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

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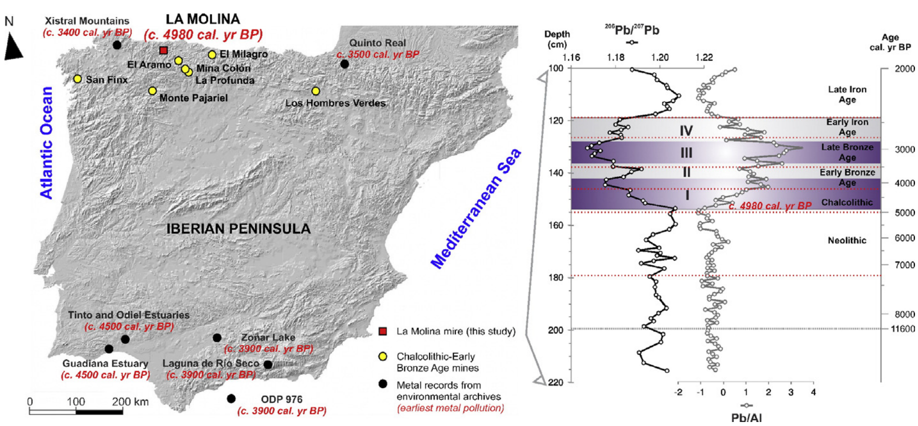
GRAPHICAL ABSTRACT



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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 ± 4 μg g^{-1}; $^{206}Pb/^{207}Pb$ 1.204 ± 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), $^{206}Pb/^{207}Pb$ decline to their lowest values (1.167) while Pb/Al and Zn/Al increase; and Early Iron Age (~2800–2470 cal. yr. BP), $^{206}Pb/^{207}Pb$ increase to 1.186, most metal/Al ratios decrease but Zn/Al shows a peak. At the beginning of the Late Iron Age, $^{206}Pb/^{207}Pb$ 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.

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 (Radivojevic 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-Ortíz 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 trifolia*, *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.