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## Environmental impact of early palaeometallurgy: pollen and geochemical analysis

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**Abstract** Interdisciplinary research was carried out in mid-level mountain areas in France with the aim of documenting historical mining and smelting activities by means of pollen and geochemical analyses. These investigations were made on cores collected in French peatlands in the Morvan (northern Massif Central), at Mont Lozère (southern Massif Central) and in the Basque Country (Pyrénées). Different periods of mining were recognised from Prehistory to modern times through the presence of anthropogenic lead in peat. Some of these were already known from archaeological dates or historical archives, especially for mediaeval and modern periods. However prehistoric ancient mining activities, as early as the Middle Bronze Age (ca. 1700 B.C.), were also discovered. They had all led to modifications in plant cover, probably related in part to forest clearance necessary to supply energy for mining and smelting.

**Keywords** France · Palaeometallurgy · Pollution · Lead isotopes · Peatland · Pollen analysis

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### Introduction

Recent geochemical analyses have demonstrated that peat bogs are potential archives not only for palaeobotanical purposes, but can also be successfully used to reconstruct historical atmospheric pollution (Shotyk 1996; and special issues of *Water, Air and Soil Pollution* 100, 1997 and *The Science of Total Environment* 202, 2002). Recent European studies conducted in the Swiss Jura (Shotyk et al. 1997; Shotyk 2002), Great Britain (Mighall et al. 2002a, b, 2004), Finland (Brännval et al. 1997), Germany (Küster and Rehfuess 1997) and Spain (Martinez Cortizas et al. 2002) suggest that lead can be used to reconstruct atmospheric pollution as it seems to be chronologically retained in hilltop peat and not vulnerable to re-mobilisation, even in non-ombrotrophic peatland (Shotyk 2002). Lead isotopic geochemistry is based on the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio concomitant with the Pb/Sc or Pb/Al ratio; it indicates the so-called anthropogenic lead (Sc and Al are among elements which behave conservatively in most geological environments). Mining and smelting activities may have affected nearby vegetation through deforestation in response to increasing energy demands. Thus, palynology associated with archaeological knowledge is a powerful tool for a better understanding of prehistoric mining and metal-working (Mighall and Chambers 1993; Küster and Rehfuess 1997; Richard and Eschenlohr 1998).

This paper summarises the results of the first interdisciplinary research in France the aim of which is to document historical mining and smelting activities using pollen and geochemical analyses. These investigations were conducted on peat cores collected in the Morvan mountains (Monna et al. 2004b), in the Lozère mountains in the southern Massif Central (Baron et al. 2005; Ploquin et al. 2003) and in the Basque Country (Pyrénées; Monna et al. 2004a; Fig. 1). They documented palaeoenvironmental impact since the beginning of those activities, in areas where archaeological and historical knowledge indicate mining

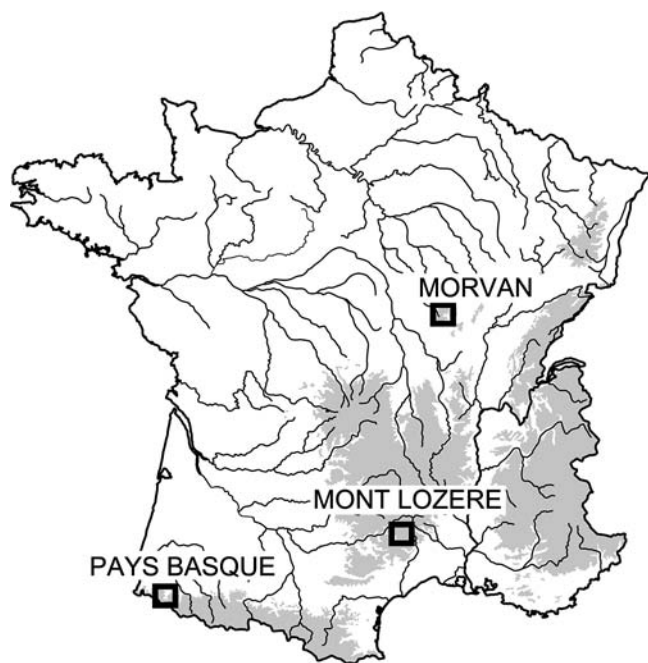


Fig. 1 Location of the sites

and/or smelting activities during several periods and where abundant mineral resources are found.

### Sampling sites and their historical context

*Mont-Beuvray (Morvan – Burgundy, 820 m a.s.l.)* is one of the highest points of the Morvan, northern Massif Central. The Morvan is a Hercynian massif mainly composed of granitic rocks, although volcano-sedimentary terrains (rhyolites and conglomerates) are also exposed. Three main types of mineral deposits were recognised: late Hercynian stratiform barytic and fluoritic outcrops (Lhégu et al. 1982), abundant polymetallic mineralisation (Pb, Zn, Ag) and, to a lesser extent, in conglomerate outcroppings at Mont-Beuvray (Delfour 1978; Marcoux 1986). At Mont-Beuvray, Bibracte, a Celtic hill fort of the Aeduan tribe, became one of the greatest and richest *oppida* in Gaul during the late Iron Age. Geomorphological anomalies such as wide trenches and gullies have recently been discovered and interpreted to be remains of mining excavation. On this basis, archaeologists have assumed that one of the factors that may have attracted early settlers is the abundance of mineral resources.

*Mont Lozère (South Massif Central, 1699 m a.s.l.)* is located in the Cevennes National Park on the southern edge of the Massif Central (Fig. 1). Mineralisation occurs all around the granitic massif in contact with the Palaeozoic or Mesozoic sedimentary cover: lead is the main metal (galena), while there are also smaller quantities of arsenic, copper, zinc, antimony and silver (Ploquin et al. 2003). On the western side of Mont Lozère, sixty deposits of slag were discovered in an area of 8 km<sup>2</sup>, all at an altitude between 1360 and 1430 m above the mineralisation. This slag is metallurgical waste indicating past smelting

activities (11th–12th century), mainly from lead and silver extraction (Ploquin et al. 2003). Several slag deposits are located near peat bogs where palaeobotanical and geochemical records are preserved. On the edge of the Narses Mortes peat bog, archaeological excavations have revealed the remains of an old furnace from the mediaeval period.

*The High Aldudes Valley (Basque Country)* contains abundant mineral resources and was widely mined during Roman times. Archaeological remains dated between the 2nd century B.C. and the 4th century A.D. testify to important metallurgical activity in this area (Galop et al. 2001, 2002; Beyrie et al. 2003). Ores of Fe, Cu, Ag, Sb and to a lesser extent of Pb and Zn, consist of sub-concordant piles or secant veins governed by fractures. Mining activity during the Middle Ages seems to have been very low, while the highest level of production, reaching more than 100 tons of copper, was registered and documented by historical sources before the French Revolution. Exploitation then collapsed during the 18th century A.D. due to a lack of wood supply sufficient for intense exploitation. During the 18th century, this area yielded more than 1200 tons of copper, and around 15 tons of silver (Beyrie et al. 2003). Marginal exploitation is recorded throughout the 19th and 20th centuries.

### Material and methods

#### Sampling

The Port-des-Lamberts peatland (Morvan) is located about 4–5 km from both Mont-Beuvray and the known ore deposit. It covers an area of about 3 ha at an altitude of 700 m a.s.l., is *Sphagnum*-dominated and organically rich at the top. The current surroundings are woodland dominated by beech forest and by a planted spruce grove.

The Narses Mortes peatland (Mont Lozère) is located at an altitude of 1400 m a.s.l. on the western side of Mont Lozère. It is a 21 ha minerotrophic peatland, mainly colonised by peat moss (*Sphagnum*) and characterised by a micro-topography of hummocks (tussocks of *Molina caerulea* or *Polytrichum*) and hollows. Marshy zones with *Cyperaceae*, *Menyanthes* and *Equisetum*, may develop temporarily. The peatland drains to the south towards the Tarn River. The surrounding vegetation consists of grassland and heath. The only trees around the bog are pines, planted during the second part of the 19th century.

The small peat bog of Quinto Real (Basque Country) is located in the High Aldudes Valley close to the Spanish border at 910 m a.s.l. It covers a surface of 400 m<sup>2</sup> of Palaeozoic terrain. The peatland is dominated by *Sphagnum* and *Cyperaceae* and surrounded by a beech forest and grazing lands.

#### Pollen analysis

The peat core from Port-des-Lamberts was collected by means of a Russian GIK-type corer, using the conventional

two-borehole technique. It consists of about 2 m of organic-rich material. Pollen analysis was performed at a sub-sampling interval of 4 cm. On the Narses Mortes peatland, two perpendicular transects of coring at regular intervals (25 m) permitted description of the geometry of peat accumulation. One sedimentary core was taken using a modified Russian Coring device (Jowsey 1966) at the centre of the peatland (central core, not presented here) where the maximum peat thickness (140 cm) was found. A second core (lateral core) of 138 cm, was collected near the edge of the site, where it was possible to examine the stratigraphy of the sediments through an incision in the peat created by a small, currently inactive stream. This lateral core provided a fine temporal resolution study of the anthropogenic period. The upper part of the core consists of a tussock of *Molinia caerulea*. Pollen analysis was carried out at 2 cm intervals for the upper part (2–74 cm), and 4 cm intervals for the lower part (74–138 cm). In the Quinto Real peatland, a 420 cm core was obtained with a Russian GIK-type corer using the two-borehole technique. Sub-sampling for pollen analysis was carried out at 4 cm intervals in the first metre and at 8 cm intervals in the lower part of the core.

Pollen preparation followed standard procedure, briefly: 10% HCl, 10% KOH, HF and acetolysis. An average of 400 vascular plant pollen grains was counted in each level. Pollen grains were identified with the aid of keys (Faegri and Iversen 1989; Moore et al. 1991), photographs (Reille 1992) and reference to a modern pollen type slide collection. Cyperaceae, spores and aquatic plants were systematically excluded from the pollen sum. In the Port-des-Lamberts peatland core, as at the Quinto Real, *Alnus* was also excluded because its over-representation could have masked the dynamics of other taxa (Janssen 1959; Wiltshire and Edwards 1994).

## Radiocarbon dating

### Geochemical analysis

The same analytical procedure was applied to the samples from Mont Beuvray and the Basque country. More details about the methodology can be found in Monna et al. (2004a, b). In brief, refractory elements, such as Sc and REE, were measured by Instrument Neutron Activation Analysis (INAA) at Actlabs (Ontario, Canada). For isotopic and heavy metal determinations, about 500 mg of powdered samples were first oxidised with H<sub>2</sub>O<sub>2</sub> and digested with a mixture of Suprapur and concentrated HCl, HNO<sub>3</sub> and HF (Merck, Germany) in closed PTX vessels with microwave assistance. An aliquot of the solution was measured by an HP 4500 inductively coupled plasma – mass spectrometer (ICP-MS) to determine Cu, Zn, Cd, and Pb concentrations. Lead from another aliquot was purified using the conventional ionic resin AG1X4 (Biorad) and measured for its isotopic composition by a quadrupole-based HP 4500 (see Monna et al. 1998, 2000 for more details about the chemical procedure and precision). Blanks and reference material standards, including NIST 1547, JSD 1, JSD 2, NIST 1547,

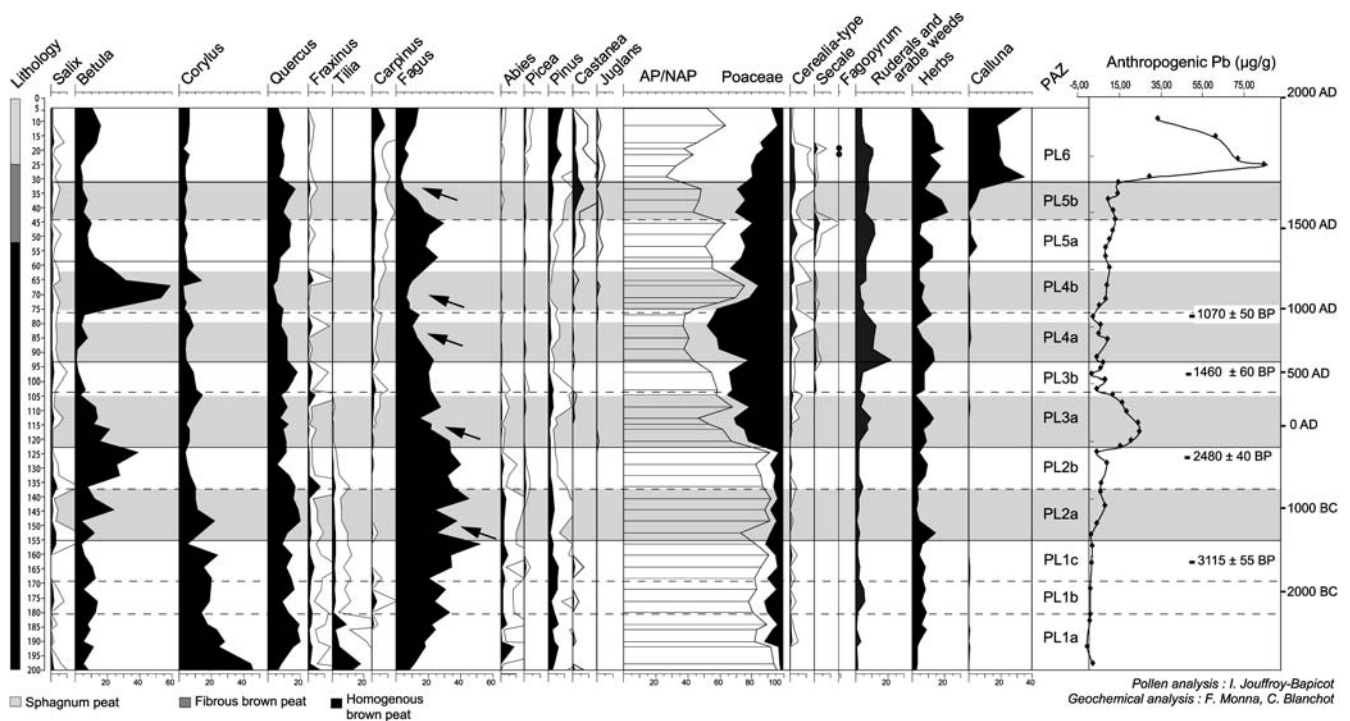
**Table 1** AMS radiocarbon dating (<sup>14</sup>C-beta counting)

Sites	Depth (cm)	Lab. No.	<sup>14</sup> C B.P.	Calibrated ages
NM	30	Poz-2011		Modern
NM	41	Poz-7048	850 ± 30	A.D. 1158–1264
NM	50	Poz-2012	1330 ± 35	A.D. 648–773
NM	53	Poz-2014	1265 ± 35	A.D. 667–868
NM	62	Poz-2015	1460 ± 35	A.D. 543–649
NM	71	Poz-2016	1635 ± 35	A.D. 264–5535
NM	90	Poz-1957	1950 ± 40	A.D. 41 B.C.–130
NM	119	Poz-1958	2200 ± 40	382–169 B.C
PL	75	Ly-10942	1070 ± 50	A.D. 888–1028
PL	97	Ly-10943	1460 ± 60	A.D. 441–664
PL	126	Ly-10944	2480 ± 40	790–407 B.C
PL	163	Ly-10945	3117 ± 54	1515–1225 B.C
QR	69–71	Beta-156998	290 ± 40	A.D. 1486–1664
QR	157–159	Ly-10587*	1895 ± 50	A.D. 3—240
QR	229–231.5	Ly-10588*	2645 ± 45	896–787 B.C
QR	283–285	Ly-10589*	3045 ± 70	1485–1051 B.C
QR	357	Beta-156997	4120 ± 40	2876–2501 B.C

Dates were calibrated (2 σ range) using Calib 4.1.3 (PL and QR) or 4.2 (NM) software (Stuiver et al. 1998); NM: Mont Lozère, “Les Narses Mortes” peat core; PL: Mont-Beuvray, “Port-des-Lamberts” peat core; QR: Basque Country, “Quinto Real” peat core; Poz: Poznan Radiocarbon Laboratory (Poland), Ly: Centre des Sciences de la Terre (University of Lyon, France), Beta: Beta Analytic Inc laboratory, Miami

PACS-1 and BCSS-1, were also systematically added to each set of unknown samples in order to check accuracy and precision Table 1.

The peat samples from the Mont-Lozère massif were powdered (300 mg) and fused in Pt crucibles along with 900 mg of ultra-pure LiBO<sub>2</sub> at 980 °C in an automatic tunnel oven. This methodology is undertaken in routine analyses in the SARM Laboratory at CRPG in Nancy. More details are available in Carignan et al. (2001). For isotopic measurements, dried peat samples (30–300 mg, according to lead concentration in each sample) were dissolved in a Teflon vessel using 2 ml of concentrated HNO<sub>3</sub> and 0.5 ml of 30% H<sub>2</sub>O<sub>2</sub>. After evaporation at 110 °C, the residue was taken up in 1 ml of concentrated HNO<sub>3</sub>, 0.5 ml H<sub>2</sub>O<sub>2</sub> and 1 ml of concentrated HF (all Merck Suprapur quality) and left at 80 °C overnight. After the last evaporation, the residue was taken up in 1 ml of 0.9 M HBr. Pb was separated from the other elements by ion exchange using the AG1X8 resin. The lead isotopic composition was measured with a MC-ICP-MS (Isoprobe, micromass, now GV Instruments). The reference materials, NIST 981 Pb and NIST 997 Tl were used to correct any instrumental mass bias. More details concerning the methodology are available in Baron et al. (2005). This technique is based on the relationship measured between Pb and Tl mass bias, according to the empirical technique used by Maréchal et al. (1999) and reported by White et al. (2000) for lead applications. Reference values used for both reference materials were taken from Thirlwall (2002). Repeated measurements of the NIST NBS 981 Pb reference material yielded accurate



**Fig. 2** Simplified pollen diagram (dominant taxa *Alnus* and Cyperaceae were removed) and anthropogenic lead concentration, from the Port-des-Lamberts peatland (Morvan, 700 m a.s.l.)

recalculated values (using the Pb-Tl relationship) with a reproducibility (2 standard deviations) better than 150 ppm for all the reported Pb isotope ratios.

## Results

In the Morvan (Fig. 2), according to radiocarbon dates and palynological spectra, the base of the core from Port-des-Lamberts may be estimated to be from the transition Neolithic/Early Bronze Age. This first period (PAZ PL1) is initially dominated by woodland taxa of mesophilous woodland: *Corylus*, *Fagus*, *Quercus* and to a lesser extent *Tilia*. Anthropogenic indicators, such as Cerealia-type and *Plantago lanceolata*, are already present in herbaceous taxa, indicating early human occupation. This was probably for agro-pastoral purposes, because the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios merely reflected natural mineral matter.

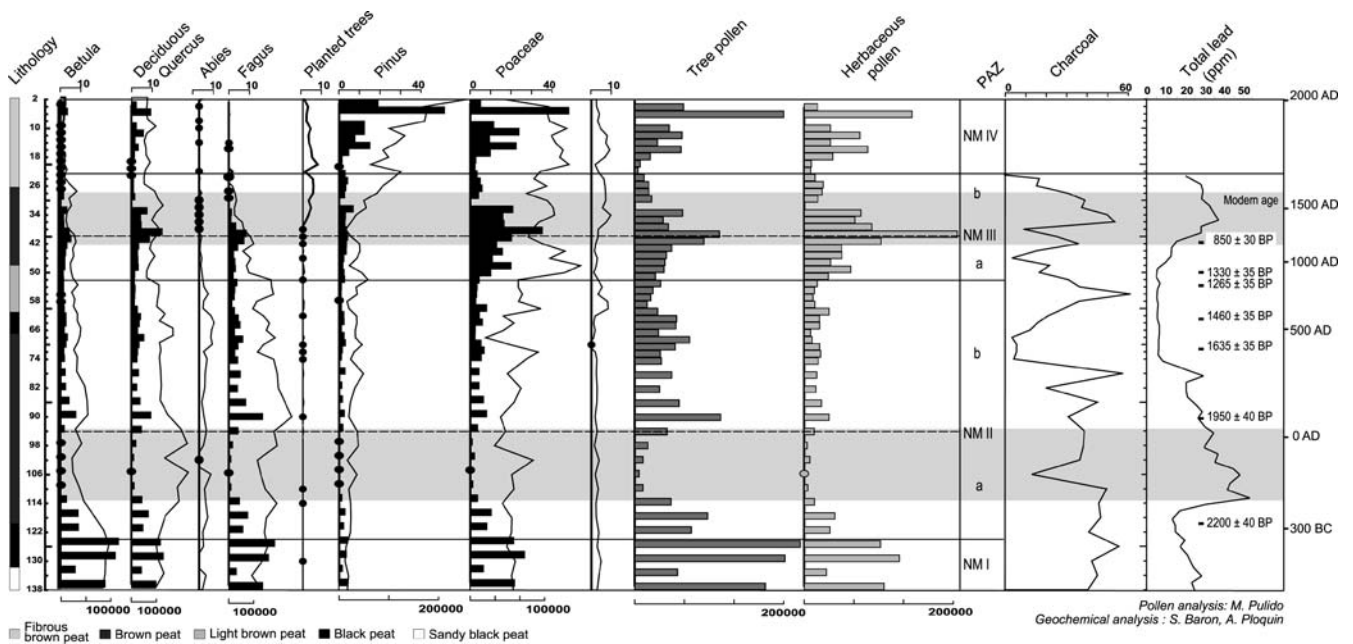
The beginning of PAZ PL2, in the late Bronze Age, shows a drastic drop in woodland taxa, especially *Fagus*. The low percentage of anthropogenic pollen indicators recorded in these levels seems to indicate that the forest clearing was not related to any agro-pastoral extension. It is precisely at this time that the earliest substantial human-derived lead input is noticed. Such a concomitance is an indication of a close connection between metallic contamination and forest clearance. This result suggests that the Mont Beuvray area was, as previously suspected by some archaeologists (Guillaumet 2001), an early mining centre. During the second part of PAZ PL2, the percentage of woodland taxa, dominated by *Fagus*, gradually increases, while anthropogenic lead concentrations remain stable. Human pressure

on the forest must have declined at that time – Iron Age, according to radiocarbon dating.

At the beginning of PAZ PL3, *Fagus* collapses again, anthropogenic herbs indicators increase, while anthropogenic lead concentrations peak during the Aeduan civilization (1st century B.C.). This result, together with the numerous metallurgical workshops discovered at Bibracte, may at least partly explain the tribe's wealth. A decline in anthropogenic pollen indicators and lead fluxes marks the beginning of our era. Bibracte was abandoned after the Roman conquest of Gaul, the population leaving the Celtic city to settle in the new city *Augustodunum*, which became the Aeduans' new smelting centre.

Archaeological knowledge from the early Middle Ages is crucially lacking, but anthropogenic indicators are already present and, what is more, their percentages are significant. At the same time, low anthropogenic inputs occurred (PAZ PL4a). Less surprising is the rise in concentration of human-derived lead and the *Fagus* representation, which drops at the beginning of PAZ PL4b, around the 11th century. This event may be synchronous with the great deforestation phase of the Middle Ages, observed on an European scale (Berglund et al. 1996), even if, on a regional scale, there is a lack of archaeological proof and historical information.

Anthropogenic lead inputs continue to increase slightly at the end of PAZ PL5 and reached a maximum at the beginning of PAZ PL6. However, the chronology established from radiocarbon dates does not allow precise dating of this phase. Locally, historical mining during the 18th and 19th centuries is well documented in archives. However the fact that *Fagus* pollen almost totally disappears at that time



**Fig. 3** Pollen diagram from the Narses Mortes peatland (Mont Lozère, 1400 m a.s.l.) and results of geochemical lead analysis. Pollen data are presented in percentages (lines) and concentrations (bars)

may be due to the intense exploitation of the Morvan forests from the 16th to the beginning of the 20th century, in order to supply Paris with firewood. However, this palynological observation may not reflect the reality of the vegetation. Harvesting for firewood was performed by means of coppice selection. There was probably still a beech-dominated forest, but pollen production might have been affected by this activity.

At Mont Lozère (Fig. 3), the age model inferred from the  $^{14}\text{C}$  dates from the marginal core from the Narses Mortes peatland (PAZ NMI) suggests that the peat expanded around 2500 years ago. At the bottom of the pollen diagram, a forest environment is deduced from relatively large percentages and the high concentrations of *Betula*, deciduous *Quercus* and *Fagus*. Some grasses (*Poaceae*) were also abundantly represented in this period, probably due to local contributions from *Molinia*. Former diagrams covering longer periods at Narses Mortes peatland (de Beaulieu 1974) clearly show a moderate opening of the beech forest to the benefit of grasslands and *Calluna* heath, at least from the Early Bronze Age, suggesting a patchy vegetation cover at Mont Lozère. At the same depth in the section, lead concentrations in the peat samples and their corresponding isotopic compositions are close to that of local granite, indicating that no anthropogenic activity occurs.

The beginning of PAZ NM II, Antiquity according to radiocarbon dates, is characterised by a reduction in the abundance of trees. A first major period of deforestation begins at this time. This deforestation was linked to an abrupt increase in lead anomalies, *Fagus* being the taxon most affected. Isotopic compositions for this lead anomaly are the same as those for ores and slag linked to mediaeval metallurgy, but no Iron Age archaeological evidence is present. This zone can be subdivided into two sub-zones

(PAZ NM IIa and PAZ NM IIb). In the sub-zone PAZ NM IIa, the tree pollen concentrations decline gradually to reach minimal values at 102 cm. Percentages of *Fagus* and *Betula* decrease equally, whereas those of *Quercus* and *Abies* increase. This synchronous decline in the pollen concentrations of all taxa (trees, shrubs and herbs) undoubtedly results from acceleration in the net peat accumulation rate as compared to the previous period, probably as a secondary effect of deforestation. In sub-zone PAZ NM IIb an increase in pollen concentrations follows. Percentages of *Fagus* and *Betula* increase while those of *Quercus* decrease. At this time, lead concentration decreases probably indicating a reduction in metallurgic pressure. At the end of PAZ NM II, during the early Middle Ages, anthropogenic pollen increases, without any connection to lead concentration and the corresponding lead isotopic composition, thus suggesting agro-pastoral activities.

PAZ NM IIIa is characterised by a second decline in the pollen percentage of *Fagus* and *Betula*. The percentage of *Quercus* remains stable in spite of a sudden reduction in the concentration of this taxon at the end of PAZ NM III. This second period of deforestation led to the drastic reduction in all tree species (*Fagus*, *Quercus*, *Betula*) found at the end of PAZ NM IIIb, whereas the pollen representation of *Poaceae* is fairly stable at high percentages and *Pinus* begins to increase at the end of this subzone. PAZ NM IIIa is probably associated with mining activities from the Mediaeval Period (at 42 cm depth). Abundant microscopic charcoal during this period is correlated with the fragmentation of the forest cover in response to anthropogenic fire events, probably linked to local metallurgy. The decrease in lead concentrations, recorded in PAZ NM IIIb (at about 34 cm depth), marks the abandonment of metallurgy and an increase in agro-pastoral activities. Indeed, a second maximum in

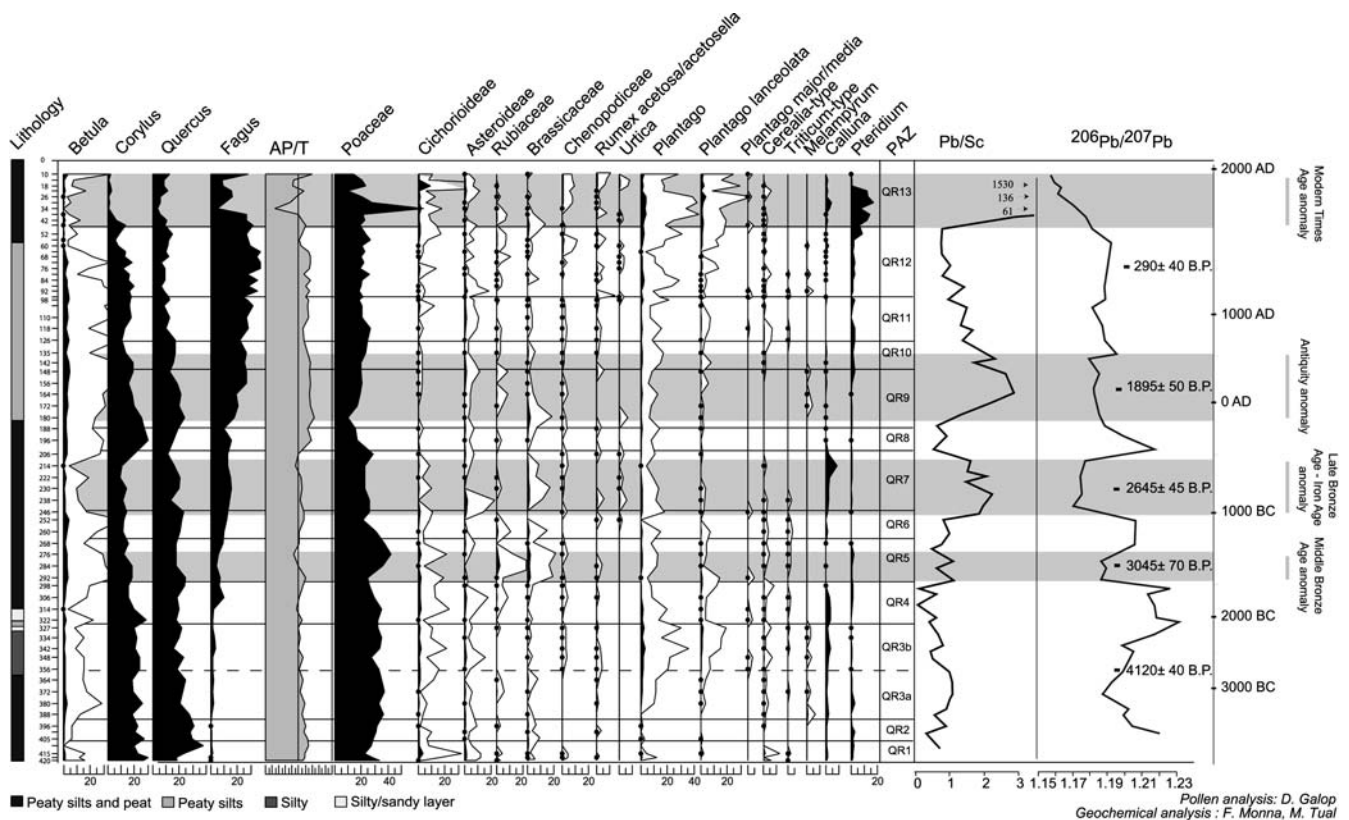


Fig. 4 Pollen diagram from the Quinto Real core (Basque Country, 910 m a.s.l.) with Pd/Sc and  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios

anthropogenic indicators and a continuous curve of planted trees are also recorded. Mediaeval human activities account for the asylvatic nature of the summit of Mont Lozère and for the abnormally low altitudinal tree-limit until the last two decades. At the end of this zone, pine (probably *Pinus sylvestris*) shows a gradual increase. In the uppermost 35 cm, lead isotopic composition indicates that modern industrial inputs overprinted the chemical signals and have thus veiled information from after the 12th or 13th century. The upper 20 cm of the sequence (PAZ NM IV) show pollen spectra marked by a balance between grasses (asylvatic vegetation, probably *Nardus stricta* meadows) and pine (influx from more or less distant plantations since the second half of the 19th century). At the top of the spectra, the pine percentages increase to more than 60% whereas Poaceae drop below 20%, illustrating local invasion by pine.

In the Aldudes Valley (Basque Country; Fig. 4), several phases of metallurgical activities linked with environmental modifications are observed between Late Neolithic and modern times (Middle Bronze Age, Late Bronze Age, Antiquity and finally modern times). In PAZ QR-1 prior to 3000 B.C. during Late Neolithic, the presence of anthropogenic indicators such as Cerealia-type, *Triticum*-type and *Plantago lanceolata* in the pollen record reveals human activities in this area. Later, the decline of oak combined with the slight extension of birch and the slow expansion of herbaceous taxa (mainly Poaceae) registered in PAZ-QR3a suggest a progressive deforestation that might have been the origin of the detrital layer recorded at 310cm depth,

around 2000 B.C. At that time the  $^{206}\text{Pb}/^{207}\text{Pb}$  and Pb/Sc ratios indicate natural mineral matter. During the Middle Bronze Age (PAZ-QR5) *Quercus* and *Corylus* declined, whereas a significant increase in herbaceous taxa, such as Poaceae and grazing indicators, is recorded. Isotopic ratios show a close concomitance between forest clearance (AP percentage drops from 60% to below 40%) and the increase in agro-pastoralism (*Rumex* is peaking) and metallic contamination. A similar relationship between lead enrichment and deforestation is noted at ca. 1000–600 B.C. during Late Bronze Age/Iron Age transition (PAZ-QR7). During this period the pollen record indicates a removal of oak forest while traces of agro-pastoral activities (*Plantago lanceolata*, *Plantago major/media*, *Rumex*, Cerealia-type) decrease or are absent. In this case, deforestation does not parallel agro-pastoral extension and may be interpreted as the result of increasing energy demands for mining and smelting purposes.

Another major anthropogenic phase is pinpointed by Pb/Sc and  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios from ca. 200 B.C. to A.D. 200 (PAZ-QR9 and QR 10). During this period, *Quercus* and *Corylus* decrease while *Fagus* seems to spread. Moderate signs of deforestation appear again without any pollen indication of significant agricultural extension. The Pb/Sc peak observed in the core corresponds well with the exploitation of iron, copper, silver and lead from the metallurgical and mining sites of the Baïgorry Valley, well known in Antiquity (Beyrie et al. 2003). During this period the decline of oak can be explained by deforestation for

metallurgical operations. Moreover, anthracological analysis performed in shaft-furnaces located near the peatland established that charcoal production within the valley focused on this species (Galop et al. 2002). After a long decline throughout the Middle Ages (PAZ-QR11 and QR12), Pb/Sc ratios increase markedly from late 16th century and early 17th century A.D., coinciding with the decrease in  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios (PAZ-QR 13). This period is an intense phase of metallurgical activities in the Basque Country, particularly in the Baïgorri Valley where the copper foundry started operating in 1747. Forest taxa (*Fagus*, *Quercus*) declined as metalworking peaked, indicating intense forest clearance linked with wood charcoal production and pastoral activities suggested by the increase of anthropogenic indicators. In this area, forests were dedicated to charcoal production, as demonstrated by abundant charcoal-kiln remains in current forest and pasture areas of the Aldudes Valley.

## Discussion

In the Morvan, as in the Basque country and the southern Massif Central, different phases of palaeometallurgy are recognised according to the presence of anthropogenic Pb in peat. Those activities of extraction and/or smelting of different metals (copper, silver or gold) would have emitted enough lead-enriched dust and gases into the atmosphere to be retained in surrounding environments.

The different phases of palaeometallurgy, recognised from the presence of anthropogenic Pb in peat, induced major modifications in plant cover. This is probably related in part to the forest clearance necessary to supply energy for mining and smelting. Vegetation cover may have been drastically affected by selective deforestation, affecting especially *Fagus* (beech) in the Morvan (Monna et al. 2004b) and at Mont Lozère (Lavoie et al. in press), while *Quercus* (oak) was preferentially used for charcoal production in the High Aldudes Valley (Galop et al. 2001; Fig. 2). Beech is well known as a good fuel for energy production.

According to the radiocarbon dates, some periods of high metallurgical activities were related to archaeological evidence of mining or smelting activities. However, some evidence of palaeometallurgy, marked by pollution and a significant fall in the pollen percentage of arboreal taxa, could not be related to archaeological knowledge, thus giving new data concerning human settlement in these areas. This might explain the forest clearance with no increase in pollen anthropogenic indicators linked to agro-pastoral activities. The results of these paleoenvironmental studies provide evidence of proximal metal activities for periods in which archaeological knowledge is lacking, for example the Bronze Age in both the Morvan and the Basque Country and during Antiquity at Mont Lozère. Where and when archaeological data or archives do exist, these paleoenvironmental studies also provide a reliable chronology and a new set of data for mining or smelting activities. The Morvan and Aeduan metallurgy,

Mont Lozère during the Middle Ages and the Basque Country during both Antiquity and modern times, are all examples.

The studies demonstrate the strength of the environmental impact on soil pollution and vegetation of pre-industrial activities, in regions which are nowadays among the less industrialised areas of France. Mining and smelting activities have had strong and long lasting effects on the forest cover. In the case of soil pollution at Mont-Beuvray, for example, about 20% of the total anthropogenic lead found there was deposited before our era, and probably about 50% of it before the 18th century (Monna et al. 2004b). The Pb concentrations in workshop-soils at Mont-Lozère, are of the same order as modern ones, but spread over a smaller area. This heritage should be taken into account in the study of present and future environmental problems.

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## References

- Baron S, Lavoie M, Ploquin A, Carignan J, Pulido M, de Beaulieu J-L (2005) Record of Metal Workshops in Peat Deposits: History and Environmental Impact on the Mont Lozère Massif, France. *Environmental Science & Technology* 39:5131–5140
- de Beaulieu J-L (1974) Evolution de la végétation sur la bordure montagnaise cévenole au postglaciaire, d'après les pollens. *Bulletin de la Société Languedocienne de Géographie* 8:347–358
- Berglund BE, Birks HJB, Ralska-Jasiewiczowa M, Wright HE (eds) (1996) Palaeoecological events during the last 15 000 years. Regional syntheses of palaeoecological studies of lakes and mires in Europe. Wiley, Chichester
- Beyrie A, Galop D, Monna F, Mougin V (2003) La métallurgie du fer au Pays Basque durant l'Antiquité. Etat des connaissances dans la vallée de Baïgorri (Pyrénées-Atlantiques). *Aquitania* 19:49–66
- Brännval ML, Bindler R, Emteryd O, Nilsson M, Renberg I (1997) Stable isotopes and concentration records of atmospheric lead pollution in peat and lake sediments in Sweden. *Water, Air, & Soil Pollution* 100:243–252
- Carignan J, Hild P, Mevelle G, Morel J, Yeghicheyan D. (2001) Routine Analyses of Trace Elements in Geological Samples using Flow Injection and Low Pressure On-Line Liquid Chromatography Coupled to ICP-MS: A study of Geochemical Reference Materials BR, DR-N, AN-G and GH. *Geostand News* 25:187–198
- Delfour J (1978) BRGM Report n°(6161)6; 78 SGN 611. BRGM, Orléans
- Fægri K, Iversen J (1989) Textbook of pollen analysis. Wiley, Chichester



- Galop D, Tual M, Monna F, Dominik J, Beyrie A, Marembert F (2001) Cinq millénaires de métallurgie en montagne basque. Les apports d'une démarche intégrée alliant palynologie et géochimie isotopique du plomb. *Sud-Ouest Européen* 11:3–15
- Galop D, Monna F, Beyrie A, Carozza L, Mougou V, Marembert F, Parent G (2002) Métallurgie et histoire de l'environnement au cours des cinq derniers millénaires en Pays basque nord (Vallée de Baigorri, Pyrénées-Atlantique, France): résultats préliminaires d'une approche interdisciplinaire. *Archeologia Postmedievale* 6:155–169
- Guillaumet JP (2001) Exploitations minières en pays éduen. *Bulletin de l'Association Française pour l'étude de l'Age du Fer* 35–37
- Janssen CR (1959) *Alnus* as a disturbing Factor in Pollen Diagrams. *Acta botanica Neerlandica* 8:55–58
- Jowsey PC (1966) An improved peat sampler. *New Phytologist* 65:245–248
- Küster H, Rehfuss K-E (1997) Pb and Cd Concentrations in a Southern Bavarian Bog Profile and the History of Vegetation as Recorded by Pollen Analysis. *Water, Air, & Soil Pollution* 100:379–386
- Lavoie M, Pulido M, Baron S, Ploquin A, de Beaulieu J-L, Bailly-Maître M-C, Carignan J, Allée P, Laurent S, Mahé-le Carlier C, Peytavin J (in press) Le plomb argentifère ancien du Mont Lozère (Massif Central): une approche historique géologique et paléoenvironnementale. In: Miras Y, Surmely F (eds) *Gestion des paléoenvironnements et stratégies d'exploitation des milieux de moyenne montagne. Actes du séminaire de Pierrefort, juin 2003*. Presses Universitaires Franc-Comtoise, Besançon
- Lhégu J, Jebrak M, Touray JC, Ziserman A. (1982) Section II, n°(6161)6; 2. In: *Bulletin BRGM*. BRGM, Orléans, pp 165–177
- Marcoux E (1986) Isotopes du plomb et paragenèses métalliques, traceurs de l'histoire des gîtes minéraux : illustration des concepts de source, d'héritage et de régionalisme dans les gîtes français: applications en recherche minière. Ed. du BRGM, Orléans
- Maréchal C, Télouk P, Albarède F (1999) Precise analysis of copper and zinc isotopic compositions by plasma-source mass spectrometry. *Chem Geol* 156:251–273
- Martinez Cortizas A, Garcia-Rodeja E, Pontevedra Pombal X, Novoa Munoz JC, Weiss D, Cheburkin A (2002) Atmospheric Pb deposition in Spain during the last (4600) years recorded by two ombrotrophic peat bogs and implications for the use of peat as archive. *The Science of The Total Environment* 292:33–44
- Mighall TM, Chambers F (1993) Early mining and metal working: its impact on the environment. *Historical Metallurgy* 27:71–83
- Mighall TM, Abrahams PW, Grattan JP, Hayes D, Timberlake S, Forsyth S (2002a) Geochemical evidence for atmospheric pollution derived from prehistoric copper mining at Copa Hill, Cwmystwyth, mid-Wales, UK. *The Science of The Total Environment* 292:69–80
- Mighall TM, Grattan JP, Timberlake S, Lees JA, Forsyth S (2002b) An atmospheric pollution history for lead-zinc mining from the Ystwyth Valley, Dyfed, mid-Wales, UK as recorded by an upland blanket peat. *Geochemistry: Exploration, Environment, Analysis* 2:175–184
- Mighall TM, Dumayne-Peaty L, Cranstone D (2004) A record of atmospheric pollution and vegetation change as recorded in three peat bogs from the Northern Pennines Pb-Sn orefield. *Environmental Archaeology* 9:13–38
- Monna F, Loizeau JL, Thomas BA, Guéguen C, Favarger PY (1998) Pb and Sr isotope measurements by inductively coupled plasma – mass spectrometer: efficient time management for precise improvement. *Spectrochim. Acta B* 59:1317–1333
- Monna F, Loizeau JL, Thomas BA, Guéguen C, Favarger PY, Losno R, Dominik J (2000) Noise identification and sampling frequency determination for precise isotopic measurements by quadrupole-based Inductively Coupled Plasma Mass Spectrometry. *Analysis* 28:750–757
- Monna F, Galop D, Carozza L, Tual M, Beyrie A, Marembert F, Chateau C, Dominik J, Grousset F (2004a) Environmental impact of early Basque mining and smelting recorded in a high ash minerogenic peat deposit. *Science of The Total Environment* 327:197–214
- Monna F, Petit C, Guillaumet J-P, Jouffroy-Bapicot I, Blanchot C, Dominik J, Losno R, Richard H, Lévêque J, Château C (2004b) History and environmental impact of mining activity in Celtic Aeduan territory recorded in a peat-bog (Morvan – France). *Environmental Science & Technology* 38:665–673
- Moore PD, Webb JA, Collinson ME (1991) *Pollen Analysis*. Blackwell Science, Oxford
- Ploquin A, Allée P, Bailly-Maître M-C, Baron S, de Beaulieu J-L, Carignan J, Laurent S, Lavoie M, Mahé-Le Carlier C, Peytavin J, Pulido M (2003) Medieval lead smelting on the Mont Lozère, southern France. In: *Archaeometallurgy in Europe*, AIM, Milan, 24–26 Septembre, Milan, pp 635–644
- Reille M (1992) Pollen et spores d'Europe et d'Afrique du Nord. *Laboratoire de Botanique Historique et Palynologie*, Marseille
- Richard H, Eschenlohr L (1998) Essai de corrélation entre les données polliniques et les données archéologiques: Le cas des forêts de Lajoux dans les Franches-Montagnes (Lajoux, Ju, Suisse). *Revue d'Archéométrie* 22:29–37
- Shotyk W (1996) Peat bog archives of atmospheric metal deposition: geochemical evaluation of peat profiles, natural variations in metal concentrations, and metal enrichment factors. *Environmental Reviews* 4:149–183
- Shotyk W (2002) The chronology of anthropogenic, atmospheric Pb deposition recorded by peat cores in three minerogenic peat deposits from Switzerland. *The Science of The Total Environment* 292:19–31
- Shotyk W, Cheburkin AK, Appleby PG, Fankhauser A, Kramers JD (1997) Lead in Three Peat Bog Profiles, Jura Mountains, Switzerland: Enrichment Factors, Isotopic Composition, and Chronology of Atmospheric Deposition. *Water, Air, & Soil Pollution* 100:297–310
- Stuiver M, Reimer PJ, Bard E, Beck JW, Burr GS, Hughen KA, Kromer B, McCormac G, van der Plicht J, Spurk M (1998) INTCAL98 Radiocarbon Age Calibration, 24,000-0 cal BP. *Radiocarbon* 40:1041–1083
- Thirlwall MF (2002) Multicollector ICP-MS analysis of Pb isotopes using a  $^{207}\text{Pb}$ - $^{204}\text{Pb}$  double spike demonstrates up to 400 ppm/amu systematic errors in TI-normalization. *Chem Geol* 184:255–279
- White WM, Albarède F, Télouk P (2000) High-precision analysis of Pb isotope ratios by multi-collector ICP-MS. *Chem Geol* 167:257–270
- Wiltshire PEJ, Edwards KJ (1994) Mesolithic, early Neolithic and later prehistoric impacts on vegetation at a riverine site in Derbyshire. In: Chambers FM (ed) *Climate change and human impact on the landscape: studies in palaeoecology and environmental archaeology*, Chapman & Hall, London New York, pp 157–168