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Abstract

More than four metres of core, covering almost 5000 years of deposition, were collected in a high ash minerogenic peat deposit located in the High Aldudes valley (Basque country), an area well known for its mineral abundance, exploited from Roman Times at least. Although minerogenic peatlands are not generally considered as the best archives to reconstruct past atmospheric metal deposition history, lead isotopic geochemistry demonstrates the integrity of the Pb record at least within the three upper meters; that is to say over the last four millennia. Zn, Cd and Cu may have been widely redistributed either by biological cycling, advective groundwater movements, or diffusional processes. Anthropogenic lead input phases are clearly pinpointed by positive shifts in Pb/Sc ratios with concomitant sharp drops in $^{206}Pb/^{207}Pb$ ratios. They are often accompanied by significant declines in tree taxa, interpreted as increasing demand for wood to supply energy for local mining and/or metallurgical operations. Periods of mining and/or smelting activity are identified during Antiquity and Modern Times, and are also confirmed by textual and field evidence. Inputs from the Rio Tinto (Southern Spain), often invoked as a major lead contributor to the European atmosphere during Roman Times, were not detected here. This remote source was probably masked by local inputs. Other mining and/or smelting phases, only suspected by archaeologists, are here identified as early as the Bronze Age. Although the durations of these phases are possibly overestimated because of detrital inputs consequent to the release of lead from polluted soils over a long period of time after major pollutant inputs, the periods at which pollution peaks occur are in good agreement with archaeological knowledge and palaeo-botanical data. The

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combination of geochemical and palaeo-botanical techniques with field archaeology, therefore provides a powerful tool in studying the interaction of early human societies with their environment, as regards early mining and smelting. © 2004 Elsevier B.V. All rights reserved.

Keywords: Pollution; Lead isotopes; Peat deposit; Atmospheric deposition; Mining; Smelting

1. Introduction

The oldest French settlement of copper miners and metalworkers (3rd millennium BC) has been recently discovered close to Montpellier–Southern France (Ambert et al., 2002). Such exploitation was probably initiated under the stimulus of populations living in the Alpine arc, themselves influenced by precursor cultures from the Balkans, Hungary, Poland and Germany (Chapman and Tylecote, 1983; Gale et al., 1991). Early metallurgical centres seem also to have existed, probably as far back as the Late Neolithic, in Northern Africa and Southern Spain, although definitive proof is still lacking (Rovira, 1998). This forces us to reconsider the relationships between populations living in Eastern and in South-West Europe from the Late Neolithic to the Bronze Age. The mineral-rich Basque country, with its key geographical position, may have interlinked both these cultures. However, even if remains of local extraction during antiquity are numerous, no proof of earlier mining has yet been found. Prehistoric mining was superficial, focusing on a simple hand-picking of minerals, and evidence may have been masked or destroyed by subsequent activities.

However, traces of historical mining or smelting may have been recorded in natural archives. The efficiency of such an environmental approach has been successfully demonstrated at least for lead, at continental scale as well as at local scale, in sediments (Brännvall et al., 1997; Schettler and Romer, 1998; Camarero et al., 1998; Brännvall et al., 1999; Monna et al., 2000a; Renberg et al., 2000, 2001; Ariès, 2001; Eades et al., 2002; Degryse et al., 2003), polar ice (Hong et al., 1994; Rosman et al., 1997), and peatlands (Glooschenko et al., 1986; Van Geel et al., 1989; Kempter et al., 1997; Weiss et al., 1997; Farmer et al., 1997; Kempter and Frenzel, 2000; Shotyk et al., 1998, 2001; Mighall et al., 2002; Martínez-Cortizas et al., 1997, 2002). Concerning peatlands, it is generally accepted that the most appropriate media are ombrotrophic peat bogs because their chemistry and hydrology tend to promote the immobility of metals deposited (Lee and Tallis, 1973; Jones and Hao, 1993; Shotyk, 1996a; Norton et al., 1997; Martínez-Cortizas et al., 1997; Shotyk et al., 1998; MacKenzie et al., 1998a). Evidence of post-depositional lead migrations has already been noticed, at the time scale of the last century, in minerogenic peatlands with ash content less than 10%, making historical interpretation impossible (MacKenzie et al., 1998b). However, at the millennia time scale, coherent lead records have also been reported in marshes featured by high ash content reaching up to 94% (Alfonso et al., 2001). Other studies performed in mineral-rich peatlands (Espi et al., 1997; Shotyk, 2002), indicate that even predominantly minerogenic sites may properly preserve the record of anthropogenic atmospheric Pb deposition or, at least, may provide a qualitative surrogate for historical pollution (Shotyk, 1996b, 2002). In all cases, anthropogenic inputs have to dominate over detrital contribution (Weiss et al., 1999), and mineral dissolution of the underlying sediments must not contribute measurably to the lead inventory (Shotyk, 2002). Invaluable information on the sources may be obtained by the measurement of lead isotopic compositions (Brännvall et al., 1997; Shotyk et al., 1998; MacKenzie et al., 1998b; Weiss et al., 1999; Dunlap et al., 1999; Renberg et al., 2000; Alfonso et al., 2001; Ariès, 2001; Weiss et al., 2002; Martínez-Cortizas et al., 2002; Shotyk et al. 2002a,b; Monna et al., 2004).

Regrettably ombrotrophic peat bogs are not available in the High Aldudes Valley, a Basque valley well known for its mineral abundance, so we had to investigate the possible use of geochemical signals archived in high ash minerogenic peatlands to constrain the history of local mining

and smelting operations. The pollen record has been investigated too. It generally mirrors the influence of climate and anthropogenic pressure, such as cultivation, pastoral activities and forest clearance (Williams, 2000), but signs of deforestation may also be related to energy demands for metal production (Galop and Jalut, 1994; Blanchot et al., 2001), unless they result from agricultural extension. All these new data are confronted to the sparse archaeological knowledge available.

2. The site and local history

Palaeozoic Basque mountains and Permo-Triassic cover contain abundant mineral resources, so that exploration was re-launched in the late 1970s (Fig. 1). Most of the ore deposits are found in upper ordovician detrital formations composed of bulky sandstones, alternation of pelites and sandstones, and black pelites. Mined from Roman Times (Galop et al., 2001; Beyrie et al., in press), 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. In the Middle Ages, this district furnished Bayonne with silver for coinage (Gapillou, 1981). Before the French Revolution, annual production reached more than 100 tons of copper, but exploitation then collapsed because of the lack of wood consequent to intense deforestation. In 1793, Spanish troops plundered the village of Banca and destroyed Cu smelting installations. Marginal exploitation is reported throughout the 19th and 20th centuries. This area yielded more than 20 000 tons of metallic copper (it is the richest district in France) and approximately 400 tons of silver.

The district of St. Martin d'Arrossa lies directly on Palaeozoic formations. It mainly consists of pile and vein stockwork of siderite, which can be locally associated with Cu. Also, mined by Romans, it was sporadically worked for iron from the 18th century, and more substantially from the late 19th century to the World War I.

The Quinto Real peat deposit (cf. Fig. 1) is located close to the Spanish border (910 m a.s.l.), almost at the interfluve of the Baztan and Aldudes valleys. It lies on a surface of approximately 1 ha on Palaeozoic terrain. *Sphagnum*-dominated at the

top, it is fed by some temporary streams originating from a small catchment area (Galop et al., 2001). The site is far from any current settlements.

3. Material and methods

3.1. Sampling

Sampling was carried out using a Russian GIK-type corer (8 cm in diameter) following the conventional two-borehole technique. The samples were wrapped in clean plastic bags in order to prevent external contamination. Sub-sampling for geochemical analysis was performed by cutting 2-cm thick sections at intervals of 4 cm, after removing with a PTFE spatula the outer parts, which could have been in contact with the corer, the tube or the plastic film. A few coarse roots, mostly present at the top, were removed using clean plastic pliers. Samples were transferred to LDPE beakers and slowly dried at 60 °C for 3 days. They were finely powdered in an automatic agate mortar pre-cleaned with diluted HCl and MilliQ water, then stored in the dark before further analyses. Sub-sampling for pollen analysis was carried out at 4 cm intervals in the first metre, and at 8 cm intervals to the bottom. These latter were kept wet until pollen preparation as described below.

3.2. Chemical composition

Lost on ignition (LOI) was performed by heating approximately 1 g of peat samples to 90 °C, and then by combustion at 450 °C for 4 h. Total organic carbon (TOC) was also measured twice on half of the samples by Nitrogen Carbon Analyser (NA 1500 W-2—Carlo Erba) at a precision of 5%. LOI and TOC were closely correlated (LOI = $1.81 \times$ TOC, $r^2 > 0.99$, $P < 0.01$). Refractory elements such as Sc, Th, Cr, Rb and La and REE were measured by instrument neutron activation analysis (INAA) at Actlabs (Ontario, Canada). Accuracy was checked within ± 10–15% on the basis of standards routinely measured and NIST 1547, PACS-1, BCSS-1 added to the set.

For complementary determinations, approximately 500 mg of powdered samples were oxidized

Fig. 1. Map of the Basque country. The ore guides and their nature have been reported.

with 4 ml of Suprapur H_2O_2 (Merck–Germany), reacting on hot plate at 40 °C overnight. Once dried, samples were digested with a mixture of Suprapur and concentrated HCl, HNO_3 and HF (Merck, Germany) in closed PTX vessels under Milestone-ETHOS microwave assistance (Monna et al., 2000a). One blank and one reference material standard (RMS), among NIST 1547, JSD 1 and JSD 2, were added to each set.

A one-third aliquot of solution was measured at the F.-A. Forel Institute by HP 4500 inductively coupled plasma–mass spectrometer (ICP-MS) for

Cu, Zn, Cd and Pb concentration determination using both external and internal (Re, Rh) calibrations. The whole procedure was performed in a clean room (US class 1000–10 000). Blanks were found negligible for all elements compared to the amount contained in the samples. Pb, Cd and Cu concentrations were in good agreement with the certified values of RMSs (within ± 10% for lead and copper, and at worst approximately ± 15–20% for Cd and Zn). Lead from the two-thirds aliquot was pre-concentrated on ionic resin AG1X4 (Biorad) and measured for isotopic abundance by HP 4500 ICP-MS (Monna et al., 1998, 2000b). Precisions of $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ ratios were approximately 0.27% and 0.31%, respectively. Seven samples were duplicated with the Perkin Elmer 6100 ICP-MS at the University of Neuchâtel. In all cases, the 95% confidence intervals overlapped. Pristine fragments of artefacts were obtained by scratching with a stainless steel tool. They were washed with a mixture of diluted Suprapur HCl and HNO_3 to remove any remains of corrosion or pollution. The fragments were dissolved and lead isotopes were measured following the procedure described above.

3.3. Radiocarbon dating

Three peat samples were dated using ^{14}C-beta counting at the Centre des Sciences de la Terre-University of Lyon (Table 1, Fig. 2), and two others by AMS at Beta Analytic Inc laboratory, Miami. All ^{14}C-dates were calibrated using Calib 4.1.3 software (Stuiver et al., 1998).

3.4. Pollen determination

Briefly, pollen preparation consists in treatments with 10% HCl, 10% KOH, HF, acetolysis and
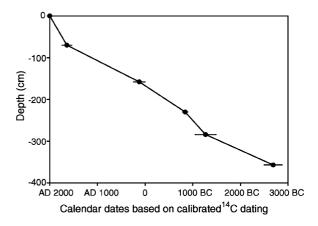

Fig. 2. Depth plotted against calibrated radiocarbon calendar dates at Quinto Real, Basque country, France.

final mounting in glycerine. More than 500 terrestrial pollen grains, defined according to Reille (1992) and Moore et al. (1986) were counted in each sample. *Cyperaceae* and spores were systematically excluded from the pollen sum, as was *Alnus*; its over-representation may mask the dynamics of other taxa (Wiltshire and Edwards, 1993). Pollen spectra have been given elsewhere (Galop et al., 2001). They will be used here only for discussion.

4. Results

4.1. Organic matter and lithophilic elements

The LOI profile (Table 2, Fig. 3) exhibits wide variations, from 7% in the layer richest in sand (321-cm depth) to 85% at the top. The first 300 cm are the most organic (avg: 60%); although two sections, at 63–86 and 134–157-cm depth, are more mineral. The uppermost 300 cm can be

Table 1

Age-depth relationship for the Quinto Real core. The data are calibrated to calendar dates AD or BC

Laboratory no.	Depth (cm)	Uncalibrated date	Calibrated date, and uncertainties (2σ)
Beta-156998	69–71	290 ± 40	1486 (1640) 1664 cal AD
Ly-10587	157–159	1895 ± 50	3 (88, 100, 125) 240 cal AD
Ly-10588	229–231.5	2645 ± 45	896 (804) 787 cal BC
Ly-10589	283–285	3045 ± 70	1485 (1368, 1362, 1315) 1051 cal BC
Beta-156997	357	4120 ± 40	2876 (2662, 2646, 2625) 2501 cal BC

Table 2
Lost on ignition (LOI), Cu, Zn, Cd, Pb, Sc contents and $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ ratios. The errors for isotopic ratios are given at 95% confidence level. See Section 3 paragraph for errors in concentration measurements

Name	Depth (cm)	LOI%	Cu $\mu g\ g^{-1}$	Zn $\mu g\ g^{-1}$	Cd $\mu g\ g^{-1}$	Pb $\mu g\ g^{-1}$	Sc $\mu g\ g^{-1}$	$^{206}Pb/$ ^{207}Pb	±	$^{208}Pb/$ ^{206}Pb	±
R 007	−7	nd	3.9	47.5	0.34	75.1	nd	1.159	0.003	2.103	0.006
R 012	−12	nd	17.9	133.3	1.35	267.6	nd	1.160	0.003	2.100	0.006
R 016	−16	nd	5.5	102.7	1.19	765.0	0.5	1.165	0.004	2.105	0.006
R 020	−20	nd	4.4	39.8	1.03	109.2	0.8	1.163	0.009	2.105	0.006
R 028	−28	85.2	10.4	30.0	1.02	140.7	2.3	1.172	0.004	2.095	0.006
R 036	−36	59.7	10.5	16.3	0.34	19.2	6.5	1.179	0.003	2.086	0.008
R 045	−45	54.1	13.4	19.8	0.32	5.4	6.5	1.183	0.002	2.102	0.005
R 055	−55	50.9	15.3	16.7	0.20	7.9	9.7	1.194	0.003	2.088	0.006
R 063	−63	42.9	7.9	7.9	0.31	8.8	10.7	1.197	0.002	2.105	0.006
R 071	−71	37.8	8.9	14.6	0.23	14.1	13.1	1.191	0.008	2.107	0.007
R 078	−78	nd	8.1	12.6	nd	10.3	12.1	nd	nd	nd	nd
R 086	−86	41.6	12.7	16.0	0.21	19.2	13.0	1.190	0.003	2.099	0.005
R 095	−95	55.6	11.2	21.6	0.23	9.2	9.1	1.190	0.003	2.105	0.005
R 101	−101	57.0	14.3	16.2	0.11	13.8	8.9	1.183	0.001	2.101	0.008
R 113	−113	62.6	12.7	10.2	0.19	10.2	7.4	1.188	0.004	2.091	0.007
R 117	−117	59.5	13.6	16.0	nd	13.3	7.7	nd	nd	nd	nd
R 124	−124	58.1	10.8	9.6	0.20	11.5	8.1	1.190	0.002	2.100	0.005
R 134	−134	45.2	8.8	9.8	0.31	nd	10.3	1.196	0.003	2.098	0.008
R 136	−136	40.4	11.8	11.2	0.15	29.0	12.2	1.180	0.003	2.109	0.006
R 140	−140	30.7	6.9	10.0	0.29	25.0	14.2	nd	nd	nd	nd
R 148	−148	43.6	10.4	9.6	0.25	32.5	12.2	1.186	0.002	2.092	0.004
R 157	−157	45.1	12.6	11.7	0.38	nd	12.0	1.183	0.003	2.099	0.006
R 161	−161	50.6	15.8	12.9	0.37	32.5	11.2	1.183	0.003	2.101	0.008
R 169	−169	76.3	10.2	11.9	0.41	13.2	5.9	nd	nd	nd	nd
R 177	−177	51.9	12.5	16.1	0.20	15.4	11.1	1.187	0.002	2.097	0.003
R 185	−185	63.4	6.5	12.8	0.29	5.0	7.5	1.190	0.004	2.093	0.008
R 192	−192	64.0	6.9	10.2	0.25	7.1	7.2	1.200	0.005	2.090	0.012
R 201	−201	57.9	9.7	11.5	0.29	5.6	9.4	nd	nd	nd	nd
R 209	−209	73.6	11.5	14.4	0.23	9.4	5.7	1.178	0.002	2.094	0.004
R 217	−217	66.9	7.1	12.0	0.23	10.6	6.7	1.177	0.005	2.099	0.011
R 221	−221	71.6	6.5	10.2	0.19	10.6	5.0	1.176	0.002	2.095	0.004
R 224	−224	68.4	7.4	12.9	nd	10.4	6.3	nd	nd	nd	nd
R 233	−233	75.6	6.6	20.6	0.21	10.6	4.6	1.177	0.003	2.095	0.008
R 241	−241	74.5	5.9	39.4	0.30	12.8	6.3	1.172	0.004	2.099	0.008
R 247	−247	59.3	7.4	29.6	nd	15.1	7.9	nd	nd	nd	nd
R 252	−252	60.2	6.3	21.5	0.21	6.2	7.2	1.207	0.003	2.087	0.007
R 261	−261	61.9	7.9	12.5	0.24	9.7	8.9	1.190	0.002	2.100	0.010
R 269	−269	52.5	7.1	9.1	0.20	7.3	9.0	1.208	0.002	2.091	0.004
R 273	−273	51.9	6.9	10.1	0.27	6.1	11.0	nd	nd	nd	nd
R 281	−281	57.1	9.6	10.7	0.19	9.6	8.3	1.188	0.004	2.101	0.008
R 285	−285	62.5	11.2	17.9	0.25	7.0	10.4	1.191	0.002	2.094	0.004
R 294	−294	40.2	21.0	21.9	0.14	14.0	12.1	1.187	0.003	2.110	0.008
R 300	−300	24.2	12.7	29.8	0.52	2.9	18.1	1.227	0.003	2.073	0.006
R 305	−305	17.0	10.8	53.3	0.12	6.7	11.7	1.215	0.004	2.083	0.006
R 313	−313	7.6	6.3	24.6	0.34	1.3	10.4	nd	nd	nd	nd
R 321	−321	7.0	6.2	34.9	0.18	6.2	9.1	1.219	0.002	2.085	0.005
R 323	−323	6.9	5.9	45.5	0.35	5.9	12.6	1.233	0.005	2.062	0.010
R 333	−333	16.9	10.7	45.1	0.28	9.9	13.4	1.218	0.004	2.087	0.009
R 341	−341	20.2	nd	nd	nd	16.3	18.9	1.199	0.003	2.106	0.009
R 345	−345	21.6	10.9	47.1	0.11	7.4	14.7	1.206	0.002	2.100	0.005
R 350	−350	21.5	10.4	40.2	nd	9.2	16.4	nd	nd	nd	nd
R 359	−359	42.6	9.1	25.2	0.24	9.2	8.8	1.200	0.003	2.094	0.005

Table 2 *(Continued)*

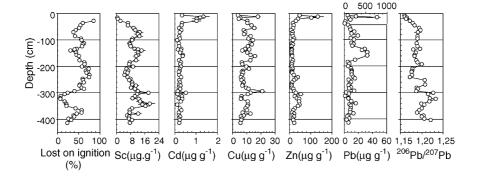| Name	Depth (cm)	LOI%	Cu μg g⁻¹	Zn μg g⁻¹	Cd μg g⁻¹	Pb μg g⁻¹	Sc μg g⁻¹	$^{206}Pb/^{207}Pb$	±	$^{208}Pb/^{206}Pb$	±
R 366	−366	57.2	10.1	17.6	0.31	8.5	7.5	1.194	0.004	2.092	0.008
R 375	−375	57.0	7.1	12.7	0.19	8.6	7.5	1.189	0.003	2.099	0.005
R 379	−379	45.6	12.6	21.8	nd	13.0	12.3	nd	nd	nd	nd
R 386	−386	37.8	7.9	14.6	0.19	5.7	6.0	1.204	0.003	2.079	0.007
R 390	−390	39.7	5.9	21.5	0.25	4.3	7.2	1.200	0.003	2.092	0.004
R 398	−398	25.8	6.7	14.5	0.19	7.1	7.1	1.206	0.004	2.083	0.008
R 403	−403	32.4	6.1	17.8	0.23	3.3	8.8	1.221	0.004	2.069	0.007
R 414	−414	23.4	5.6	22.5	0.21	6.0	7.6	nd	nd	nd	nd

nd: Not determined.

Fig. 3. Lost on ignition, scandium, cadmium, copper, zinc, lead and $^{206}Pb/^{207}Pb$ ratios plotted against depth. Note the break in the lead concentration axis. Most of errors represent less than the size of dots; otherwise the error bars represent a confidence level of 95%.

classified as peat and muck interbedded (Kivinen, 1980; Moris, 1989) or as low-ash carbonaceous sediments with interbedded high ash carbonaceous sediments and peat layers (Andrejko et al., 1983), but this latter classification rather matches the use of peat as fuel for industry (Wüst et al., 2003).

Considering the whole core, Sc content is inversely correlated to LOI ($r^2 = 0.46$, $P < 0.01$), but the correlation is improved if only the uppermost 300 cm are taken into account ($r^2 = 0.89$, $P < 0.01$) (Fig. 4). The same observation is made with other lithophilic elements (La, Th, Cr, Rb and REE not presented here), which are all strongly correlated with Sc ($r^2 > 0.85$, $P < 0.01$ for Rb and $r^2 > 0.96$ for the others).

4.2. Heavy metals

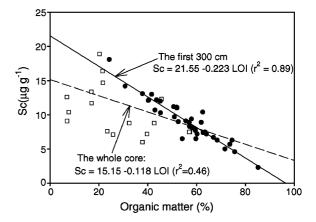Cd, Zn and Pb concentrations increase in the topmost 40 cm and peak in approximately the

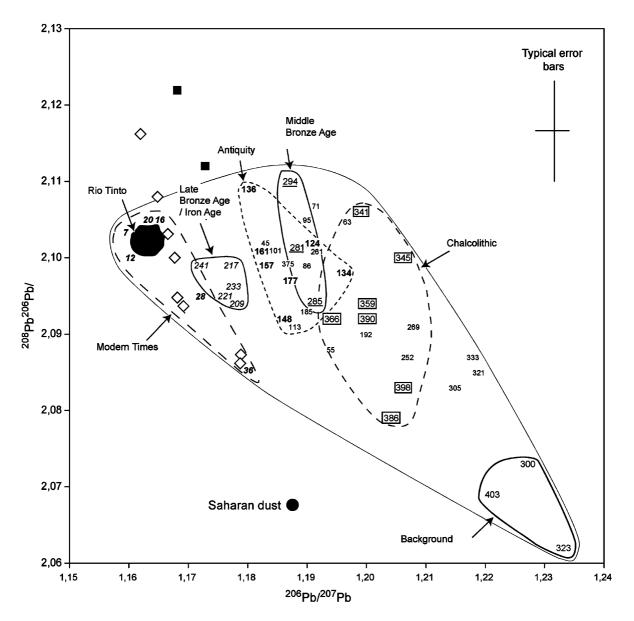Fig. 4. Scandium content plotted against organic matter content; (●): the 300 cm topmost samples, (□): the others.

Fig. 5. $^{208}Pb/^{206}Pb$ vs. $^{206}Pb/^{207}Pb$ diagram. The peat samples are represented by their depth. Five clusters have been defined among the horizons featuring high Pb/Sc and low $^{206}Pb/^{207}Pb$ ratios on the basis of the cultural periods in which they appear (see text for more details). The isotopic compositions of artefacts dating from the Late Bonze Age ($\diamond$) and antiquity ($\blacksquare$) (this study), and those of Saharan dusts ($\bullet$) (Grousset et al., 1995) and Rio Tinto (Stos-Gale et al., 1995) are also plotted for further comparison.

same horizon at 1.35 μg g^{-1}, 133 μg g^{-1} and 765 μg g^{-1}, respectively, then decrease to the surface (Fig. 3). Below, the Cd profile is rather flat, whereas Zn exhibits smooth variations with

two peaks at 241 and 305–350-cm depth. Pb rises more or less from the bottom to approximately 150-cm depth, except for a fall in the detrital horizon (310-cm depth), before decreasing to 5

$\mu g\ g^{-1}$ at 45-cm depth. No clear tendencies are detected in the Cu profile. Its maximum value (21 $\mu g\ g^{-1}$) does not occur in the top horizons, but at 294-cm depth. Cd, Cu and Pb do not present any relationship with LOI as indicated by insignificant Spearman's coefficient values, whereas Zn shows a weak inverse correlation ($r_{sp} = -0.347$, $P < 0.01$).

4.3. Lead isotopic compositions

$^{206}Pb/^{207}Pb$ ratios vary widely from 1.233, in the most detrital layers (300–320-cm depth), to 1.159 at the top (Fig. 3). This evolution is not regular but presents five major shifts toward low $^{206}Pb/^{207}Pb$ ratios: (i) at approximately 375-cm depth; (ii) between 280 and 290-cm depth; (iii) between 209 and 241-cm depth; (iv) at 160-cm depth; and finally (v) an almost linear decline, from 63 cm to the top. Reported on a $^{208}Pb/^{206}Pb$ vs. $^{206}Pb/^{207}Pb$ diagram (Fig. 5), peat samples form a triangle rather than falling on a characteristic binary mixing line. The samples from the most detrital horizons (300, 403, 323-cm depth) define the first summit of the triangle featured by highest $^{206}Pb/^{207}Pb$ and lowest $^{208}Pb/^{206}Pb$ ratios. The second summit corresponds to samples having high $^{208}Pb/^{206}Pb$ ratios (approx. 2.105) with intermediate $^{206}Pb/^{207}Pb$ values (approx. 1.19–1.20). The last one matches the uppermost samples (7–20-cm depth) with the lowest $^{206}Pb/^{207}Pb$ ratios (<1.17) and $^{208}Pb/^{206}Pb$ ratios of approximately 2.100–2.105. Artefacts produced during the Late Bronze Age and Antiquity are also reported on the diagram for further comparison.

5. Discussion

5.1. Origin of mineral material and assessment of anthropogenic contribution

Previous studies have shown that mineral matter may affect the distribution of metals in a peat core (Shotyk, 1996a,b; Weiss et al., 1997). The extent of anthropogenic contribution by comparison to natural contribution can, however, be estimated by normalising total metal concentrations to a conservative element, which has no anthropogenic origin. Lithophilic elements such as Sc, but also Zr, Ti, Al (Martínez-Cortizas et al., 1997, 2002; Schettler and Romer, 1998; Kempter and Frenzel, 2000; Shotyk et al., 2001, 2002a,b; Shotyk, 2002; Weiss et al., 2002) or ash content (West et al., 1997; Alfonso et al., 2001) are generally used for normalisation. This procedure implicitly assumes that natural Metal/Sc ratios of natural inorganic material are constant over time. However, atmospheric inorganic matter derives from sources, which may vary according to climate and human land occupation, thus affecting the consistency of natural Metal/Sc ratios (Shotyk et al., 2002a). As a matter of fact, large variations in ratios of lithophilic elements, such as La/Sc, were reported in an ombrotrophic peat bog in the Jura Mountains, and were interpreted as being the result of changes in the nature of atmospheric mineral inputs (Shotyk et al., 2001).

In the mineral-dominated Quinto Real core, the La/Sc and Th/Sc ratios exhibit only small variations around upper continental crust (UCC) values (La/Sc = 4.61 and Th/Sc = 1.47, Wedepohl, 1995) (Fig. 6). Moreover, when normalized to the shales, REEs display typical flat patterns (not shown here), reflecting a constant crust-derived origin. Thus, local inputs have presumably always predominated, suggesting constant REE patterns and Metal/Sc ratios over time. The values of these latter could be defined as reference before any enrichment factor or anthropogenic flux calculations. They will preferably be drawn from a given location rather than from earth crust compositions, because a global average cannot account for the local variations in rock chemistry (Weiss et al., 1997). In addition, chemical fractionation of the elements by physical fractionation during dust transport has been suggested, so that using crustal proportions as reference value for normalization may be meaningless (Martínez-Cortizas et al. 2002). At Quinto Real, samples do not exhibit constant Metal/Sc values at the bottom of the core (Fig. 7). Had they been present, suggesting uncontaminated horizons, they could have been used as reference values. In Fig. 4, the deficit in scandium below 300 cm by comparison to the organic matter
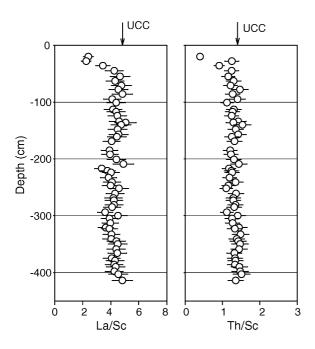
Fig. 6. Evolution of La/Sc and Th/Sc ratios with depth in the Quinto Real core. The values of the upper continental crust (UCC) (Wedepohl, 1995) are also given. The error bars represent a confidence level of 95%.

content would rather indicate the presence of an authigeneous mineral phase, possibly resulting from water circulation as minerotrophic peatlands

are not hydrologically isolated from the substratum (Shotyk, 1996a,b). For these reasons, consistent values for natural Metal/Sc ratios are difficult to determine and enrichment factor or anthropogenic fluxes cannot be properly calculated. Since quantitative information is not available, our aim is now to determine if the Metal/Sc ratio profiles can at least be interpreted qualitatively. Even if our suggestion that Metal/Sc ratios of natural inorganic material are constant over time were to prove unfounded, it is still logical to suppose that any variations would not significantly affect overall Metal/Sc ratios observed in polluted peat samples.

5.2. Evaluation of metal record integrity

In a $^{208}Pb/^{206}Pb$ vs $^{206}Pb/^{207}Pb$ diagram, the natural (or background) end-member corresponds to samples possessing highest $^{206}Pb/^{207}Pb$ (1.22–1.23) and lowest $^{208}Pb/^{206}Pb$ ratios (2.06–2.07) (Fig. 5). Such values are comparable to those previously published for atmospheric inputs of crust-derived lead in Western Europe ($^{206}Pb/^{207}Pb$: 1.195–1.275) (Shotyk et al., 1998; Dunlap et al., 1999; Camarero et al. 1998; Alfonso et al., 2001; Martínez-Cortizas et al., 2002). The other horizons have been affected by one (or several) less radiogenic components. Five clusters can be defined
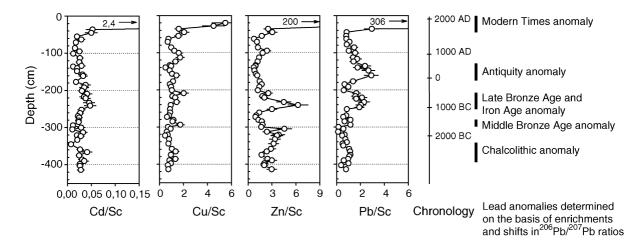

Fig. 7. Cd/Sc, Cu/Sc, Zn/Sc and Pb/Sc ratios vs. depth in the Quinto Real core. The error bars represent a confidence level of 95%.

among the horizons featuring high Pb/Sc and low ^{206}Pb/^{207}Pb ratios on the basis of the cultural periods in which they appear (cf. Figs. 7 and 8): Chalcolithic (samples at 341, 345, 359, 366, 386, 390, 398-cm depth), Middle Bronze Age (281, 285, 294 cm depth), Late Bronze Age–Iron Age (209, 217, 221, 233, 241-cm depth), Antiquity (124, 134, 136, 148, 157, 161, 177-cm depth) and Modern Times (7, 12, 16, 20, 28, 36-cm depth) (Fig. 5). It is clear that the lead enrichments observed in Chalcolithic horizons cannot be explained by a simple mineral dissolution of the substratum because their isotopic compositions are significantly different from those of the background. Similarly, Saharan dust inputs, very frequent in the Basque country, cannot be invoked given that the isotopic signature of this source (Grousset et al., 1995) does not fit with the data (Fig. 5). The presence of a sandy horizon at approximately 310 cm depth may have strongly facilitated the downward post-depositional translocation of lead from the Middle Bronze Age horizons. The intermediate position of the Chalcolithic group between the Middle Bronze Age horizons and the background well supports this thesis. Another possible scenario would be the real occurrence of anthropogenic inputs starting as early as the Chalcolithic. The interruption in the Pb/Sc trend observed approximately 310-cm depth in Fig. 7 would, therefore be due to the dilution of anthropogenic inputs by strong deposition of detrital inorganic matter. The study of a nearby core presenting no such variation in organic matter content could help resolve this question.

It is noteworthy that the above-mentioned clusters and the background as a whole form a triangle rather than a line (Fig. 5). The sequence in which the clusters appear, from low to high ^{206}Pb/^{207}Pb signatures (Modern Times, Late Bronze Age, Antiquity, Middle Bronze Age), does not correspond to any chronological order, so that it is impossible to explain their position as the result of a major migration of lead. It implies rather the result of a change in the type of mineral exploitation during these periods. Other works have already reported a very limited downward migration for Pb (Dumontet et al., 1990; Farmer et al., 1997; Vile et al., 1999), in part because almost all

of the cationic species of this metal are bound to organic phase, which considerably reduces its mobility in peat (Shotyk, 1996b; Vile et al., 1999). Even in a mineral-dominated marsh in Aquitaine (with ash content up to 94%), the lead isotopic record yielded similar results to those obtained in ombrotrophic peat bogs and ice cores (Alfonso et al., 2001), and were quite consistent with the well-accepted assessment of world lead production during the last 5000 years (Settle and Patterson, 1980). Similarly, the comparison of both ombrotrophic and minerotrophic peat deposits in the Jura Mountains also demonstrated the relative immobility of lead and the possibility of using its record in minerogenic peatlands as a surrogate of past anthropogenic inputs in certain circumstances, such as the predominance of anthropogenic inputs over both detrital contribution and mineral dissolution of the substratum (Shotyk 1996a,b; Weiss et al., 1999; Shotyk, 2002). Although our core presents high ash content, the lead record at the considered time resolution appears to be well preserved, at least within the uppermost 300 cm. However, the duration of identified pollution phases may have been overestimated because of the release of lead from polluted soils over a long period of time after major atmospheric inputs.

For other metals the situation is more complex and different behaviours have been suggested depending on organic matter content, pH and fluctuations in redox potential (Shotyk, 1996b). Although copper ore deposits have been extensively mined in the valley since at least Roman Times, no clear trend in Cu/Sc ratios can be observed along the profile, except at the surface (Fig. 7). The present core does not seem suitable for the reconstruction of past atmospheric Cu inputs, unlike others previously reported (Kempter and Frenzel, 2000; Mighall et al., 2002). Like copper, Zn is an essential constituent for plants, and bioaccumulation processes may influence its distribution pattern, so that it is generally considered as a mobile metal, or at least as more susceptible to post-depositional redistribution than lead (Martínez-Cortizas et al., 1997). Here the Zn/Sc ratio profile also exhibits positive shifts in the Late Bronze Age/Iron Age and Modern Times but none is observed during Antiquity. Cadmium is not
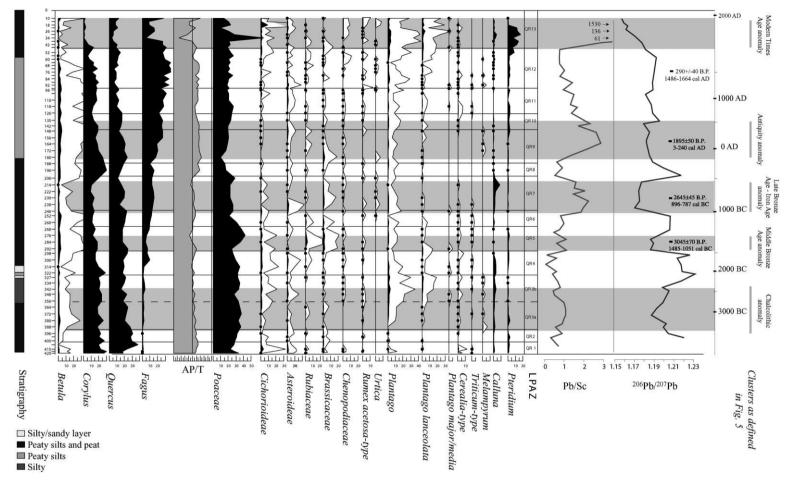
Fig. 8. Pollen record of the Quinto Real core (from Galop et al., 2001). Pb/Sc and ^{206}Pb/^{207}Pb ratios are reported to make easier historical reconstruction. The relative pollen diagram is divided into Local Pollen Assemblage Zones (LPAZ) based on relative change in land-use pollen indicators according to Behre (1981) and on relative change between trees and open-land indicators.

influenced as much as zinc and copper by plant uptake, which makes it closer to lead. Positive anomalies occur during the Late Bronze Age/Iron Age and Modern Times, as with Zn and Pb, but none is observed during Antiquity and the Middle Ages. In any case, it is hazardous to use the Zn, Cu and Cd profiles for historical purposes because these elements do not possess isotopic features comparable to lead, which would allow their degree of migration to be assessed.

5.3. Towards a historical interpretation

5.3.1. Prehistoric record

In QR 1 (cf. Fig. 8), or in other words prior to ca 3000 BC, the presence of *Cerealia*-type, *Triticum*-type and *Plantago lanceolata* in the pollen record shows significant cereal cultivation and human settlements. Later, the decline of oak (*Quercus*) combined with the extension of birch (*Betula*), a heliophilic tree, suggest a progressive deforestation which could be at the origin of the detrital layer recorded at 310-cm depth, around cal. 2000 BC.

The $^{206}Pb/^{207}Pb$ and Pb/Sc ratios of the Middle Bronze Age (QR5) and Late Bronze Age/Iron Age (QR 7) samples, respectively, cal. 1500–1300 BC and cal. 1000–600 BC, indicate significant anthropogenic inputs. Simultaneously, oak and hazel (*Corylus*) diminish while traces of agropastoral and slash-and-burn activities (*Plantago lanceolata*, *Plantago major/media*, *Melampyrum*, *Rumex*) decrease or are simply absent. Between these two phases (QR6, cal. 1300–1000 BC), Pb/Sc and $^{206}Pb/^{207}Pb$ ratios are more crustal, and signs of reforestation are observed. Both geochemical and pollen records are in good agreement with the sparse archaeological knowledge available. In the Middle Bronze Age, and more precisely during the 15th and 14th centuries BC, metallurgical activity increased in the Southern French Atlantic region, with high production of bronze alloys (Coffyn et al., 1995). Regional smelting and/or mining probably decreased from 1100 BC (Cantet, 1991), to start again in the Final Bronze Age, as proved by the abundant production of ornamental artefacts. The wealth of copper in the polymetallic district of Banca may, therefore have attracted early miners, although direct field evidence of Bronze Age exploitation is still lacking in the valley, apart from the discovery of a prehistoric mallet used to crush minerals (Dupré et al., 1993). Prehistoric exploitations are likely to have suffered from considerable alteration due to a humid climate on steep slopes, or more certainly to have been destroyed by later occupation. At that time lead was not exploited for itself but was emitted into the atmosphere in significant amounts subsequent to mineral extraction and smelting of other metals, so it could be a good marker for local or regional prehistoric metallurgy. Such contaminations dating as far back as the Bronze Age have been recorded in natural archives in the Jura Mountains (Weiss et al., 1997), the North-Western Iberian Peninsula (Martínez-Cortizas et al., 1997, 2002), the overbank sediments of the River Weser (Monna et al., 2000a), and in the French Morvan massif (Blanchot et al., 2001). The isotopic signatures of Late Bronze Age/Iron Age peat samples fall into line with those of contemporary bronze and copper artefacts (rings, a bracelet, pins, a sword, and other bronze fragments) recently found in the Basque country (Fig. 5), even though they may have been produced using metals locally extracted or acquired by trading. Significant changes in metalworking practices are also suggested by the change of isotopic signatures between Middle and Late Bronze Age (Fig. 5), but the strongest clue to local metalworking occurrence is given by the concomitance of anthropogenic lead enrichments and deforestations. As the latter are not consecutive to agro-pastoral extensions, they are interpreted as the result of mounting energy demands for mining and smelting, like those already reported in several parts of Pyrenees (Galop and Jalut, 1994), in the Swiss Jura Mountains for iron metallurgy (Richard and Eschenlhor, 1998), and more recently in the French Morvan massif (Blanchot et al., 2001; Monna et al., 2004).

5.3.2. Antiquity

Another major anthropogenic phase is pinpointed by Pb/Sc and $^{206}Pb/^{207}Pb$ from ca cal. 200 BC to approximately 200 AD (Fig. 7). At that time, oak and hazel decrease while beech seems to spread. Moderate signs of deforestation appear

again without any indication of significant agricultural extension. Such an intensification of anthropogenic atmospheric inputs in Antiquity has already been reported at the continental scale, in the Pyrenean region (Ariès, 2001) as well as far beyond the Mediterranean area, as demonstrated by the studies performed in Greenland (Hong et al., 1994; Rosman et al., 1997), Sweden (Brännvall et al., 1999; Renberg et al., 2000, 2001), Northern Spain (Martínez-Cortizas et al., 2002) and the Jura Mountains (Shotyk et al., 1998). In fact, these signals are so ubiquitous in Southern and Western Europe that certain authors have suggested their use as a chronological marker in sediment deposits (Alfonso et al., 2001; Renberg et al., 2001). They are often interpreted as the result of long-range transport of contaminants originating from Spain, especially when local mining is lacking and lead isotopic compositions are compatible with those of Rio Tinto, Southern Spain, one of the major mining sites (Stos-Gale et al., 1995); *Hispania* accounting for almost 40% of the worldwide Pb production during the Roman Empire (Nriagu, 1983).

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 Baïgorri Valley well known in Antiquity (Machot, 1995). Apart from Roman industrial activity, numerous other small workshops were found throughout the valley of Urepel (Beyrie et al., in press). Because of the abundance of this indigenous exploitation and the incompatibility of lead isotopic signatures in peat samples with those of the Rio Tinto district (cf. Fig. 5), major influence from remote sources is not to be considered here. Any long-range input was undoubtedly masked by dominating anthropogenic local inputs. This is in good agreement with another recent study undertaken in the Lake Redó, Central Pyrenees–Spain, which clearly identified a phase of pollution, attributed to local mining operations, starting approximately 670 BC and reaching a maximum at approximately 660 AD; in other words peaking after Roman times, a period in which lead production was at a minimum in Europe (Camarero et al., 1998). Long-range transport of lead from the Rio Tinto region should appear on the

flank of this peak but was not noticeable, probably because this source was also masked by dominant local emissions. The isotopic compositions of metallic tool fragments found in the Roman gallery of the Banca mine support this hypothesis since such signatures might correspond to the anthropogenic end-member which shifted isotopic ratios of peat samples towards less radiogenic signatures (cf. Fig. 5). The decline of oak can be explained by deforestation for metallurgical operations. Moreover, anthraco-analysis has established that charcoal production within the valley mainly focussed on this species (Galop et al., in press).

Human-derived lead deposition lasted for at least 400 years and did not collapse as brutally as elsewhere at the fall of the Roman Empire, possibly because the Romanisation of the Basque country had never been intense. Another explanation could also be a delay due to weathering of polluted soils by small streams, which temporarily feed the Quinto Real peatland area.

5.3.3. Medieval to modern time

After a long decline throughout the Middle Ages, Pb/Sc ratios increase markedly from the late 16th and early 17th century AD, coinciding with the decrease in $^{206}Pb/^{207}Pb$ ratios (Fig. 8). This period is abundantly mentioned in textual archives as an intense phase of metallurgical activity in the Basque country, and more particularly in the Baïgorry valley. The copper foundry of Banca started operating in 1747. Most Basque forests were dedicated to charcoal production, as demonstrated by abundant charcoal-kiln remains in present forest areas of the Aldudes valley. Yet metalworking almost totally collapsed in the middle of the 19th century. Forest taxa slump when metalworking peaked, demonstrating intense wood charcoal consumption for energy production. Recent pollution has been recorded too, but its chronology is difficult to reconstruct accurately because ^{14}C-based chronology is not detailed enough in topmost horizons. However, isotopic signatures at the surface of the core ($^{206}Pb/^{207}Pb =$ 1.159) probably illustrate the impact of allochtoneous less radiogenic anti-knock compounds added until recently to leaded gasoline.

6. Conclusion

Although the origin of the earliest geochemical anomaly, recorded in Chalcolithic levels, remains unknown, two later anomalies, identifiable in Bronze Age levels, are almost certainly related to mining and smelting. The first episode, dating from the Middle Bronze Age, would probably not have been detected by the sole measurement of concentrations. Lead isotopes, however, are very sensitive to such low contaminations (Munksgaards and Parry, 1998), so that their use offers new possibilities for the recognition of precursor mining operations. The second episode occurred during the Late Bronze Age/Iron Age, at a time when metalworking was growing in magnitude throughout Western Europe. Both of these phases are accompanied by local signs of deforestation, not strictly related to agro-pastoral extensions. The strong impact of human activity during Antiquity in the nearby surroundings is clearly traced by geochemical and, to a lesser extent, pollen records. Lead emitted locally has dominated over remote sources, such as lead ore deposits intensively exploited by the Romans in Southern Spain. This latter source, often invoked as a major contributor to lead anomalies observed in European natural archives, has perhaps sometimes been overestimated because the presence of minor, but local, exploitations may have acted as point-sources. In Modern Times, human activity in the valley, in part related to mining and smelting, strongly impacted the nearby environment, as demonstrated by the drastic modification of plant cover and considerable metal pollution, with lead reaching concentrations up to 765 μg g^{-1}.

Combining geochemistry, palynology, and archaeological knowledge allows interpretations to be extended. If the trustworthiness of the metal record can be verified, high ash minerogenic peatlands may be successfully used to document ancient mining exploitation and metallurgy, even though the information they provide is more qualitative than quantitative. The duration of pollution phases might be overestimated because of the release of lead from polluted soils over a long period of time after mining and/or smelting operations ceased. However, in addition to the evidence furnished by lead isotopic signatures, the good agreement, in our case, between interpretations from field data and archaeological knowledge (acquired independently) confirms the reliability of the lead signal, at least over the last four millennia.

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