



HAL
open science

History and environmental impact of mining activity in Celtic Aeduan territory recorded in a peat-bog (Morvan – France)

Fabrice Monna, Christophe Petit, Jean-Paul Guillaumet, Isabelle Jouffroy-Bapicot, C. Blanchot, J Dominik, R. Losno, Hervé Richard, Jean Lévêque, Carmela Château

► To cite this version:

Fabrice Monna, Christophe Petit, Jean-Paul Guillaumet, Isabelle Jouffroy-Bapicot, C. Blanchot, et al.. History and environmental impact of mining activity in Celtic Aeduan territory recorded in a peat-bog (Morvan – France). *Environmental Science and Technology*, 2004, 38 (3), pp.665-673. hal-00293665

HAL Id: hal-00293665

<https://hal.science/hal-00293665v1>

Submitted on 20 May 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

History and Environmental Impact of Mining Activity in Celtic Aeduan Territory Recorded in a Peat Bog (Morvan, France)

F. MONNA,^{*,†,‡} C. PETIT,[‡]
J.-P. GUILLAUMET,[‡]
I. JOUFFROY-BAPICOT,[§] C. BLANCHOT,[†]
J. DOMINIK,^{||} R. LOSNO,[⊥] H. RICHARD,[§]
J. LÉVÊQUE,[†] AND C. CHATEAU[#]

Laboratoire GeoSol, UMR INRA-Université de Bourgogne, Bat. Gabriel, F-21000 Dijon, France; Archéologies, Cultures et Sociétés, Bourgogne et France Orientale du Néolithique au Moyen Age, UMR 5594 CNRS-Université de Bourgogne, Bat. Gabriel, F-21000 Dijon, France; Laboratoire de Chrono-écologie, UMR 6565 CNRS, UFR des Sciences et Techniques, Université de Besançon, 16 route de Gray, F-25030 Besançon Cedex, France; Institut F.-A. Forel, Université de Genève, 10 route de Suisse, CH-1290 Versoix, Switzerland; LISA, Universités Paris 7 and Paris 12, CNRS, Faculté des Sciences, 61 av. du Gal de Gaulle F-94010 Créteil Cedex, France; and Centre des Sciences de la Terre, Université de Bourgogne, Bat. Gabriel, F-21000 Dijon, France

The present study aims to document historical mining and smelting activities by means of geochemical and pollen analyses performed in a peat bog core collected around the Bibracte oppidum (Morvan, France), the largest settlement of the great Aeduan Celtic tribe (ca. 180 B.C. to 25 A.D.). The anthropogenic Pb profile indicates local mining operations starting from the Late Bronze Age, ca. cal. 1300 B.C. Lead inputs peaked at the height of Aeduan civilization and then decreased after the Roman conquest of Gaul, when the site was abandoned. Other phases of mining are recognized from the 11th century to modern times. They have all led to modifications in plant cover, probably related in part to forest clearances necessary to supply energy for mining and smelting. Zn, Sb, Cd, and Cu distributions may result from diffusional and biological processes or from the influence of groundwater and underlying mineral soil, precluding their interpretation for historical reconstruction. The abundance of mineral resources, in addition to the strategic location, might explain why early settlers founded the city of Bibracte at that particular place. About 20% of the anthropogenic lead record was accumulated before our era and about 50% before the 18th century, which constitutes a troublesome heritage. Any attempts to develop control strategies in accumulating environments

should take into account past human activities in order to not overestimate the impact of contemporary pollution.

Introduction

When dealing with current metal pollution in accumulating environments such as soils, sediments, or peatlands, reliable information about the extent and origin of the anthropogenic impact at a regional scale is an essential prerequisite for choosing among the environmental strategies available: remediation, restriction of pollutant emissions, or isolation of the contaminated environment from the surroundings. The estimate of 'pristine' natural conditions therefore constitutes a preliminary step because a reference level is needed for any further comparisons with current environments. This assessment obviously presents a strong historical connotation because it is supposed to reflect a period at which mankind did not significantly affect, at least for metals, the surrounding environment. However, the introduction of history into the environmental sciences goes much further. Knowledge of local history may help to resolve the complex question of pollutant origin in soils by distinguishing recent emissions from those inherited from earlier human societies, as metals accumulate indistinctly in surface horizons. The possession of historical data also allows the use of natural analogues to determine the long-term behavior of past pollution from field studies and, hence, by extension the fate of our current emissions. This is particularly significant with lowly mobile metals such as lead, for which any migration rate determination is problematic at the human time scale in natural field conditions. Archaeologists and palaeobotanists are also interested in any fingerprint of early human activity on the environment because it may help to elucidate the organization and development of primitive societies. Although the ultimate objectives of environmentalists, palaeobotanists, and archaeologists may be different, their attempts to understand the interaction of man and environment may be mutually enriching. In this light, the present study intends to reconstruct local metalwork history at the largest settlement of the vast Aeduan territory through its impact on the environment. Described by Caesar in "*De Bello Gallico*" in 58 B.C. as one of the greatest and richest oppida of Gaul, Bibracte was located upon Mount Beuvray, one of the highest points of the granitic Morvan. This strategic site corresponds to the limit of the Saône, Loire, and Seine watersheds in central France. The Celtic city, with its thousands of inhabitants, was founded ca. 180 B.C. and spread over approximately 200 ha. It was an important trade center, including metalworking, as the presence of numerous bronze and iron workshops demonstrates (1). Under Roman Empire domination (ca. 25 A.D.), the population gradually left Bibracte to settle 25 km away, in the new city of *Augustodunum* (2), nowadays known as Autun. Evidence of settlements before Celtic occupation is rare, except for some artifacts dating from the Neolithic, Late Bronze Age, and Early Iron Age (3). This can partly be explained by geographical conditions: the agricultural potential of acidic soils is low, climate conditions are rugged (precipitations, 1500 mm; mean temperatures, 8.5°C), slopes are steep, and valleys are narrow (4). Geomorphological anomalies, such as wide trenches and gullies, have recently been found on the site and interpreted as remains of mining excavations. On this basis, archaeologists have assumed that one of the reasons which may have attracted early settlers is the abundance of

* Corresponding author phone: +33 (0)3 80 39 63 50; fax: +33 (0)3 80 39 63 87; e-mail: Fabrice.Monna@u-bourgogne.fr.

[†] Laboratoire GeoSol, Université de Bourgogne.

[‡] Archéologies, Université de Bourgogne.

[§] Université de Besançon.

^{||} Université de Genève.

[⊥] Universités Paris 7 and Paris 12.

[#] Centre des Sciences de la Terre, Université de Bourgogne.

mineral resources. However, this assumption is not yet an established fact because of the lack of clear field evidence, the extent of the current forest making difficult any pedestrian or aerial geophysical prospecting. Remains of early local mining exploitation may also have been destroyed, buried, or masked either by the building of Bibracte or by any further metal extraction up to and including that of the 20th century. In such a situation of successive periods of mining activity, the reconstruction of the industrial history of the site may be envisaged through the geochemical analysis of peat bogs (cf. *The Science of the Total Environment, Special Issue, 2002*, vol. 292, 1–2), which also provides quantitative information about the environmental legacy. Elemental compositions were therefore measured in a peat core sampled around Mount Beuvray ('Port-des-Lamberts', Glux-en-Glenne, Nièvre). However, metals buried in peatlands may possibly result from a combination of multiple sources (5), while postdepositional migrations, already observed at decadal scale, may totally preclude any utilization for historical reconstruction (6, 7). That is why lead isotopic composition, which can help to dispel such ambiguities, is nowadays often determined (5, 7–11). Lead has the advantage of being one of the less mobile metals in such an environment. Its isotopic geochemistry is based on the atom ratio differences existing between natural and anthropogenic sources, the latter depending on U/Pb and U/Th ratios and the age of the ore deposits from which the metal derives (12). Mining may also have affected nearby vegetation through possible deforestation performed in response to increasing energy demands for metalworking (13, 14). Geochemistry was therefore supplemented by pollen analyses.

Given this new set of data, we will examine the earliest signs of extensive mining and smelting to establish whether mineral abundance in the area acted as a magnet for the first Aeduan settlers, an important question recently raised by archaeologists. From an environmental point of view, we will try to quantify the weight and behavior of the contaminant heritage, and the impact on vegetation of past metalwork in a rural area which today presents no major industrial activity.

Setting

Mount Beuvray is located in the Morvan, northern Massif Central. It is a Hercynian massif (900 m, asl maximum at Haut Folin) mainly composed of granitic rocks, although volcano-sedimentary terrains (rhyolites and conglomerates) are also exposed (Figure 1). The whole massif is crosscut by several microgranitic and quartz veins. Three main types of mineral deposits were recognized: (i) late Hercynian stratiform barytic and fluoritic outcrops, such as those of the Argentolle district mining area (15); (ii) abundant polymetallic mineralization (Pb, Zn, Ag) in NNW–SSE and NNE–SSW veins, and, to a lesser extent, (iii) in conglomerates outcropping on Mount Beuvray (16, 17). Although the presence of ancient mining activities has already been suggested in the Mount Beuvray region, textual and field evidence indicates exploitation of fluorine, Barite, and lead from the late 18th century, which continued until the mid-1980s.

The Port-des-Lambert peat deposit (cf. Figure 1) is situated at about 4–5 km from both Mount Beuvray and known ore deposits (Figure 1) and lies on a surface of about 3 ha. *Sphagnum*-dominated and organic-rich at the top, it is fed by some temporary streams originating from a small catchment area.

Material and Methods

Sampling. The peat column was collected in October 2000 following the conventional two-borehole technique with the help of a Russian GYK-type corer. It consists of about 2

m of organic-rich material. The core, well preserved in a plastic bag to protect against contamination and evaporation, was subsampled a few hours later in 2-cm-thick subsections using an acid precleaned PTFE spatula. The outer part was systematically discarded, as it could have been polluted by contact with any metallic parts of the corer or plastic bag. A fraction of subsamples was kept wet for pollen analysis, while the remainder was transferred to precleaned LDPE beakers and dried for 3 days at 60 °C. Once dried, the subsamples were powdered in an automatic agate mortar systematically precleaned with diluted HCl and Milli-Q water.

Geochemical Analyses. Total organic carbon (TOC) and nitrogen contents were measured by elemental analyzer (NCS 1500, Carlo Erba). The whole procedure from preparation to measurement for isotopic and elemental concentration determination by inductively coupled plasma–mass spectrometry (ICP-MS) and inductively coupled plasma–atomic emission spectrometry (ICP-AES) was performed in US class 1000–10000 clean rooms. About 200 mg of samples were first oxidized overnight using 4 mL of Suprapure H₂O₂ (Merk, Germany) and dried. Two millimeters each of Suprapure-grade HCl, HNO₃, and HF (Merk, Germany) was then added. The dissolution was achieved under microwave assistance Ethos (Milestone). One blank and one reference material standard (RMS), Peach leaves NIST 1547 or JSD 1–2, were added to each set of seven unknown samples.

Pb, Zn, Cd, and Cu contents were measured after external and internal (Re, Rh) calibrations on an HP 4500 ICP-MS. The same elements together with Sb, Al, and S were also determined on one-half of the samples by ICP-AES using a micronebulizer or conventional Scott chamber. Both methods always yielded similar results within ±10% of RMS certified values. Lead was first purified from an aliquot of the solution on AG1 × 4 ionic resin (Biorad). Isotopic ratios were then determined on quadrupole-based HP 4500 ICP-MS. Mass bias correction was operated by bracketing several NIST 981 lead standards every five samples. Further details about the complete procedure and instrumental settings can be found elsewhere (18, 19). Blank corrections were never required as they appeared negligible compared to the total amount of lead in the aliquots. Precisions of ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁶Pb ratios were about 0.27% and 0.31%, respectively. Previous comparisons between isotopic measurements made by quadrupole-based ICP-MS and more precise thermo ionization mass spectrometry (TIMS) always demonstrated the accuracy of the ICP-MS results, within 95% confidence intervals (19).

Refractory elements such as Sc, Th, La, and Ce were precisely measured by instrumental neutron activation (INAA) at Actlabs (Ontario, Canada). Routinely measured standards and Peach Leaves NIST 1547 added as blind samples yielded results within about ±10–15% of certified values.

Pollen analyses were performed at a subsampling interval of 8 cm. Preparation followed a standard procedure, according to a physicochemical protocol adapted to this type of sediment to eliminate mineral and organic matrix (namely, the Frenzel method, explained elsewhere (20)). There were no sterile levels, and palynomorphs were well preserved. Pollens were identified with the aid of keys (21), photographs (22), and reference to a modern-type slide collection. At least 400 pollen grains, in addition to dominant taxa, were counted in each level.

Radiocarbon Dating. Four peat samples were dated using ¹⁴C. They were measured by beta counting at the Centre des Sciences de la Terre–University of Lyons (Table 1, Figure 2). All dates were calibrated using Calib 4.1.3 software (23).

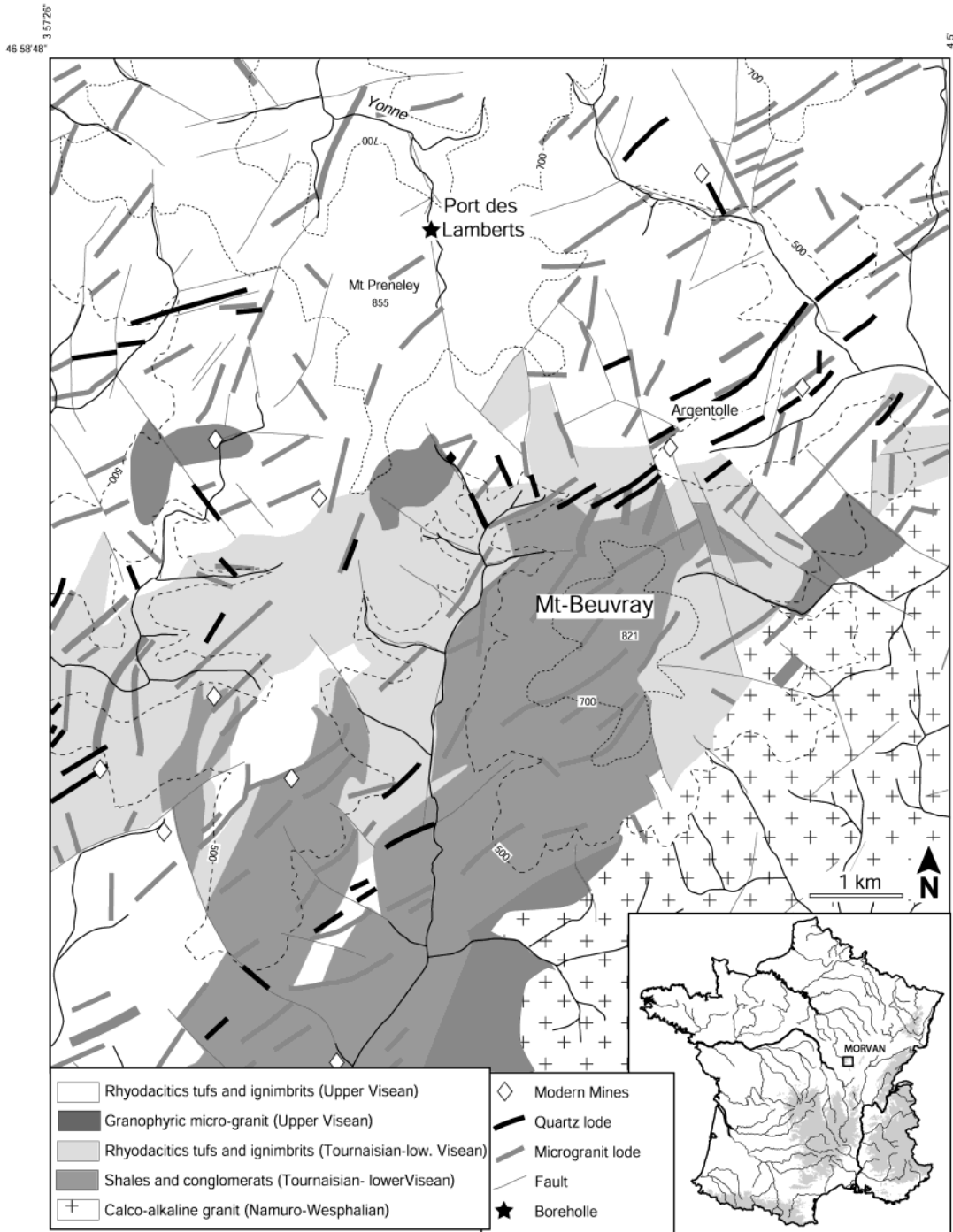


FIGURE 1. Map of the Morvan and location of sampling site; major mining exploitations and archaeological sites are also represented.

TABLE 1: Age–Depth Relationship for the ‘Port-des-Lamberts’ Peat Core

name	lab name	¹⁴ C BP	calibrated dates ^a	max. probabilities
PDL 75	LY-10942	1070 ± 50	888–1028 A.D.	984, 905, 965, 1015
PDL 97	LY-10943	1460 ± 60	441–664 A.D.	605, 617, 635, 585, 565
PDL 126	LY-10944	2480 ± 40	790–407 B.C.	–583, –643, –661, –587, –544
PDL 163	LY-10945	3117 ± 54	1515–1225 B.C.	–1406, –1325, –1425, –1355, –1485

^a The data are calibrated to calendar dates A.D. or B.C..

Results and Discussion

Trophic Status of the Core. Total organic carbon concentration is mostly in the range 45–50%, which indicates a high organic matter content between 80% and 95% (Figure 3). On

this basis, the deposit can be classified as peat (24). Organic matter exhibits inverse variations to that of Sc or other lithophilic elements such as Al, Th, or rare earth elements (not shown here). C/N ratios slightly decrease from the bottom to the top, respectively, from 24 to 17. Such values,

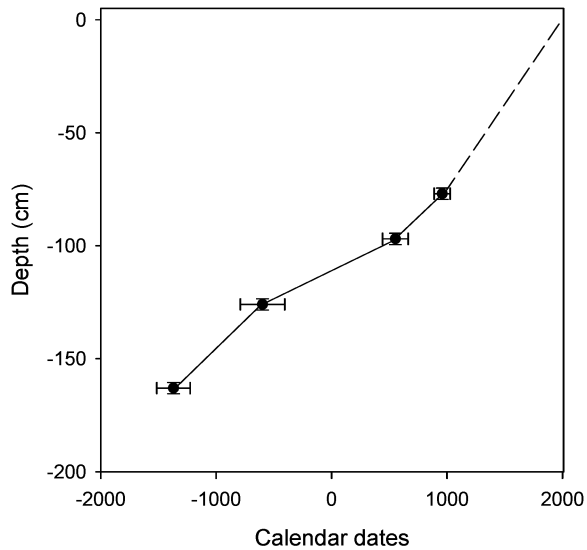


FIGURE 2. Depth vs ¹⁴C-based calibrated calendar dates. The error bars are given at 95% confidence level.

together with those of organic matter, are characteristic of minerotrophic fen peat (25).

Chronology. ¹⁴C-Derived dates are coherent with the depth at which they were determined (Table 1, Figure 2). Although no complementary dating was available within the topmost 75 cm, the extrapolation of the dated sequence acceptably fits the top of the core (dashed line on graph 2). However, the growth rate was probably slower between ca.

cal. 500 B.C. and cal. 1000 A.D., as indicated by a significant change in the curve slope.

Data Preparation. Total concentration profiles are often used for a direct historical reading, but such an operation must be undertaken with care because (i) the distribution of metals in the core can be affected by variations in inorganic matter content (8, 26), (ii) changes in vegetation, compaction, or primary production (6), and (iii) in minerotrophic peatlands, the redistribution of metals after postdepositional migrations may occur (7, 27). Inputs from groundwater are also possible when peatlands are not hydrologically isolated from the substratum (5, 28). The elimination of mineral matter influence and further calculation of anthropogenic metal contents is theoretically operated by subtracting the detrital contribution from the total amount (5). Mineral contribution is evaluated by taking as a reference a refractory lithophilic element, such as Sc, or Zr, REE, Th, Al, Ti, which is considered to be conservative in peat profiles and has no anthropogenic origin (26, 29)

$$M_{\text{anthr.}} = M_{\text{sample}} - Sc_{\text{sample}} \cdot \left(\frac{M}{Sc} \right)_{\text{natural}} \quad (1)$$

with $M_{\text{anthr.}}$ being the anthropogenic metal content; M_{sample} and Sc_{sample} , respectively, are the total metal and scandium concentrations, and $(M/Sc)_{\text{natural}}$ is the natural ratio assumed to be constant. $(M/Sc)_{\text{natural}}$ values are generally assimilated to those of the continental crust or upper continental crust (UCC) or may alternatively be deduced from the bottom of the core, provided it fully reflects natural inputs.

In the present core, Pb/Sc ratios roughly decrease from the top to the bottom. An almost constant $(Pb/Sc)_{\text{sample}}$ ratio

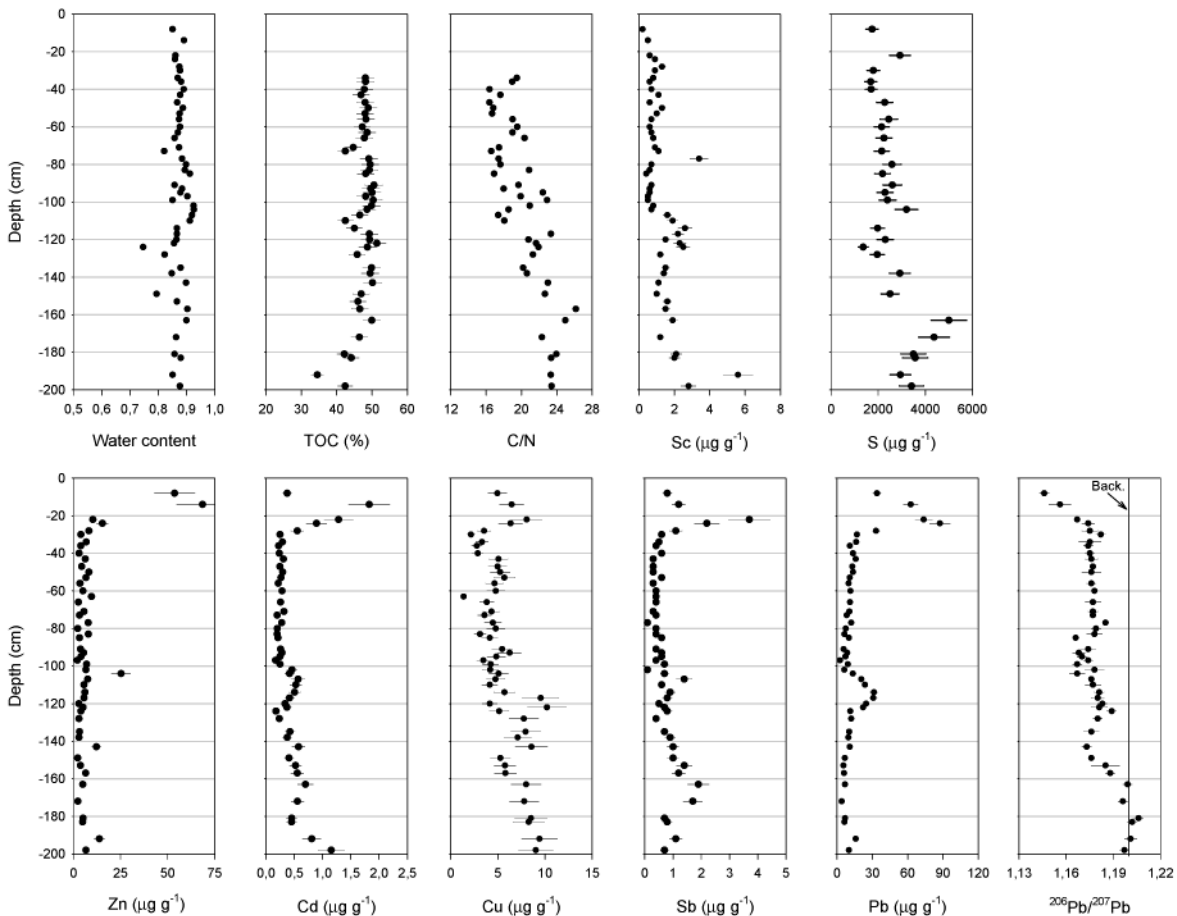


FIGURE 3. Water content, C/N and ²⁰⁶Pb/²⁰⁷Pb ratios, total organic carbon (TOC), and Sc, Pb, Zn, Cd, Cu, Sb, and S concentrations versus depth. The error bars correspond to a 95% confidence level.

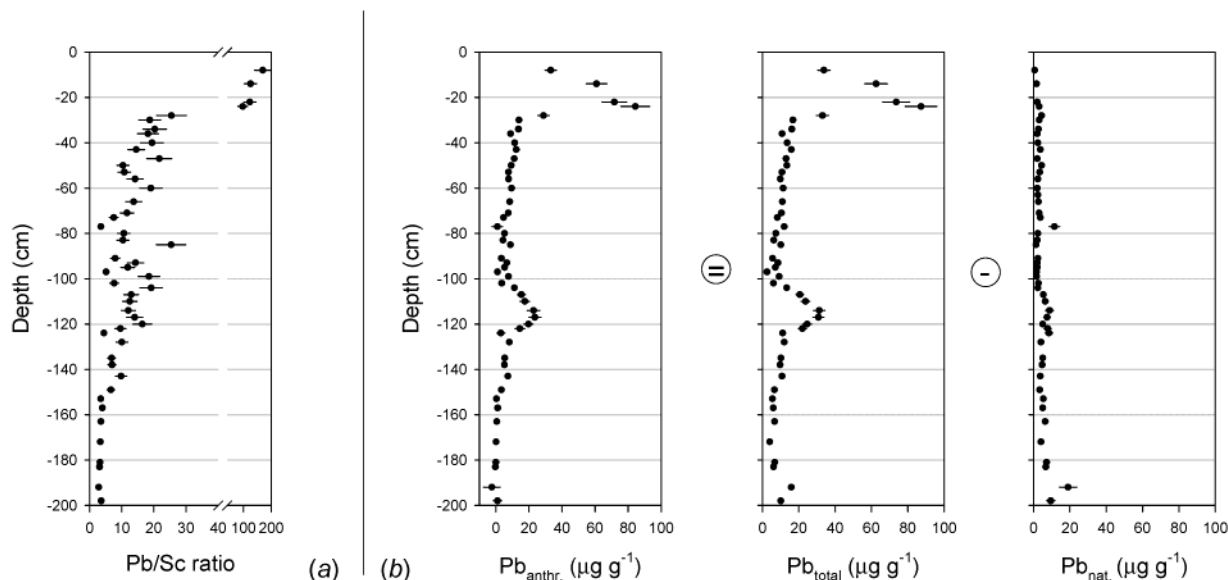


FIGURE 4. (a) Pb/Sc ratios versus depth (cm). (b) Calculation of anthropogenic lead concentration ($Pb_{anthr.}$) by subtracting natural lead ($Pb_{nat.} = Sc \times 3.3$; see text for details) from total lead concentration (Pb_{total}). The error bars correspond to a 95% confidence level.

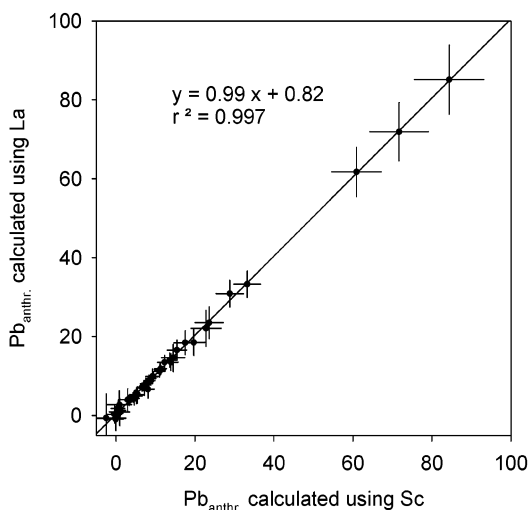


FIGURE 5. Comparison of anthropogenic lead concentrations calculated using Sc or La as reference element. See text and Figure 4 for $(Pb/Sc)_{natural}$ determination, $(Pb/La)_{natural}$ ratio taken at ~ 0.82 from the last 40 cm of the core (against 0.53 for the UCC value, 37). The error bars correspond to a 95% confidence level.

value of 3.3 ± 0.7 (2σ) is found within the deepest 40 cm (Figure 4a), while $^{206}Pb/^{207}Pb$ signatures (ca. 1.20, Figure 3) are typical of preindustrial sediments in France (10, 30). Using the value of 3.3 ± 0.7 (2σ) for $(Pb/Sc)_{natural}$ enables the minor oscillations observed in the last 40 cm of the total lead profile to be filtered (cf. Figure 4b), because they can be attributed to a significant addition of mineral matter from underlying sediments. In fact, all the other lithophilic refractory elements measured, La, Th, Ce, Sc, and Al, are strongly intercorrelated ($r > 0.9$, $p < 0.001$), similar to what was found elsewhere (26), and yield similar calculations of anthropogenic lead contribution when their reference ratio is derived from the bottom of the core (i.e., the comparison calculation operated using Sc and La in Figure 5). The difference between the Pb/Sc ratio taken as reference (3.3) and that of UCC (2.4) (31) might be explained by a fractionation between heavy and light particles occurring during long-range atmospheric transportation (26) or by the preponderant influence of local background characterized by a higher Pb/Sc ratio. In any

case, our calculation of anthropogenic lead will be not affected because our reference values, obtained from the core and not from a theoretical crust, already integrate such a potential fractionation. As a consequence, the positive anomaly of lead content around 120 cm depth cannot solely be explained by the amount of mineral matter (Figure 4). A dominant anthropogenic component has to be considered, also confirmed by $^{206}Pb/^{207}Pb$ signatures at this depth (~ 1.18) which indicate the presence of human-derived lead.

Regrettably, applying the same procedure for Zn, Cu, Sb, or Cd profiles (Figure 3) is far from straightforward, in part because these elements have no isotopic features which would allow zones without any anthropogenic contribution to be clearly identified. Zn and Cu are also essential nutrients for plants, which recycle them into the root zone. That is why their good preservation in peat bogs is generally difficult to observe, except in cases where pollution has been strong (32, 33). After eliminating the polluted topmost 30 cm samples Cu, Sb, and Cd profiles show an overall decreasing trend from the bottom to the top (Figure 3), which might result from the influence of groundwater and underlying mineral soil. In these horizons, Sb and Cd are significantly correlated to S ($r_{pearson} = 0.74$, $p < 0.001$ and $r_{pearson} = 0.63$, $p < 0.001$, respectively), suggesting that they may also have been partly redistributed in the core, to be finally associated with stable sulfur. Zn does not vary disproportionately to Sc except in the topmost horizons, where recent anthropogenic inputs have been such that they are still present. If large amounts of anthropogenic zinc were deposited in the past, they are no longer visible because of major translocation. Although, above 130 cm depth, cadmium almost matches the lead profile (cf. Figure 3) and presents variations out of proportion with those of Sc, the data suggest that none of these metals can be used as an appropriate monitor for atmospheric input reconstruction.

Isotopic Signature Contribution. Concerning lead, invaluable information about its possible postdepositional migration and hence about its utility for past industrial history reconstruction is provided by its isotopic composition. The procedure to determine graphically the isotopic signatures of anthropogenic inputs consists generally in representing the samples in a diagram of $^{206}Pb/^{207}Pb$ vs $1/[Pb]_{tot}$ (12). The background is considered as a constant end member, and the isotopic composition of anthropogenic lead of one

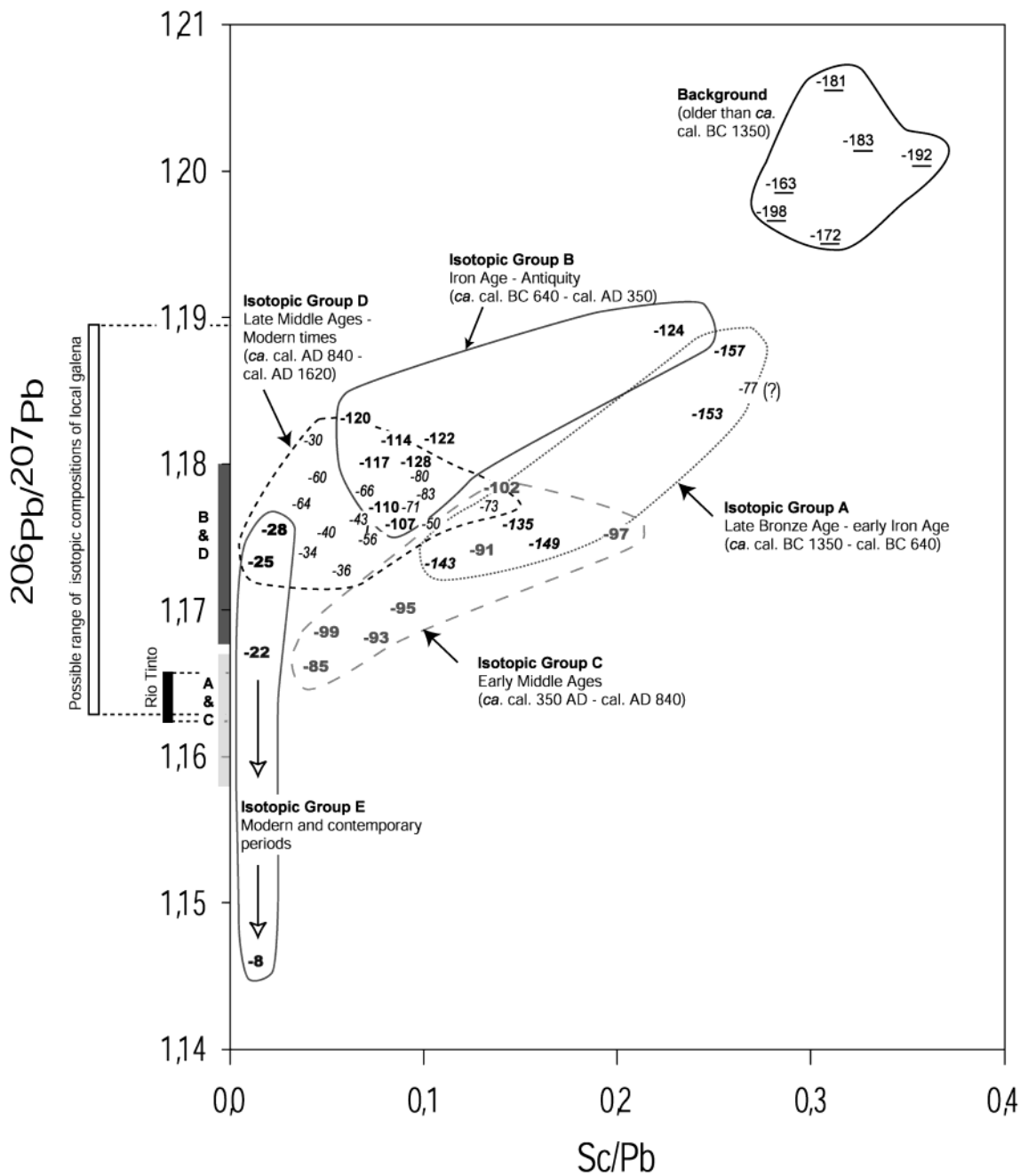


FIGURE 6. $^{206}\text{Pb}/^{207}\text{Pb}$ versus Sc/Pb ratios. Samples are represented by their depth and grouped on the basis of their isotopic characteristics and the cultural periods to which they belong. The latter is assessed using the curve presented in Figure 2.

contaminated sample can be read at the Y-axis intercept of the straight line linking the background domain and the sample. However, the use of $[\text{Sc}]_{\text{tot}}/[\text{Pb}]_{\text{tot}}$ in place of $1/[\text{Pb}]_{\text{tot}}$ on the X-axis produces a considerably more restrained background domain when natural Pb concentrations vary subsequently to changes in mineral matter contents. In such a situation, both Pb and Sc concentrations evolve proportionally, so that the $[\text{Sc}]_{\text{tot}}/[\text{Pb}]_{\text{tot}}$ ratio remains almost constant. For polluted samples, the procedure also eliminates dispersions due to variations in natural lead content on the X-axis, while the Y-axis intercept is interpreted as an end member featured by no Sc and high Pb content, in other words as the isotopic signature of the pure anthropogenic component. In our core, this representation is particularly well adapted since mineral matter content varies enough along the peat column not to be neglected (Figure 4b). The set of data does not fall on a line, which would have been

an indicator of a unique anthropogenic source (or possibly multiple sources possessing the same isotopic signature), but widens close to the Y-axis, suggesting changes in exogenous lead sources (Figure 6). Six groups of samples can be graphically defined from their isotopic characteristics and the cultural periods to which they belong: the background end member before cal. B.C. 1750 (Group Background in Figure 6), late Bronze Age—early Iron Age, where anthropogenic lead inputs start (Isotopic Group A), Iron Age—Antiquity (Isotopic Group B), early Middle Ages (Isotopic Group C), late Middle Ages—Modern times (Isotopic Group D), and finally modern and contemporary samples (Isotopic Group E), although the age of the latter are rough estimations obtained by considering a constant accumulation rate between the 11th century and the present (see Figure 2).

The position of these groups in Figure 6 indicates that the isotopic compositions of the pollutant inputs have oscillated

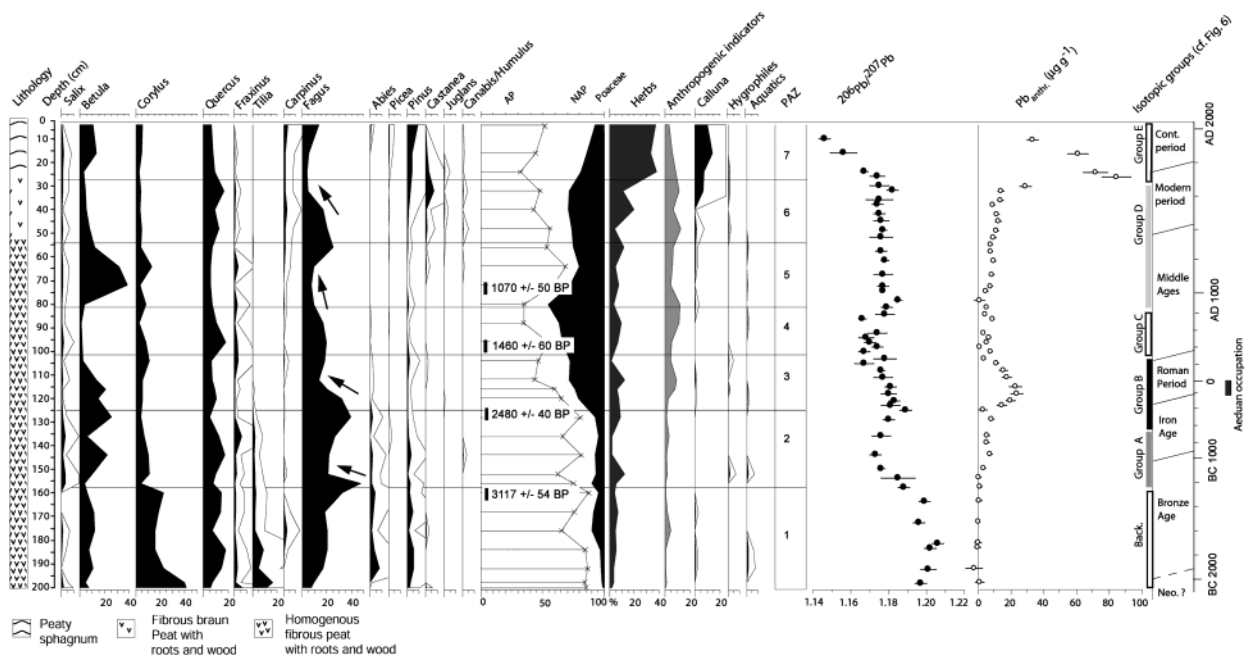


FIGURE 7. Lithology and pollen diagram organized in pollen assemblage zones (PAZ) according to major plant communities. For better legibility, dominant taxa *Alnus* and *Cyperaceae* were removed to form a simplified palynological diagram expressed as a percentage of taxa (34). $^{206}\text{Pb}/^{207}\text{Pb}$ ratios and anthropogenic lead concentrations are also represented on the depth scale accompanied by a chronological scale.

between low ($^{206}\text{Pb}/^{207}\text{Pb}$, 1.160–1.165 for phase A and C) and higher radiogenic signatures ($^{206}\text{Pb}/^{207}\text{Pb}$, 1.165–1.180 for phase B and D). The chronological order in which these phases appear is incompatible with any postdepositional migration of lead within the profile. As an example, the isotopic signature of the anthropogenic contribution corresponding to phase B cannot be explained by a translocation of lead from underlying or overlying horizons, simply because the anthropogenic lead buried during phases A and C is not radiogenic enough. The good integrity of both lead concentrations and isotope profiles is unambiguously demonstrated, at least at this time resolution; therefore, the lead record can be used for monitoring historical pollution. For comparative purposes, isotopic and anthropogenic lead concentration profiles are juxtaposed to palynological data organized in pollen assemblage zones (PAZ) according to major plant communities (Figure 7).

History Reconstruction. The Early Bronze Age is initially dominated by woodland taxa: *Corylus* (hazel), *Fagus* (beech), *Quercus* (oak), and to a lesser extent *Tilia* (lime) (Figure 7, PAZ 1). Anthropogenic indicators, such as cereal-type pollens, are already present in herbaceous taxa (35, 36) and testify to early local human occupation. While the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of ~ 1.20 in PAZ 1 merely reflect natural mineral matter (Background Isotopic Group), anthropogenic lead inputs start to be detected from PAZ 2 (ca. cal. B.C. 1300) by a significant fall in $^{206}\text{Pb}/^{207}\text{Pb}$ ratios and a slight rise in anthropogenic lead concentrations. The beginning of PAZ 2 in the late Bronze Age shows a drop in *Fagus*, *Corylus*, and *Quercus* taxa percentage. The low percentage of anthropogenic pollen indicators recorded in these levels seems to indicate that forest clearing was not related to any agropastoral extension. It is precisely at that time that the earliest substantial human-derived inputs are noticed by means of sizable anthropogenic lead concentrations while $^{206}\text{Pb}/^{207}\text{Pb}$ ratios continue to decline toward more anthropogenic values (Isotopic Group A). Such a concomitance is a hint of a close connection between metallic contamination and forest clearance. Moreover, as we shall see later, *Fagus* decline is systematically associated with anthropogenic input intensification, so that

these observations in Late Bronze Age horizons, when metalworking developed in Western Europe (37), are not fortuitous. More locally, in Blanot, 30 km from the site, an abundant set of metallic artifacts dating from this period has been discovered (38). Vegetation cover may have been drastically affected by selective deforestation operated in response to an increasing demand in energy for mining and smelting, as noticed elsewhere (13, 14). This suggests that this anthropogenic lead did not originate from remote areas after long-range atmospheric transport but was primarily emitted locally. Our results tend therefore to confirm that the Mount Beuvray area was, as previously suspected by some archaeologists, an early mining center. Extraction and smelting of copper, silver, or gold would have emitted into the atmosphere enough lead-enriched dust and gases to be archived in surrounding environments.

Throughout the Iron Age, the percentage of woodland taxa, dominated by *Fagus*, gradually increases (PAZ 2) while anthropogenic lead concentrations remain stable. Human pressure on the forest must have declined at that period. A turning point in this tendency is, however, observed in the Late Iron age (beginning of PAZ 3): *Fagus* taxa collapse again, anthropogenic herb indicators increase, while anthropogenic lead concentrations peak at the apogee of Aeduan civilization (first third of PAZ 3). Large forest openings probably enhanced erosion and accumulation of mineral matter in peat deposits (39), so that the reduction in accumulation rate (Figure 2) and the Sc anomaly (cf. Figure 3) pinpointed during the Aeduan occupation are not surprising. Intensification of lead anthropogenic inputs has been often documented between ca. B.C. 500 and A.D. 500 in multiple European environments (8, 10, 39, 40), as far as Scandinavia (11, 41) and Greenland (42, 43). In the absence of dominating local sources, they are attributed, at least partly, to long-range transport of polluted airborne particulate matter coming from Southern Spain (8, 43), this region accounting for up to 40% of worldwide lead production during the Roman Empire (44). At that time, the use of this metal was such that it was aptly called the Roman metal (45). Nonetheless, if there is no longer any doubt about the importance of lead of Spanish origin in high latitude

regions, this source must not be overestimated in continental Europe, where local emissions may have acted as point sources even overriding the temporal pattern of large-scale pollution emission (9, 14). Here, the isotopic signatures of the pollutant buried in peat (Isotopic Group B) are distinctly more radiogenic than those of Rio Tinto (1.162–1.166, 46, 47) (cf. Figure 6), while high anthropogenic lead concentrations come with major forest clearance, underlying their indigenous character. The Aeduans are well-known to have been fine metalworkers. Our results suggest the presence of major mining activity which, together with the numerous metallurgical workshops found out at Bibracte, could at least partly explain the tribe's wealth. Isotopic signatures of anthropogenic emissions clearly indicate variations in primary origin of lead between the Bronze Age and Antiquity (Figure 6), which might result from changes in the type of minerals exploited, although direct archaeological evidence is still lacking. Unfortunately, except for two values yielding $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of 1.188–1.189 (17), there are no isotopic measurements available for local galena in the literature. However, by southward extension to the Massif Central, where much work has been done on similar Mesozoic galena, one can reasonably expect $^{206}\text{Pb}/^{207}\text{Pb}$ ratios comprised between 1.164 and 1.189 (48) (cf. Figure 6). This range, despite its size, is nevertheless compatible with the values of the anthropogenic inputs determined from the position of the different isotopic groups in Figure 6.

A decline in anthropogenic pollen indicators and lead fluxes (mid PAZ 3) marks the beginning of our era. Concurrently, the percentage of *Fagus* taxa stabilizes or even increases. After the Roman conquest of Gaul, the entire population of Bibracte was transferred 25 km away, to found the new city of *Augustodunum* (2). Local mining and smelting probably declined since mineral resources could have been provided by trade with the Romans and smelting transferred to *Augustodunum*, which became a metallurgical center. However significant anthropogenic lead fluxes are noticed at least until A.D. 300, which might signify persistent minor activities in the area or simply be the result of the release of lead from polluted soils over a long period of time after Aeduan mining operations ceased.

No remarkable change in geochemical is observed during the early Middle Ages (PAZ 4). For that period, archaeological knowledge is crucially lacking, so that the origin of the low anthropogenic inputs is rather uncertain. Following the fall of the Roman Empire, ancient industrial techniques were partially abandoned or even forgotten, which is probably what happened here. Around the 12th century (PAZ 5), human-derived lead concentrations rise, *Fagus* representation drops, and *Betula* (birch), a heliophilous and pioneer tree, dominates woodland cover. Such a renewal is contemporary with the great deforestation phases observed at the European scale (49). Almost everywhere, Roman mines were progressively reopened, while new ones were discovered (i.e., Germany, Balkans, etc.) (33, 50). Anthropogenic inputs continue in PAZ 6 and even amplify drastically later (PAZ 7), although the chronology established from ^{14}C does not allow a precise dating of this phase. The peak of anthropogenic lead concentration at almost $80\ \mu\text{g g}^{-1}$ probably corresponds to the phase of local mining exploitation, which is well documented by textual archives during the 18th and 19th century. The fact that *Fagus* pollen almost totally disappears at that time tends to support this thesis. Such a fall may also be due to the intense exploitation of Morvan forests from the 16th to the beginning of the 20th century, which were operated to furnish Paris with firewood (51). The sequence seems to be diluted in the topmost centimeters, as suggested by the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio measured at 14 cm depth (1.156), supposedly dating from 1900, which actually reflects the recent use of nonradiogenic lead for industry. Apart from

these persistent doubts in the most recent samples, the new set of geochemical and pollen data presented here is in good agreement with the archaeological and historical knowledge available. The use of isotopic geochemistry combined with the Sc correction of total lead measurements enables controlled distinction and apportioning of anthropogenic versus natural materials. The isotopic signal was found, as previously (52), to be more sensitive than the sole measurement of concentrations when anthropogenic contribution is low. This technique makes possible here a fine recognition of early contaminations dating as far back as the Late Bronze Age. They are interpreted as the first signs of local metallurgy, which may have attracted later settlers who founded Bibracte, its indigenous character being underlined by the correspondence with the pollen record. By combining geochemical and palaeobotanical techniques with archaeological knowledge, the past seems therefore to become less opaque.

In the sequence studied, about 20% of the total anthropogenic lead was deposited before our era and probably about one-half of the pool before the 18th century. Together with the archaeological answers exposed above, the importance of the environmental impact of our ancestors' industrial activities has been demonstrated in a region which is nowadays one of the less industrialized areas of France. This heritage should be taken into account when evaluating the quality of the environment in order to not overestimate the impact of modern pollution. The reconstruction of the interactions which existed between early societies and their environment is a key factor, which may well be of assistance in the management of current and future environmental problems.

Acknowledgments

We thank Pierre Yves Favargé, Sylvie Philippe, Marie-Jeanne Milloux, and Davide Vignati for their technical assistance. We also thank four anonymous reviewers who greatly improved the manuscript by their thoughtful comments.

Literature Cited

- (1) Gruel, K.; Vitali, D. *Gallia* **1999**, *55*, 1.
- (2) Rebourg, A. *Gallia* **1999**, *55*, 141.
- (3) Gran-Aymerich, J. In *La civilisation de Hallstatt, bilan de la rencontre de Liège*; Etudes et recherches archéologiques de l'université de Liège; 1989; E.R.A.U.L. no. 36; pp 343–355.
- (4) Buchsenchutz, O.; Richard, H. In *L'environnement du Mont Beuvray*; Centre archéologique européen du Mont Beuvray; Glux-en-Glenne, 1996; Collection Bibracte no. 61616; 1, p 207.
- (5) Weiss, D.; Shoty, W.; Appleby, P. G.; Kramers, J. D.; Cheburkin, A. K. *Environ. Sci. Technol.* **1999**, *33*, 1340.
- (6) Urban, N. R.; Eisenreich, S. J.; Grigal, D. F.; Schurr, K. T. *Geochem. Cosmochem. Acta* **1990**, *54*, 3329.
- (7) MacKenzie, A. B.; Logan, E. M.; Cook, G. T.; Pulford, I. D. *Sci. Tot. Environ.* **1998**, *223*, 25.
- (8) Shoty, W.; Weiss, D.; Appleby, P. G.; Cheburkin, A. K.; Frei, R.; Gloor, M.; Kramers, J. D.; Reese, S.; Van Der Knaap, W. O. *Science* **1998**, *281*, 1635.
- (9) Camarero, L.; Masqué, P.; Devos, W.; Ani-Ragolta, I.; Catalan, J.; Moor, H. C.; Pla, S.; Sanchez-Cabeza, J. A. *Water Air Soil Pollut.* **1998**, *105*, 439.
- (10) Alfonso, S.; Grousset, F.; Massé, L.; Tastet, J.-P. *Atmos. Environ.* **2001**, *35*, 3595.
- (11) Renberg, I.; Bindler, R.; Brännvall, M.-J. *Holocene* **2001**, *11*, 511.
- (12) Faure, G. *Principles of Isotope Geology*, 2nd ed.; Wiley: New York, 1986.
- (13) Richard, H.; Eschenhor, L. *Rev. d'archéométrie* **1998**, *22*, 29.
- (14) Galop, D.; Tual, M.; Monna, F.; Dominik, J.; Beyrie, A.; Marembert, F. *Sud Ouest Eur.* **2001**, *11*, 3.
- (15) Lhégu, J.; Jebrak, M.; Touray, J. C.; Ziserman, A. *Bulletin BRGM*; BRGM, Orléans, 1982; section II, no. 61616; 2, pp 165–177.
- (16) Delfour, J. *BRGM report no. 61616*; 78 SGN 611, BRGM: Orléans, 1978; p 11.
- (17) Marcoux, E. Ph.D. Thesis, University of Clermont-Ferrand II, 1986; p 299.
- (18) Monna, F.; Loizeau, J.-L.; Thomas, B. A.; Guéguen, C.; Favarger, P.-Y. *Spectrochim. Acta B* **1998**, *59*, 1317.

- (19) Monna, F.; Loizeau, J.-L.; Thomas, B.; Guéguen, C.; Favarger, P.-Y.; Losno R.; Dominik, J. *Analisis* **2000**, *28*, 750.
- (20) Moore, P. D.; Webb, J. A.; Collinson, M. E. *Pollen analysis*, 2nd ed.; Blackwell: Oxford, 1991.
- (21) Feagri, K.; Iversen, J.; *Textbook of Pollen Analysis*; John Wiley & Sons: New York, 1989.
- (22) Reille, M. *Pollen et spores d'Europe et d'Afrique du Nord*; Laboratoire de Botanique Historique et Palynologie, URA CNRS 1152: Marseille, 1992; p 550.
- (23) Stuiver, M.; Reimer, P. J.; Bard, E.; Beck, J. W.; Burr, G. S.; Hughen, K. A.; Kromer, B.; McCormac, F. G.; Plicht, J.; Spurk, M. *Radiocarbon* **1998**, *40*, 1041.
- (24) Würst, R. A. J.; Bustin, R. M.; Lavkulich, L. M. *Catena* **2003**, *751*, 1.
- (25) Zeitz, J. In *Geochemie und Umwelt*; Matschullat, J., Tobschall, H. J., Voight, H.-J., Eds.; Springer-Verlag: Heidelberg, 1997; 443p.
- (26) Shotyk, W.; Weiss, D.; Kramers, J. D.; Frei, R.; Cheburkin, A. K.; Gloor, M.; Reese, S. *Geochim. Cosmochim. Acta* **2001**, *65*, 2337.
- (27) Jones, J.; Hao, J. *Environ. Geochem. Health* **1993**, *15*, 67.
- (28) Bozkurt, S.; Lucisano, L.; Moreno, L.; Neretnieks, I. *Earth Sci. Rev.* **2001**, *53*, 95.
- (29) Shotyk, W. *Environ. Rev.* **1996**, *4*, 149.
- (30) Monna, F.; Lancelot, J. R.; Croudace, I. W.; Cundy, A. B.; Lewis, J. T. *Environ. Sci. Technol.* **1997**, *31*, 2277.
- (31) Wedepohl, K. H. *Geochim. Cosmochim. Acta* **1995**, *59*, 1217.
- (32) Mighall, T. M.; Abrahams, P. W.; Grattan, J. P.; Hayes, D.; Timberlake, S.; Forsyth, S. *Sci. Tot. Environ.* **2002**, *292*, 69.
- (33) Kempster, H.; Frenzel, B. *Water Air Soil Pollut.* **2000**, *121*, 93.
- (34) Janssen, C. R. *Acta Bot. Neerlandia* **1959**, *8*, 55.
- (35) Behre, K.-E. *Anthropogenic indicators in pollen diagrams*; Balkema: Rotterdam, 1986.
- (36) Richard, H. In *L'homme et la dégradation de l'environnement*; XVème Rencontres Internationales d'Archéologie et d'Histoire d'Antibes; APDCA: Gap, 1995.
- (37) Huth, C. Metals make the world go round. In *Metal circulation, communication and tradition of craftsmanship in Late Bronze Age and Early Iron Age Europe*; Pare, C. F. E., Ed.; Oxbow Books: Oxford, 2000.
- (38) Thévenot, J. P. *Revue archéologique de l'Est et du Centre-Est*; Dijon, 1991; 11th supplément.
- (39) Van Geel, B.; Bregman, R.; van der Molen, P. C.; Dupont, L. M.; Van driel-Murray, C. *Acta Bot. Neerl.* **38**, 467.
- (40) Martínez-Cortizas, A.; García-Rodeja, E.; Pontevedra-Pombal, X.; Nóvoa Muñoz, J. C.; Weiss, D.; Cheburkin, A. *Sci. Tot. Environ.* **2002**, *292*, 33.
- (41) Renberg, I.; Wik-Persson, M.; Emteryd, O. *Nature* **1994**, *368*, 323.
- (42) Hong, S.; Candelone, J.-P.; Patterson, C. C.; Boutron, C. F. *Science* **1994**, *23*, 1841.
- (43) Rosman, K. J. R.; Chisoholm, W.; Hong, S.; Candelone, J.-P.; Boutron, C. F. *Environ. Sci. Technol.* **1997**, *31*, 3413.
- (44) Nriagu, J. O. *Lead and lead poisoning in Antiquity*; Wiley: New York, 1983.
- (45) Nriagu, J. O. *Environment* **1990**, *32*, 7.
- (46) Stos-Gale, Z.; Gale, N. H.; Houghton, J.; Speakman, R. *Archaeometry* **1995**, *37*, 407.
- (47) Pomiès, C.; Cocherie, A.; Guerrot, C.; Marcoux, E.; Lancelot, J. *Chem. Geol.* **1998**, *144*, 137.
- (48) Brévar, O.; Dupré, B.; Allègre, C. J. *Econ. Geol.* **1982**, *77*, 429.
- (49) Berglund, B. E.; Birks, H. J. B.; Ralska-Jasiewiczowa, M.; Wright, H. E. *Palaeoecological events during the last 15 000 years. Regional syntheses of palaeoecological studies of lakes and mires in Europe*; John Wiley & Sons: New York, 1996.
- (50) Brännvall, M.-L.; Bindler, R.; Renberg, I.; Emteryd, O.; Bartnicki, J.; Billström, K. *Environ. Sci. Technol.* **1999**, *33*, 4391.
- (51) Vigreux, M. *Courrier du Parc naturel régional du Morvan* **1994**, *25*, 9.
- (52) Munksgaards, N. C.; Parry, D. L. *Sci. Tot. Environ.* **1998**, *217*, 113.

Received for review July 3, 2003. Revised manuscript received November 3, 2003. Accepted November 6, 2003.

ES034704V