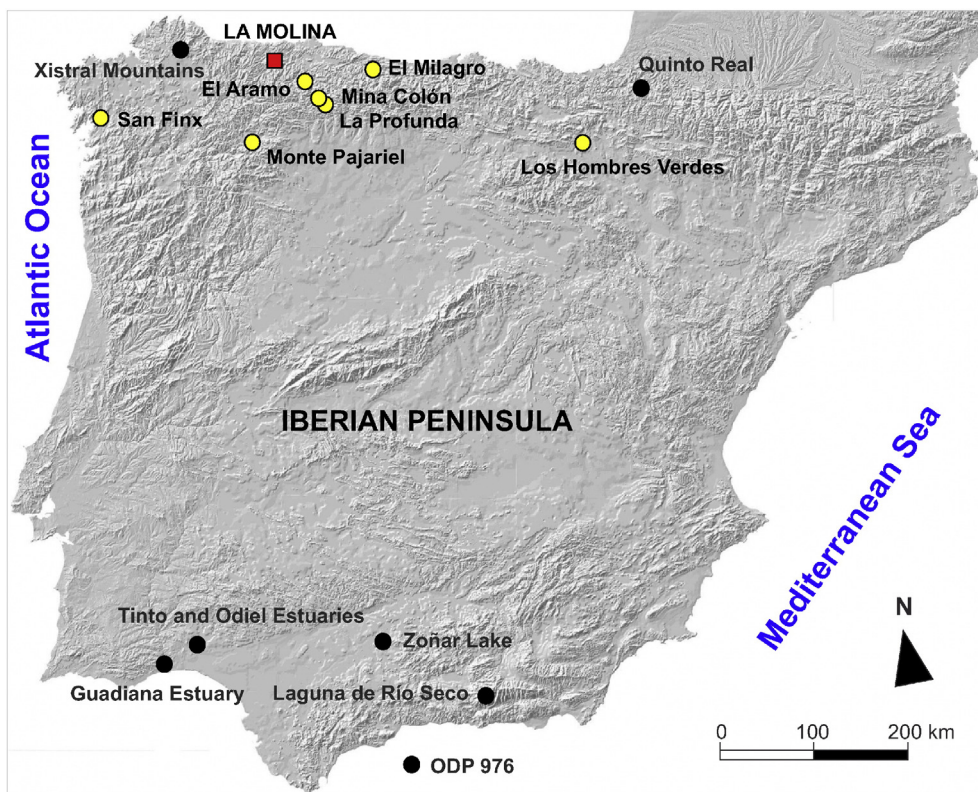


Fig. 1. Map of the Iberian Peninsula showing the location of La Molina mire (red square), the known prehistoric mines of northern Spain according to Vidal (2012) (yellow circles), and other paleo-environmental research on prehistoric metal pollution cited in the text (black circles). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

La Molina is close to a historical complex of four Roman mines known as Ablaneda (Domergue, 1987), as well as to the Narcea and Pigüeñas basins, where gold deposits were exploited during Roman times (Perea and Sánchez-Palencia, 1995; Fernández Mier, 1999). At a more regional level, the mire is also close to several Chalcolithic–Early Bronze Age mines namely, El Aramo, El Milagro, La Profunda, and Mina Colón (Fig. 1), so it is particularly well placed in relation to ancient mining and metallurgical activities.

2.2. Sampling and bulk density

A 215-cm-deep peat profile was collected in July 2005 using a Russian peat corer (50-cm-long and 5 cm in diameter). Peat sections were placed in PVC tubes, protected in plastic guttering and stored under cold conditions (4 °C) prior to laboratory sub-sampling and analysis. The core was sectioned into continuous 1 cm thick slices. The present work deals with data obtained for samples below 100 cm (pre-Roman), as the upper metre of the core was presented in detail in Martínez Cortizas et al. (2013).

Bulk density was determined in triplicate by taking 1 cm thick plugs with a 2 cm diameter cylinder. The peat was dried at 105 °C until constant weight and the density expressed as the average dry mass per volume unit (cubic centimetre).

2.3. Elemental composition

Subsamples were dried at 105 °C and ground to fine powder (<50 µm) using an automatic agate mortar (pre-cleaned with diluted HCl and MilliQ water) and homogenized. Total carbon content was determined using a Leco-Truspec CHNS analyser. Because the mire is acidic no carbonates are present in the peat and the values are assumed to represent total organic carbon. Concentrations of lithogenic elements (Si, Al, Ti, Zr) and trace metals (Cr, Cu, Zn, Pb) were obtained by energy

dispersive X-ray fluorescence (EMMA-XRF) analysis (Cheburkin and Shoty, 1996; Weiss and Shoty, 1998). The instruments are hosted at the RIAIDT (Infrastructure Network for the Support of Research and Technological Development) facility of the University of Santiago de Compostela (Spain). Standard reference materials were used for the calibration of the instruments. Quantification limits were 0.001% for Ti, 0.01% for Al and Si, 0.5 µg g⁻¹ for Pb, 10 µg g⁻¹ for Cr and 1 µg g⁻¹ for Zr, Cu, and Zn. Replicate measurements were performed on one of every five samples in order to account for reproducibility; all replicates agreed within 5%.

2.4. Isotopic analyses

Lead stable isotopes were determined using Quadrupole ICP–MS (Perkin–Elmer ELAN 6100; Umeå University, Sweden) after strong acid digestion (HNO₃ + HClO₄, 10:1 at 130 °C) of 0.15–0.25 g of dried (105 °C) sample in open Teflon vessels (Renberg et al., 2002). Dwell times of 50 ms were used and isotopic values were corrected empirically for fractionation by repeated analysis of NIST SMR 981 reference Pb material (1.081 ± 0.0033 per a.m.u.). Within-run accuracy was confirmed by analysis of a reference lake sediment, IAEA SL-1 (Bindler et al., 2004), and was ±0.0025 unit.

2.5. Radiocarbon dating and chronology

Nine radiocarbon ages, spanning the section of interest, were used to build the age model. This age dating information has been reported previously by López-Merino (2009) and Carrión et al. (2015). The analyses were performed at the Ångström Laboratory (Uppsala University, Sweden) and the Centro Nacional de Aceleradores (CSIC, Spain) by the AMS technique. The ¹⁴C dates were calibrated using the IntCal13.14C calibration curve (Reimer et al., 2013) (SM_Table 1), and they were used to produce an age-depth model using the Clam.R software

(Blaauw, 2010) (SM_Fig. 1). The best fit was obtained with a fourth order polynomial. The bottommost part of the core corresponds to pre-Holocene lacustrine sediments, while the rest of the core is composed of peat. Peat accumulation commenced after the 8200 cal. yr. BP event. The missing part of the Early Holocene period was probably eroded during the event, which would account for the sharp sedimentological change occurring at c. 198 cm depth (López-Merino, 2009).

2.6. Changepoint modelling

Changepoint (CP) modelling was applied to the $^{206}\text{Pb}/^{207}\text{Pb}$ and metal/Al ratios in order to detect periods of changes in the record statistically. This approach is based on Bayesian transdimensional Markov chain Monte Carlo (Gallagher et al., 2011) and has been previously applied to research on peatlands (Kylander et al., 2013).

3. Results

Based on the observed changes in the lithology (such as from lake sediment to peat) and in the geochemistry (such as changes in stable lead isotopes) of the La Molina record, supported by the probability of change inferred from the CP modelling, the results of the analyses are presented in three distinct sections: i) basal sediments/peat transition (≥ 195 cm); ii) mid-Holocene peat layers (195–154 cm), characterized by almost stable Pb isotope ratios; and iii) an upper section (154–100 cm) defined by a sustained decline in $^{206}\text{Pb}/^{207}\text{Pb}$ isotope ratios. The latter has been divided into four pollution phases based on changes in stable Pb isotopes, but also on trace metal/Al ratios.

3.1. Basal sediments and peat transition (215–195 cm; >8000 cal. yr. BP)

Lacustrine sediment found in the deepest part of the profile is pre-Holocene in age. A few centimetres below the sediment-peat boundary at 206 cm depth, the bulk sediment is dated to c. 12,660 cal. yr. BP, whereas the peat accumulating on top of the sediment starts after the 8200 cal. yr. BP event. The transition from sediment to peat is characterized by a rapid decline in bulk density from >0.8 g/cm $^{-3}$ to about 0.4 g/cm $^{-3}$ (Fig. 2). Along with the decline in bulk density an equally rapid change occurs in geochemistry from a mineral-rich to an organic-

rich composition. Silicon declines from 35% to about 20% and Zr from 400 to 200 $\mu\text{g g}^{-1}$, whereas C increases from $<5\%$ to $>20\%$ (Fig. 2).

Lead (15 ± 1 $\mu\text{g g}^{-1}$) and Zn (20 ± 3 $\mu\text{g g}^{-1}$) concentrations are relatively constant in the lacustrine sediment and in the transition to peat. Copper varies from 10 to 30 $\mu\text{g g}^{-1}$ in the sediment, but increases to 40 $\mu\text{g g}^{-1}$ (Fig. 3) along with the increase in C. The stable Pb isotopic composition of the sediment varies slightly (Fig. 3), suggesting some mineralogical variations in the mineral matter delivered to the sediment, but values centre around 1.19–1.20 for $^{206}\text{Pb}/^{207}\text{Pb}$ and 2.08 for $^{208}\text{Pb}/^{206}\text{Pb}$. With the transition to peat the isotopic composition remains similar, although with less variation.

3.2. Mid-Holocene peat (195–154 cm; c. 8000–4980 cal. yr. BP)

This section shows changes in the relative proportions of organic and mineral matter. Carbon varies two-fold from 17 to 34% and Zr inversely from 220 to 110 $\mu\text{g g}^{-1}$ (Fig. 2). Most of the variation in trace metals (Fig. 3) reflects these changes in relative proportions; normalizing the trace metals to aluminium reduces much of this variation and indicates no (Pb/Al) or little (Cu/Al, Cr/Al) variation in metal inputs to the peat (Fig. 4). There is a general increase in Zn/Al above 170 cm depth, but this change is unaccompanied by any other metal.

The stable Pb isotopic composition shows limited variation with $^{206}\text{Pb}/^{207}\text{Pb}$ ratios centred on 1.199 ± 0.005 (Fig. 3). A slight increase in the ratio to 1.204 ± 0.006 occurs at 162–154 cm and coincides with a slight decline in Pb/Al (Fig. 4).

3.3. Early mining/metallurgy (154–100 cm; c. 4980–2470 cal. yr. BP)

The main feature defining this section is a sustained change in stable Pb isotopic composition from 154 to 117 cm. Below and above this section $^{206}\text{Pb}/^{207}\text{Pb}$ ratios are >1.20 , similar to the basal sediments, but within this section they are <1.20 . Based on changes in stable Pb isotopic composition and metal/Al ratios, this period has been divided into four phases.

Phase I (154–144 cm; c. 4980–3700 cal. yr. BP) corresponds to the Chalcolithic and is characterized by decreasing $^{206}\text{Pb}/^{207}\text{Pb}$ ratios (to 1.175), with local minimum values at c. 4030–3700 cal. yr. BP. This

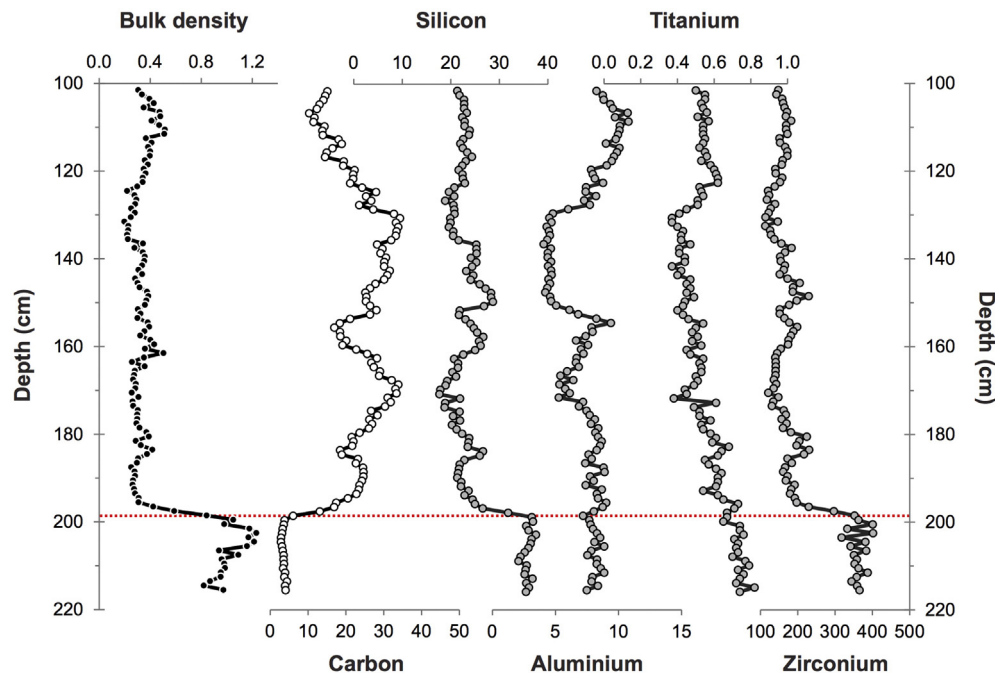


Fig. 2. Depth records of bulk density (g cm $^{-3}$), C (%) and lithogenic elements (Si, Al and Ti in %, Zr in $\mu\text{g g}^{-1}$).

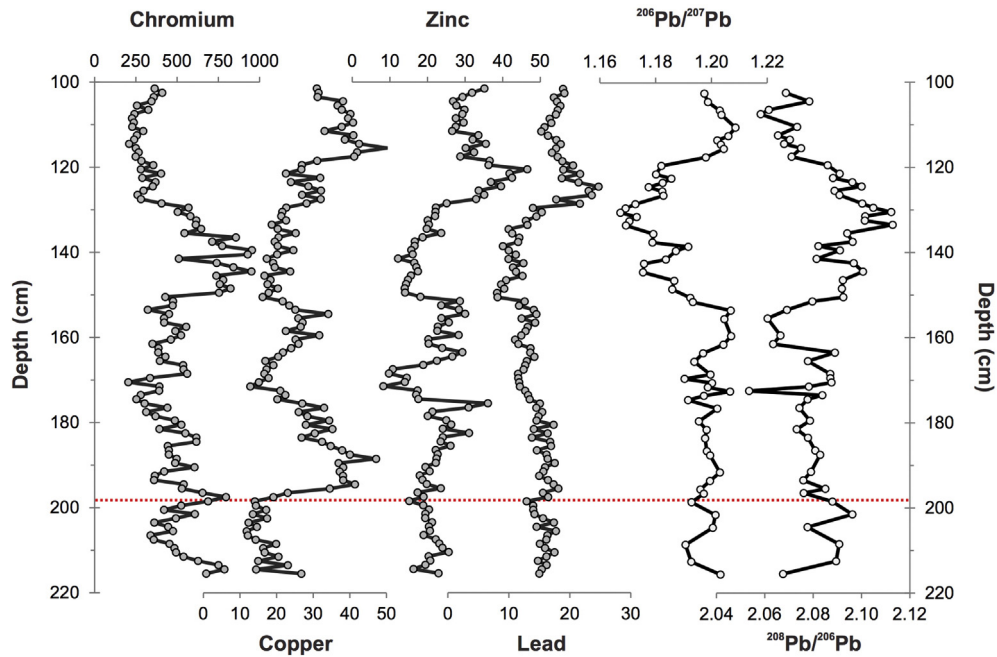


Fig. 3. Depth records of metals (in $\mu\text{g g}^{-1}$) and Pb isotopic composition.

decline is accompanied by increases in Pb/Al, Cu/Al and Cr/Al ratios, but without any increase in Zn/Al ratio (Fig. 4).

Phase II (144–136 cm; c. 3700–3500 cal. yr. BP) is relatively brief and corresponds to the Early Bronze Age. It is characterized by an increase in

$^{206}\text{Pb}/^{207}\text{Pb}$ ratios (to 1.192) and continued enrichments in Pb, Cu, and Cr (Fig. 4).

Phase III (136–127 cm; c. 3500–2800 cal. yr. BP) corresponds to the Late Bronze Age. This period contains the lowest $^{206}\text{Pb}/^{207}\text{Pb}$ ratios (to

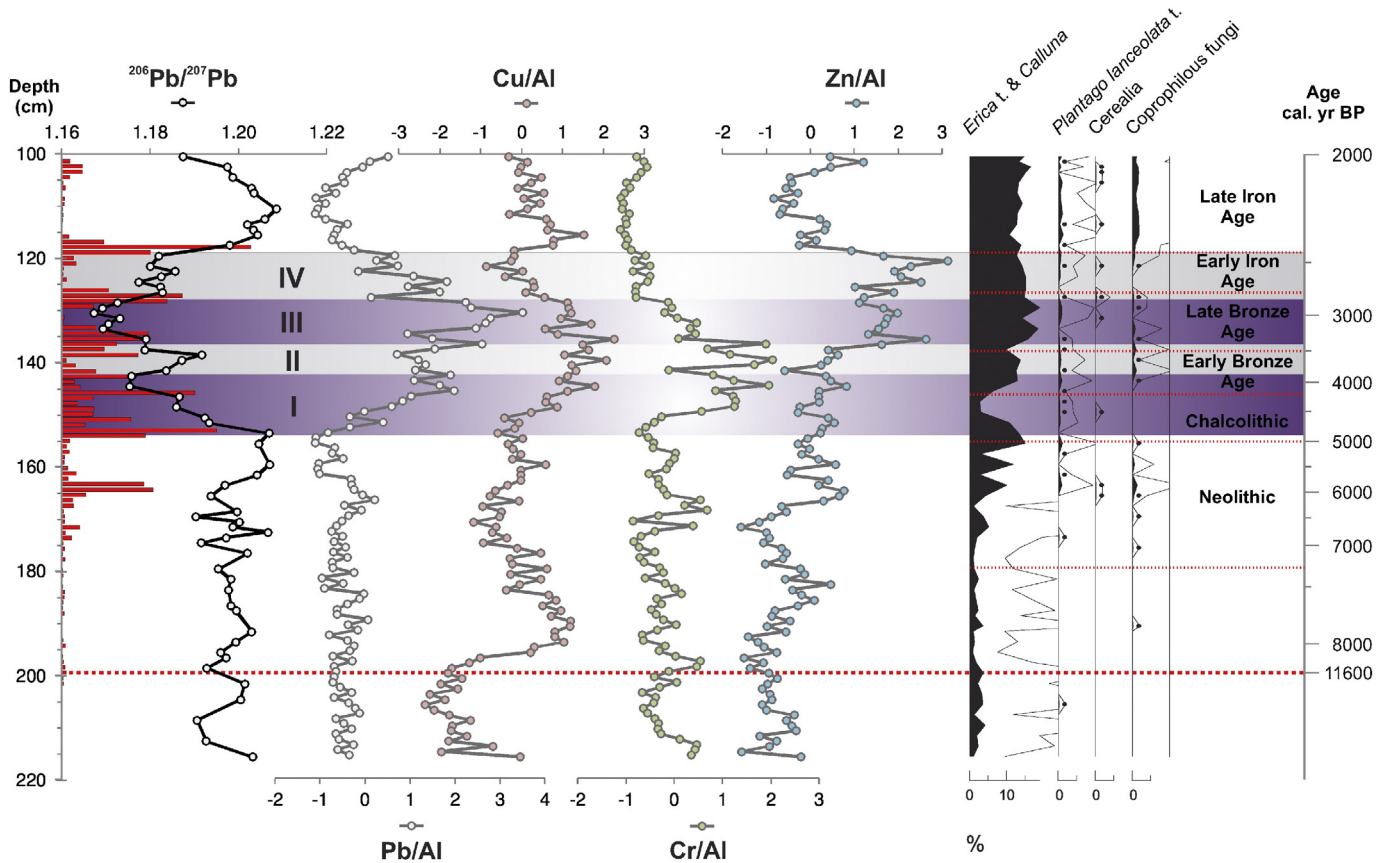


Fig. 4. Record of metal pollution detected by the Pb isotopic composition and standardized metal/Al ratios of pre-Roman times in La Molina mire. The shaded areas indicate the prehistoric metal atmospheric pollution phases described in the text. The palynological curves of some taxa indicators of human impact are also plotted (López-Merino, 2009), together with the cultural periods. Horizontal red bars in the leftmost panel represent the probability of a change point ($p(c)$) occurring at a given depth.

1.169) with local minimum values at 3160–2860 cal. yr. BP. In addition to the decline in isotope ratios, Pb/Al increases further, Cu/Al remains at a similar level, Cr/Al declines and Zn/Al increases sharply (Fig. 4).

Phase IV (127–117 cm; c. 2800–2470 cal. yr. BP) corresponds to the Early Iron Age and is characterized by increasing $^{206}\text{Pb}/^{207}\text{Pb}$ ratios (to 1.186). Enrichments in Pb, Cu and Cr all decrease (Fig. 4), whereas Zn/Al reaches its peak values.

Finally, above 117 cm (<2470 cal. yr. BP) the composition of the peat returns largely to values similar to those below 154 cm (pre-4980 cal. yr. BP). This includes $^{206}\text{Pb}/^{207}\text{Pb}$ ratios >1.20 and low metal/Al ratios.

4. Discussion

Interpreting metal records from peat cores largely relies on the assumption that their content has not been significantly altered by diagenetic processes, due to the chemical instability of the hosting mineral phases in the acidic and the dominant anoxic environment of the peat. If remobilisation is extensive, then the record of metals cannot be soundly interpreted chronologically. This has been shown for elements with intense redox behaviour, such as Fe and Mn (see for example, Chesworth et al., 2006), and also speculated for bio-essential metals as Cu and Zn (Biester et al., 2012). Amongst the metals we have analysed, Pb has been shown to be subject to little or no remobilisation at all (see the review by Kylander et al., 2006), but Cu, Zn and Cr may be, on theoretical grounds, affected by diagenesis. On the other hand, studies on inorganic particles found in peat have also shown a lack of significant weathering of most mineral phases (including feldspars), apart from calcite and apatite (Bennett et al., 1991; Le Roux et al., 2006; Sapkota et al., 2007; Smieja-Król et al., 2010).

Peat organic matter turnover is another process that has been shown to affect the content of chemical elements in peat. In a study of the elemental composition of peat from mires of the Harz Mountains (Germany), Biester et al. (2012) showed that the investigated elements were strongly affected by peat decomposition: i) elements hosted in mineral particles (Zr, Ti, Si) and organically bound elements (Cl and Br) were enriched, ii) redox sensitive elements (Fe, Mn, Cr) and mobile nutrients (Ca, Zn) were released and recycled, while iii) some metals (Pb, As, and Hg) were dominated by historically elevated atmospheric anthropogenic fluxes. In an attempt to overcome these uncertainties, metal ratios to conservative elements (e.g., Al, Ti, Zr or Sc) and enrichment factors have been proposed as an alternative approach (Shotyk, 1996); although their use has also been subjected to criticism (Reimann and De Caritat, 2000; Kylander et al., 2006).

For the specific questions of this study we rely mostly on the Pb isotope record but also consider metal/Al ratios. In the studied section of La Molina core, the metal ratios are highly correlated to the isotopic ($^{206}\text{Pb}/^{207}\text{Pb}$ ratios) composition (Pb/Al $r = 0.88$) but not to the C/N ratio (used as a proxy for peat decomposition; data not shown), lending support to their interpretation. On the other hand, the contrasting metal/Al ratios records in the detected pollution phases are consistent with previous archaeological research on the exploitation of metals in Iberia. Thus, although some diagenetic imprint cannot be completely ruled out, we believe that it is reasonable to assume that no extensive metal remobilisation has taken place in the La Molina peats and that the chronology of the observed changes does in fact correspond to the pace of atmospheric metal pollution, which is linked to prehistoric human activities (i.e. mining and metallurgy).

4.1. Sourcing metal pollution

The isotopic composition of the pre-Holocene basal sediment samples of the La Molina core show both high $^{206}\text{Pb}/^{207}\text{Pb}$ and low $^{208}\text{Pb}/^{206}\text{Pb}$ ratios (Fig. 5) (Martínez Cortizas et al., 2013). Peat samples older than c. 4980 cal. yr. BP have similar values to those of the basal sediment, which most likely represent the local geologic signature.

These values are lower than those found for pre-pollution times in other peat records from NW Spain ($^{206}\text{Pb}/^{207}\text{Pb} \geq 1.25$; Martínez Cortizas et al., 2002; Kylander et al., 2005) but comparable to those from other areas of Europe ($^{206}\text{Pb}/^{207}\text{Pb} \approx 1.20$; Kylander et al., 2010). The $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios of samples with ages between c. 4980 and 2470 cal. yr. BP fall on a mixing line that overlaps with the isotopic fields of ores from N, NW and SW Spain (Fig. 5). This has been identified previously for samples from the La Molina Roman period (Martínez Cortizas et al., 2013). In fact, the lowest $^{206}\text{Pb}/^{207}\text{Pb}$ ratio reported here (1.169) is identical to the average ratio of the phase of the Late Roman period (AD c. 280–500) with the highest metal atmospheric pollution and comparable to the lowest isotope ratio found for the last few centuries (Fig. 5).

The isotopic signature of ores from northern Spain mines that are known to have been exploited during the Chalcolithic and Bronze Age is clearly different from that of La Molina (Fig. 5). $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios of azurite/malachite recovered from the walls and waste mineral heaps of the galleries of El Aramo mine, located 35 km SE of La Molina (Figs. 1 and 5), range between 1.199–1.287 and 1.905–2.070, respectively (Huelga-Suárez et al., 2012); and similar ratios, 1.209–1.271 and 1.934–2.034, respectively, have been measured for ores from El Milagro mine (Figs. 1 and 5), located some 100 km east (Huelga-Suárez et al., 2014). Only two samples of El Milagro mine fall within the range of pre-pollution samples of La Molina, but these still lie outside the range recorded in the samples indicating higher atmospheric metal pollution (Fig. 5). Thus, other mining activities than those developed in El Aramo and El Milagro mines seem to have been responsible for the accounted atmospheric metal pollution. La Profunda and Mina Colón mines (Fig. 1) also located nearby could be suitable candidates, although lead isotopic analyses are required in order to prove it. Unknown, non-excavated local mines are the most likely source of this early pollution, as other northern Iberian long-term metal records do not identify such ancient pollution (Gallego et al., 2013).

4.2. Chronology of the changes in prehistoric atmospheric metal pollution

Based on the age-depth model (SM_Fig. 1) and the probability of a change obtained with CP-modelling (Fig. 4), the first significant change in Pb isotopic composition occurred at c. 6000 cal. yr. BP, during Neolithic times (Fig. 4). No archaeological evidence has yet been found of mining activity for this age, but the change could in fact have been linked to human activities because the palynological record from La Molina mire (López-Merino, 2009; Carrión et al., 2015) shows increasing values of heather (*Erica* t. and *Calluna*) and the appearance of indicators related to agriculture (*Cerealia*) and grazing (*Plantago lanceolata* t. and coprophilous fungi) (Fig. 4). These activities, both in the surroundings of the mire and in distant places, probably resulted in subtle changes in the source areas of dust deposited in the mire.

The change in Pb isotopic composition by c. 4980 cal. yr. BP (c. 5140–4840 cal. yr. BP, 95% probability) provides clear evidence of early atmospheric metal pollution (Fig. 4). This sustained period, with lower $^{206}\text{Pb}/^{207}\text{Pb}$ ratios together with enhanced metal/Al ratios, extends from the Chalcolithic until the end of the Early Iron Age (c. 2470 cal. yr. BP), and can be further subdivided into four phases that coincide with known cultural periods in northern Iberia. These include the Chalcolithic and Early Bronze Age (Phases I and II, respectively), Late Bronze Age (Phase III), Early Iron Age (Phase IV) and Late Iron Age (after c. 2470 cal. yr. BP) (Fig. 4). The chronology of these four phases in La Molina's peat record coincides not only with cultural periods, but also with the Pb pollution record in southern Iberia related to prehistoric mining and/or metallurgy. Based on two sediment records, García-Alix et al. (2013) dated the main phases of human activity as: Chalcolithic (c. 5150–4150 cal. yr. BP), Early Bronze Age (c. 4150–3500 cal. yr. BP), and Late Bronze Age (c. 3500–2800 cal. yr. BP).

Seven prehistoric mines have been found in northern Iberia (Fig. 1): San Finx (200 km W of La Molina), Monte Pajariel (90 km S), Mina Colón

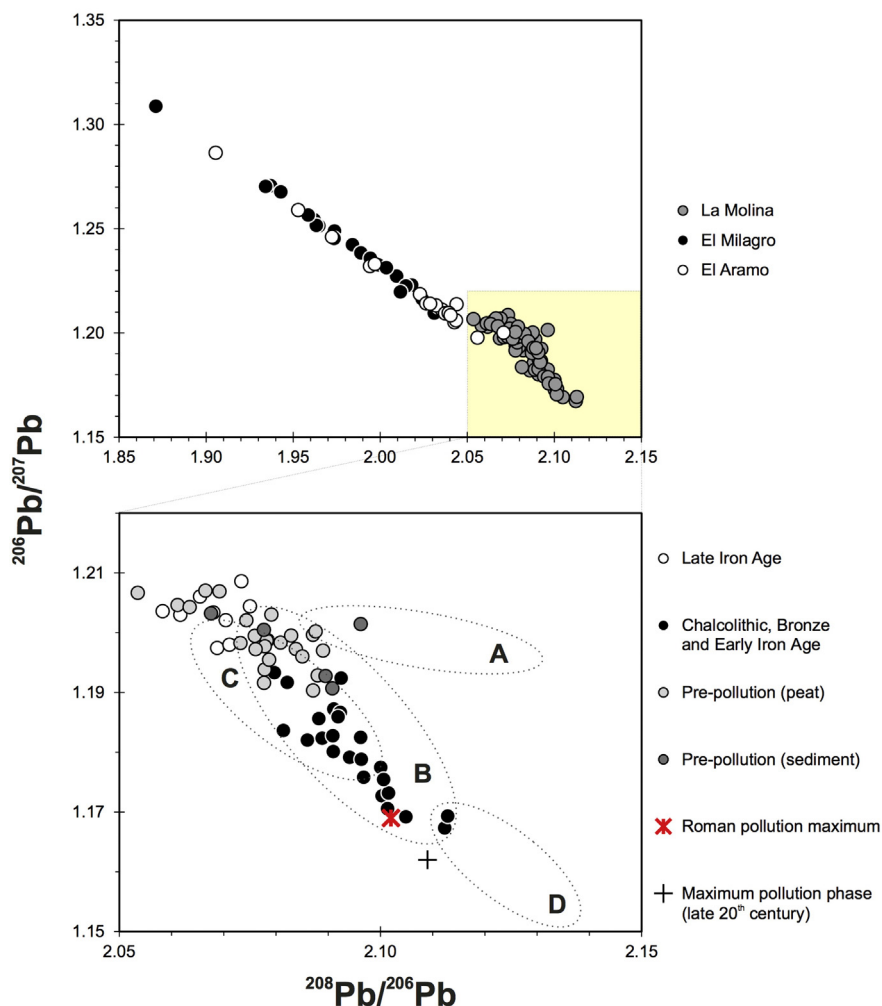


Fig. 5. Upper panel) Three-isotope plot of the pre-Roman isotopic composition of the peat samples of La Molina core and reference samples (azurite/malachite) from the Bronze Age El Milagro and El Aramo (Fig. 1) mines (from Huelga-Suárez et al., 2012, 2014). Lower panel) Three-isotope plot of the pre-Roman isotopic composition of La Molina core, reference isotopic fields for Iberian ores and soil (A: NW Spain soils; B: SW Spain ores; C: N Spain ores; D: NW Spain ores) as well as Roman and post-Roman periods of La Molina core (from Kylander et al., 2005; Martínez Cortizas et al., 2013).

and La Profunda (60 and 75 km SE), Los Hombres Verdes (350 km SE), El Aramo (35 km SE) and El Milagro (100 km E) (Vidal, 2012). All of these are thought to have been mined in either the Chalcolithic or the Bronze Age. However, only El Aramo, El Milagro and La Profunda have well-constrained chronologies based on radiocarbon dating of animal (horns and bones used as tools for mining) and human (bones in burials) remains (de Blas, 1996, 2005, 2011; de Blas and Suárez Fernández, 2009). In these cases, mining seems to have occurred in two main phases: from 4500 to 4000 cal. yr. BP and from 3900 to 3500 cal. yr. BP (de Blas, 2005) with the exploitation of copper minerals (azurite/malachite) stretching over a millennium. El Aramo in particular is regarded as the largest prehistoric mine complex in Western Europe (de Blas, 2005). The date obtained at La Molina for the start of metal atmospheric pollution (c. 4980 cal. yr. BP) is in agreement with studies in southern Spain that suggest a significant impact of mining/metallurgy on the environment during the Chalcolithic (Nocete et al., 2005, 2007).

Despite this, other researchers consider that clear evidence of anthropogenic pollution does not appear until the Early Bronze Age, by c. 3900 cal. yr. BP (García-Alix et al., 2013). In north-eastern Spain, the earliest evidence of metal pollution (indicated by Pb enrichments and a decrease in $^{206}\text{Pb}/^{207}\text{Pb}$ ratios) found in a mire located 400 km E of La Molina (Fig. 1) in the Pyrenees (Quinto Real, Basque Country, Monna et al., 2004) is dated to c. 3500–3300 cal. yr. BP. In southern Iberia, Chalcolithic metallurgy is thought to have been practised on a small

scale, producing low emissions, and Pb seems to have been absent (Hunt-Ortiz 2003; Costa Caramé et al., 2010; García-Alix et al., 2013). Thus, the La Molina record may reflect local impacts or, because Pb is present in Chalcolithic metallurgy in France (García-Alix et al., 2013), it may also reflect a northern Iberia tradition connected to that of other areas of southern Europe. Regardless, all investigations from northern and southern Spain to date – including the La Molina record here – reveal a consistent increase in metallurgical activities during the Early Bronze Age (c. 4100–3500 cal. yr. BP).

La Molina record shows a relative increase in the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios and a decrease in Pb, Cr, and Zn enrichments (Fig. 4) in Phase II (c. 3700–3500 cal. yr. BP). This is in agreement with a decrease in metallurgical activity by c. 3500 cal. yr. BP in southern Spain (García-Alix et al., 2013; Lull et al., 2010). The isotopic composition of the Pb of the nearby El Aramo and the more distant El Milagro (Huelga-Suárez et al., 2012, 2014) is different from that of the La Molina record (Fig. 5), which excludes these mines as possible sources for the Pb deposited on the mire. At La Molina, the isotopic trend found for the prehistoric metal pollution phases follows that observed for Roman times (Martínez Cortizas et al., 2013), suggesting that active mines from the Chalcolithic to the Early Iron Age were possibly located in the surroundings of the mire. Up to present, no prehistoric mines have been reported for this area despite intensive mining having occurred during Roman times. This is not surprising because Roman ore exploitation in northern

Spain may have reworked and expanded activities in already known prehistoric mining areas (Lewis and Jones, 1970), and later, modern mining operations destroyed or severely altered most of the prehistoric mines (de Blas, 1996).

The peat record from La Molina indicates that the highest levels of atmospheric metal pollution in prehistoric times, and thus also the more extensive phase of mining and/or metallurgy, occurred during the Late Bronze Age (Phase III, c. 3500–2800 cal. yr. BP). Compared to the Chalcolithic and Early Bronze Age, the Late Bronze Age shows an increase in Pb and Zn, continued enrichment in Cu and a decline in Cr (Fig. 4), which suggests changes in the metals that were targeted during this period. García-Alix et al. (2013) also point to an important change in the metallurgical technology by c. 3200 cal. yr. BP, which agrees with the largest enrichment in Pb and lowest $^{206}\text{Pb}/^{207}\text{Pb}$ ratios between c. 3160 and 2860 cal. yr. BP found here. Hunt-Ortiz (2003) suggests that trade networks in Iberia largely expanded during this period, including the Atlantic area. The start of this phase marks the end of the exploitation of the largest copper mines in northern Spain, at El Aramo and El Milagro. Given the proximity of the former to La Molina (35 km), this evolution provides evidence for significant local exploitation of mines in northern Spain during prehistory.

Although evidence of mining/metallurgy still exists in the Early Iron Age (c. 2800–2470 cal. yr. BP), the record from La Molina suggests a decrease in its intensity. The significant, sharp increase in Pb isotope ratios to pre-pollution values, together with the abrupt decrease in Pb and Zn accumulation by c. 2470 cal. yr. BP, suggest a collapse of mining/metallurgy in the area for almost a century. Atmospheric pollution does not resume until c. 2300 cal. yr. BP in the transition to the Late Iron Age (Martínez Cortizas et al., 2013). A similar situation was reconstructed for southern Spain by García-Alix et al. (2013), suggesting a progressive decline of traditional mining areas due to depletion of ore outcrops or a change in the main areas of exploitation.

5. Conclusions

Previous paleo-environmental investigations in NW Iberia have dated metal pollution back to 3400–3500 cal. yr. BP, although archaeological studies conclude that mining and/or metallurgy commenced in the Chalcolithic and Early Bronze Age. The record from La Molina reconciles this mismatch, showing evidence that atmospheric pollution in northern Iberia started as early as 4980 cal. yr. BP years ago. The chronology of the observed changes in Pb isotopic composition and enrichment in metals (particularly for Pb) is remarkably similar to that of southern Iberia and mirrors well-known cultural periods. In contrast to southern Iberia, the record from La Molina points to the regular use of Pb or Pb-containing ores in metallurgy, likely connecting northern Spain with other areas of Europe (such as southern France).

Our results are in agreement with what has been suggested by previous investigations, but also indicate a sizeable, local mining/metallurgy surrounding La Molina during the Chalcolithic and the Early Bronze Age, evidenced not least by the Pb isotopic signature and its difference from known mines active at that time, but with more widespread activity in the Late Bronze Age. These results also have implications regarding the distribution of prehistoric mines that can be reconstructed with the direct available archaeological evidence. It may be possible that many prehistoric mines were destroyed by later activities biasing the present record. Thus, paleo-environmental archives, when properly located and studied, can also be useful in assisting archaeological programmes to build up a record of the development of prehistoric mining and metallurgy.

Acknowledgements

This work was funded by the projects CGL2010-20672 and HAR2008-06477-C03-03/HIST (Plan Nacional I + D + i, Spanish Ministerio de Economía y Competitividad), 10PXIB200182PR (General Directorate of

I + D, Xunta de Galicia), and CDS-TCP (CSD2007-00058, Programa Consolider-Ingenio 2010). We are grateful to José Antonio López-Sáez, Fernando Gil Sendino, Carmen Fernández Ochoa and Roberto Zapico for their collaboration and assistance during the fieldwork, to José Rodríguez Racedo for helping with the geochemical analyses, and to Suzanne Leroy for perceptive comments on an earlier draft.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2015.12.078>.

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