

# Medieval lead making on Mont-Lozère Massif (Cévennes-France): Tracing ore sources using Pb isotopes

Sandrine Baron <sup>a,\*</sup>, Jean Carignan <sup>a</sup>, Sarah Laurent <sup>b</sup>, Alain Ploquin <sup>a</sup>

<sup>a</sup> CNRS–CRPG Centre de Recherches Pétrographiques et Géochimiques, 15 rue Notre Dame des Pauvres, BP 20, 54501, Vandoeuvre lès Nancy, France

<sup>b</sup> Université Louis Lumière Lyon II, 18 quai Claude Bernard, 69007 Lyon, France

Received 23 August 2004; accepted 20 September 2005

Editorial handling by R.S. Harmon

Available online 15 December 2005

## Abstract

This study aims to document the origin of metallurgical activities on the Mont-Lozère Massif (Cévennes Mountains, South of Massif Central, France), which is the largest medieval site of Pb–Ag metallurgical activities in France. These activities are characterised by more than 70 sites comprising numerous dispersed slags. Related charcoal samples dated by <sup>14</sup>C have yielded a medieval, ca. XI–XII th. C. age. Numerous ore deposits, now mostly old mine tailings, surround the granitic massif and are possible candidates for suppliers of the old smelting activities. In Western Europe, Pb–Ag mines were of primordial importance for the medieval monetary system. Mines were intensively coveted by Lords, Bishops and Kings, and their exploitation was strictly regulated by each owner. The scarcity of ancient manuscripts makes it impossible to use a historical approach to determine the ore source regions related to a given metallurgical activity.

The ore sources for this metallurgical activity were traced by comparing the Pb isotopic composition of slags and that of galena deposits surrounding the Mont-Lozère. The range of Pb isotopic compositions measured in slag samples is restricted and included in the field defined by galena from surrounding ores in Pb–Pb isotope diagrams. It is shown that, although direct tracing of the ore supplies is not straightforward, many ancient mine areas must be excluded, whereas some others seem highly likely. These old mines are not necessarily the closest to the smelting sites, suggesting that the choice of metal making location was constrained by several factors, including type of wood (here beech) and water proximity, but more importantly land ownership.

© 2005 Elsevier Ltd. All rights reserved.

## 1. Introduction

The department of Lozère is situated in the South of the Central Massif, southern France. It corresponds to the *Gabales* Antique region, the territory

of a Gallic Tribe which was conquered by Rome in 52 BC and assimilated into the Aquitaine province.

In medieval times, the *Gabales* territory was the diocese of Mende or Gévaudan. In 1161 AD, a charter (a “Bulle d’Or Papale”) was granted by the King of France, Louis VII, to the Bishop of Mende, Aldeberg III. By this action, the King granted all of the “operating rights” (including mining and coinage laws) to the Bishop and he submitted the Gévaudan

\* Corresponding author. Tel.: +33 492353984.  
E-mail address: [sbaron@crpg.cnrs-nancy.fr](mailto:sbaron@crpg.cnrs-nancy.fr) (S. Baron).

diocese to the episcopal jurisdiction. At the same time, the Grèzes Viscount owned part of the same territory. During the Albigeois Crusade (beginning in 1209 AD), the Bishop (taking the advantage of this troubled period) kept the Grèzes Viscount in order to increase his power to face the King. During fifty years, conflicts of interest were continuous between the King, the Viscount and the Bishop. It was not until 1307 AD that an “agreement” (acte de paréage) was concluded and the Gévaudan diocese was divided into three parts: the first for the King, the second for the Bishop and the last for both. This organisation remained until the French Revolution in the XVIII century (Laurent, 2005).

In this historical context, this region was of great interest because of its numerous mineral resources, specifically the Pb–Ag ores which have been mentioned since antiquity (Strabon, book IV, 2.2). Because the medieval monetary system was exclusively based on Ag coins (i.e. deniers), Ag mine exploitation was intensively regulated (Bailly-Maître, 2002). Medieval texts on mining activities, generally lawsuit manuscripts, show the interest of these exploitations for the lords. The “Acte of paréage” (sharing act) specified that the Bishops could enrich themselves, and thus increase their power.

One of the most important paleo-metallurgical sites of Europe for Pb smelting is found at the Mont-Lozère (ML), and testifies to mining activities in this area during medieval times. In order to locate the sectors formerly exploited, historical industrial and survey documents were studied (Laurent, 2005). Unfortunately, the old texts are very scarce and imprecise. Based on fieldwork, many mines were located but a large number of old underground sites are now filled up. It seems that the smelting activities were not in close proximity to the exploited mines. Indeed, many slag sites, interpreted as evidence for metallurgical activities, are found only on the ML. These are located within a limited altitude range, between 1340 and 1430 m (Ploquin et al., 2003).

By combining archaeological/historical knowledge with geochemical data, the aim of this study is to document the historical mining and smelting activities on the ML massif. Because of the complex political situation in Gévaudan at that time, it is historically important to document which mining areas supplied the smelters. Very few studies integrate data from ores, historical mining wastes (mine tailings), metallurgical wastes (slags) and records of activity (Ettler et al., 2004; Niederschlag et al., 2003). Lead isotopes are commonly used for source

tracing in different samples such as: (i) ices cores (Rosman et al., 1994, 1997), (ii) sedimentary cores (Alfonso et al., 2001; Farmer et al., 1996), (iii) peat bogs (Shotyk et al., 1996, 1998; Weiss et al., 1999) and also in archaeological studies (Monna et al., 2000; Nieminem et al., 2002). This study reports the Pb isotopic compositions of slags and of surrounding ore deposits in order to estimate the source areas that supplied the Medieval metallurgical activities at the ML.

## 2. Field context

### 2.1. The Mont-Lozère Pb ores

The ML massif is part of the French Central Massif, which results from the Hercynian orogeny (Bouladon, 1960). The late Hercynian ML granite (about 300 Ma) caused low-grade metamorphism at its contact with the host Paleozoic basement, producing the “schistes cévenols” (Fig. 1). The ore deposits associated with the ML granite are dominated by galena, but include some other minerals such as sphalerite and tetrahedrite. Gangue minerals are barite, quartz and minor fluorite. Deposits occur as veins crosscutting the basement (schists), and the overlying rocks (dolomitic Lias), but also occur as stratiform impregnations in the overlying rocks (dolomitic Lias and Bajocian). The veins are mostly located at the edge of the granitic massif (Fig. 2(a)), both in the contact metamorphic zone and within the overlying rocks. The ore zones follow the horst faults and are rarely found within the granite itself. In these rare cases, the ore fades rapidly into sterile veins.

### 2.2. Metallurgical sites

More than 70 archaeological sites (slag fields) were found on the ML (Fig. 2(b)). These were the locus of smelting activities of Pb–Ag ores, possibly to produce metal for coinage. Two main types of slags, black and white-coated, occur at each site. The black slags are often vitreous and contain inclusions of quartz and feldspar whereas the white-coated ones are crystallised. The matrix of both types of slags contains ~25% to 35% Pb (Ploquin et al., 2003). The slags also contain Pb balls inside their matrix. Some of these balls have been dispersed into the environment, due to the breakage of slag pieces.

The present-day vegetation around these sites reflects the environmental impact of these old metal-

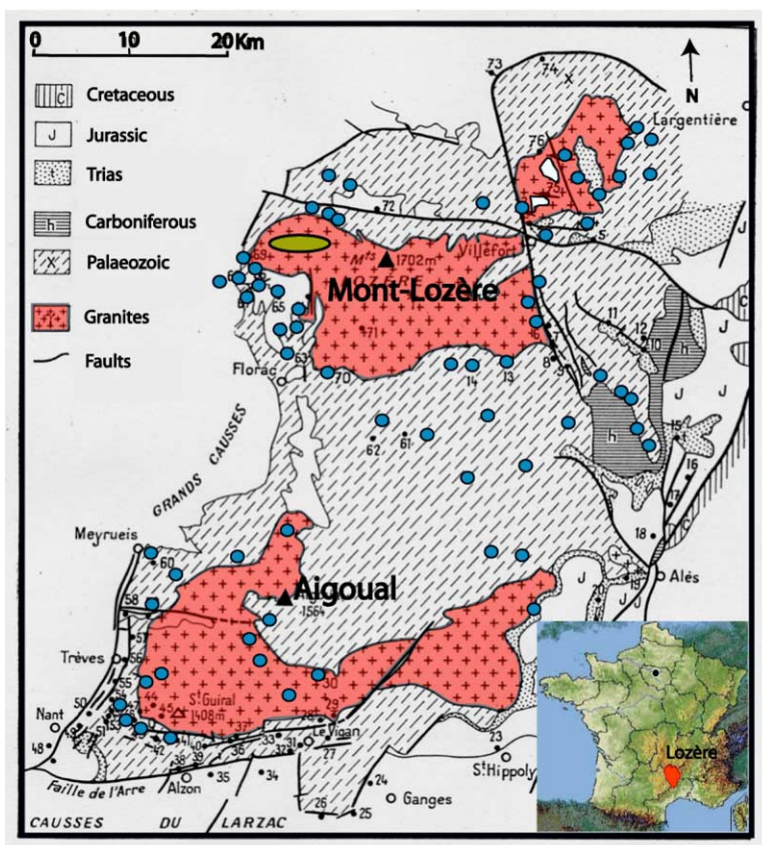


Fig. 1. Geological setting of the ML massif (in the Cévennes mountains) in southern France. ML is in part in the National Park of Cévennes. The Margeride Massif is located north of the ML and the “Cévenole border” is located at the south of the ML (close to Mont-Aigoual). The ancient metallurgical area is located in the northwestern part of the ML granite (oval). Dots report ancient mines. Map modified from Routhier, 1963.

lurgical activities. Indeed, whenever vegetation is present, trees, bushes and grass are often in poor condition and usually smaller than those growing in unpolluted zones.

### 3. Materials and methods

#### 3.1. Sampling

Galenas from different areas all around the ML were sampled, mainly in mine tailings because of the scarcity of mineralised outcrops and the inaccessibility of old mines. Slag sites were sampled during the general survey or during archaeological investigation. Furthermore, in two sites, galena samples were found among the slags (Sites 8 and 22). Thirty five galena samples and 27 slag samples were selected from different sites throughout the investigated area. At some of these sites, charcoal stratigraphically related to slag horizons was sampled

for geochronological purposes. These horizons represent slag remobilized by erosion, into which associated charcoal residues were included. Most of the charcoal samples are beechwood and likely represent combustion fuel for ore smelting (Allée, 2003). Beech trees are almost absent in the area today. Five charcoal samples, covering most of the studied area, were dated by the  $^{14}\text{C}$  method.

#### 3.2. Isotopic analyses

Lead balls were manually extracted from the slag matrix and a ca. 0.1 mm diameter grain was put in a Teflon cup along with 200  $\mu\text{L}$  of concentrated distilled  $\text{HNO}_3$  (15 molar). The closed cup was placed on a heating plate (140  $^\circ\text{C}$ ) overnight. The sample was then evaporated at 80  $^\circ\text{C}$ . This procedure was repeated 3–4 times and was also used for galena samples. The residue was dissolved in dilute  $\text{HNO}_3$  (0.3 molar) to obtain a

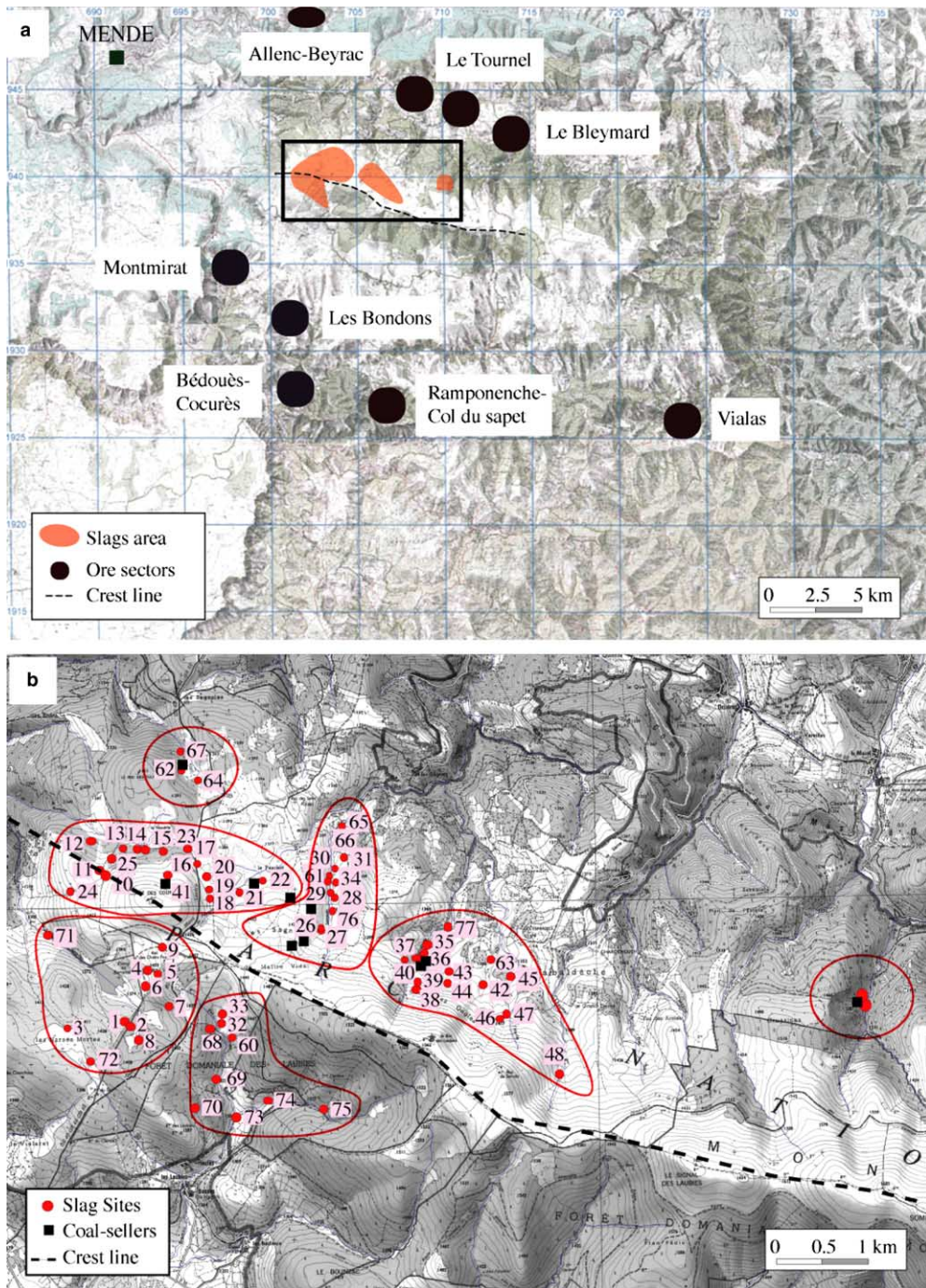


Fig. 2. (a) Focus on the ML Massif (illustrated by its crest line) surrounded by its mineralised sectors. The corresponding names of mines for each sector are reported in Table 3. Most of the sites (inside the rectangle) are located on the north side. (b) Focus on the slag area (a large wooded area has not yet been fully prospected). The corresponding numbers are reported in Table 4.

300  $\mu\text{g/L}$  Pb solution in order to fit the concentration of the Pb reference solution for the isotopic analysis.

The Pb isotopic composition was measured with a MC-ICP-MS (Isoprobe, micromass, now GV Instruments) equipped with nine Faraday cups

Table 1  
Results obtained on NIST NBS 981 Pb from the three analytical sessions

	$^{208}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{206}\text{Pb}/^{204}\text{Pb}$
<b>SRM 981 Pb<sup>a</sup></b>	<b>2.16768 ± 23</b>	<b>0.91483 ± 07</b>	<b>36.722 ± 08</b>	<b>15.4980 ± 25</b>	<b>16.9408 ± 21</b>
<b>02/10 (CRPG)</b>	<b>2.16800</b>	<b>0.91491</b>	<b>36.720</b>	<b>15.4962</b>	<b>16.9374</b>
2*sd <sup>#</sup> (n = 43)	0.00032	0.00007	0.009	0.0022	0.0023
RSD ppm	149	77	237	140	133
<b>02/12 (CRPG)</b>	<b>2.16791</b>	<b>0.91486</b>	<b>36.723</b>	<b>15.4972</b>	<b>16.9394</b>
2*sd <sup>#</sup> (n = 22)	0.00029	0.00009	0.009	0.0029	0.0025
RSD ppm	135	103	250	184	145
<b>01/03 (CRPG)</b>	<b>2.16772</b>	<b>0.91485</b>	<b>36.722</b>	<b>15.4977</b>	<b>16.9402</b>
2*sd <sup>#</sup> (n = 36)	0.00026	0.00006	0.008	0.0029	0.0028
RSD ppm	119	61	220	184	168

<sup>a</sup> DS-TIMS (Royal Holloway) (Thirlwall, 2002).

<sup>#</sup> 2 \* Standard deviation.

Table 2  
The  $^{14}\text{C}$  ages of five charcoal samples related to metallurgical sites

Site number	Site nature	Layer content	$^{14}\text{C}$ datation	Age cal. AD	Lab Refs.
26	Colluviation	Coals-slags	940 ± 25 BP	1025–1160	Ly 11758
60	Colluviation	Coals-slags	940 ± 45 BP	1025–1205	Ly 6856
35	River deposits	Coals-slags	930 ± 45 BP	1030–1210	Ly 8034
12	River deposits	Coals-slags	995 ± 45 BP	985–1155	Ly 8032
61	Colluviation	Coals-slags	800 ± 30 BP	1195–1280	Ly 11759

Dating has been performed at the  $^{14}\text{C}$  laboratory of the University of Lyon I, France. Ly 6856, Ly 8032 and Ly 8034 have been calibrated using the calibration curve published in radiocarbon review, Calibration issue, vol. 28, n 2B (1986). Ly 11758 and 11759 were calibrated using the calibration curve of the Quaternary Isotope Laboratory, University of Washington (Stuiver et al., 1998).

allowing the measurement of all the Pb isotopes, Tl isotopes and  $^{200}\text{Hg}$  simultaneously. The NIST NBS 981 Pb and NIST 997 Tl were used to correct for instrumental mass bias, according to the empirical technique used by Maréchal et al. (1999) and reported by White et al. (2000) for Pb applications. This technique is based on the relationship measured between Pb and Tl instrumental mass bias. Reference values used for both reference materials were taken from Thirlwall (2002). For reference solutions and samples, the  $^{208}\text{Pb}$  beam intensity during the three analytical sessions needed for this study was between 3.5 and 5 V. A Pb/Tl ratio of 10 was used for both the reference solution and samples and Pb concentration was matched to better than 10% between samples and bracketing reference solutions (every 2–4 samples). Over a single session, repeated measurements of the NIST NBS 981 Pb reference material allowed determination of the Pb–Tl instrumental fractionation relationship, which was used to calculate the Pb isotope ratios of samples according to the measured Tl ratio. The composition of the NIST NBS 981 Pb was also recalculated according to the Pb–Tl frac-

tionation relationship. Results obtained for individual sessions are accurate within uncertainties of the reference values. Recalculated ratios and related uncertainties are reported in Table 1.

The isotopic homogeneity of Pb from a single ore (MO 11, Neyrac) and a single slag (SO 42, site 13) fragment was checked by preparing these samples for each of the three different analytical sessions (Tables 3 and 4). The results for the three aliquots agree within uncertainty, as defined by repeated measurements of NIST NBS 981, suggesting isotopic homogeneity of Pb at this scale.

## 4. Results and discussion

### 4.1. Age of the metallurgical activities

Five radiocarbon ages (Allée, 2003) are reported in Table 2. Four sites out of five charcoal yielding  $^{14}\text{C}$  ages ranging from 930 to 995 BP and all identical within uncertainties ( $\pm 45$ ), i.e. 1025–1210 AD cal. One sample from site 61 yielded a slightly younger age of  $800 \pm 30$  BP (i.e. 1195–1280 AD cal.).

Table 3  
The Pb isotopic compositions of galena samples found around the ML Massif

Sectors	$^{208}\text{Pb}/^{206}\text{Pb}$	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{206}\text{Pb}/^{204}\text{Pb}$
<i>Allenc-Beyrac</i>						
Le Beyrac	2.08674	1.18540	0.84360	38.786	15.680	18.587
Allenc	2.08421	1.18412	0.84451	38.690	15.677	18.563
Eygas	2.09476	1.18014	0.84735	38.999	15.775	18.617
<i>Ramponenche/Col du sapet</i>						
Ramponenche Mines 1	2.10303	1.17146	0.85364	38.639	15.684	18.373
Ramponenche Mines, bridge	2.09306	1.18113	0.84665	38.760	15.678	18.518
Ramponenche Mines 2	2.10175	1.17208	0.85318	38.623	15.679	18.377
Col du sapet	2.08910	1.17864	0.84844	38.609	15.680	18.481
<i>Le Tournel</i>						
Le Tournel West	2.08582	1.18376	0.84476	38.718	15.681	18.562
Orcières	2.08383	1.18441	0.84430	38.698	15.679	18.571
Le Tournel East	2.08396	1.18403	0.84457	38.713	15.689	18.577
<i>Bédouès-Cocurès</i>						
La Baume	2.09828	1.17693	0.84967	38.695	15.669	18.441
La Passerelle	2.09408	1.18039	0.84718	38.753	15.678	18.506
Ravin des Agudes 2	2.09574	1.17843	0.84859	38.727	15.681	18.479
<i>Vialas</i>						
Bosviel	2.09750	1.17228	0.85304	38.536	15.672	18.372
Le Colombert B	2.09957	1.17143	0.85366	38.545	15.672	18.359
Le Colombert A	2.09722	1.17220	0.85310	38.524	15.671	18.369
<i>Le Bleynard</i>						
Cubières	2.08281	1.18462	0.84415	38.683	15.678	18.572
Bleynard-Mazel (upper part)	2.07914	1.18831	0.84153	38.747	15.683	18.636
Malecombe	2.07958	1.18625	0.84299	38.693	15.685	18.606
Neyrac (MO 11)	2.08454	1.18362	0.84486	38.677	15.676	18.554
(2sd) $n = 3^a$	0.00033	0.00008	0.00008	0.014	0.005	0.005
Cubierettes	2.08193	1.18644	0.84285	38.715	15.674	18.596
<i>Les Bondons</i>						
Lozerettes 4	2.09926	1.17185	0.85335	38.704	15.673	18.437
Les Colobrières	2.09779	1.17586	0.85044	38.684	15.670	18.440
Ferrier	2.09558	1.17129	0.85376	38.678	15.673	18.457
Les Bondons	2.09858	1.17646	0.85001	38.686	15.670	18.435
Malaval 1	2.09205	1.18007	0.84741	38.679	15.667	18.489
Malaval 2	2.08915	1.18199	0.84603	38.715	15.678	18.531
<i>Montmirat</i>						
Le Devois	2.09305	1.17954	0.84779	38.683	15.668	18.481
Le Montet	2.09974	1.17152	0.85359	38.661	15.664	18.412
Le Montet West	2.08873	1.18293	0.84536	38.706	15.677	18.531
Le Marazeil	2.08677	1.18368	0.84482	38.712	15.680	18.551
Lonjagnes	2.09548	1.17830	0.84868	38.708	15.677	18.472
Les Combettes	2.09130	1.18031	0.84724	38.683	15.671	18.497
Combe de la baume	2.08117	1.18595	0.84320	38.715	15.686	18.603
La Louve 2	2.08511	1.18409	0.84453	38.692	15.671	18.556

For location of the sectors: see Fig. 5.

<sup>a</sup> Three aliquots of the Neyrac galena sample (isotopic homogeneity of ore).

These ages are medieval and may be interpreted as reflecting the time at which metallurgical activities took place in the area. This also partly corresponds to the period the King of France gave all

the “operating rights” to the Bishop of Mende (1161 AD). The latter may have then exploited mines of the ML area for coinage (and/or other purposes).

#### 4.2. Isotopic compositions of galena

Thirty-five galena samples have been measured and the results are listed in Table 3. Taken together, the galena samples are isotopically relatively homogeneous, although some areas may be individualised because of the high precision of the measurements. The veins of the Montmirat sector are the most heterogeneous, with variations of up to 1% for the  $^{206}\text{Pb}/^{204}\text{Pb}$  ratio. This might be due to the fact that different generations of galena from the same mine were analysed. Because most samples were collected within mine tailings, it is not possible to establish structural relationships between veins. The analysed samples may or may not be representative of the composition of the main exploited ore body. This situation shows the limitations of ore source tracing. On the other hand, Vialas, Le Tournel, Le Bleyard and Bédouès-Cocurès are the most homogeneous sectors, and related veins show a small dispersion of their isotopic ratios, but distinguishable from one sector to another (Table 3).

Previous Pb isotope studies of galena from the ML granite itself are scarce. Literature data is available for only three of the mineralised sectors analysed in this study: (i) veins in the Vialas sector (Marcoux, 1986; Brévar et al., 1982), (ii) one vein in the Bleyard sector (Brévar et al., 1982), and (iii) one vein in the Montmirat sector (Brévar et al., 1982). These few Pb isotopic data from the literature are comparable to those presented here (Table 3).

On the other hand, many data for galena samples from the South-Eastern Massif Central may be found in the literature: (i) the Margeride massif (to the north of the ML) (Marcoux and Brill, 1986), (ii) the South Cévenole border (LeGuen and Lancelot, 1989), and (iii) the entire Cévennes and the Montagne Noire massif (Brévar et al., 1982). All these mineralisations are believed to be linked to the Hercynian orogenesis or subsequent events (Bouladon, 1960; Brévar et al., 1982; Marcoux and Brill, 1986; LeGuen and Lancelot, 1989). Their Pb isotopic compositions are reported in Fig. 3 in  $^{208}\text{Pb}/^{204}\text{Pb}$  vs  $^{206}\text{Pb}/^{204}\text{Pb}$  and  $^{207}\text{Pb}/^{204}\text{Pb}$  vs  $^{206}\text{Pb}/^{204}\text{Pb}$  diagrams. Galena samples from the ML massif form a restricted field, which is distinguishable from those defined by galena from the other areas. The Pb isotopic compositions of samples from the South Cévenole border define the most restricted field, with lower  $^{208}\text{Pb}/^{204}\text{Pb}$ ,  $^{206}\text{Pb}/^{204}\text{Pb}$  and  $^{207}\text{Pb}/^{204}\text{Pb}$  ratios. This difference in composition is well outside the typical uncertainty reported

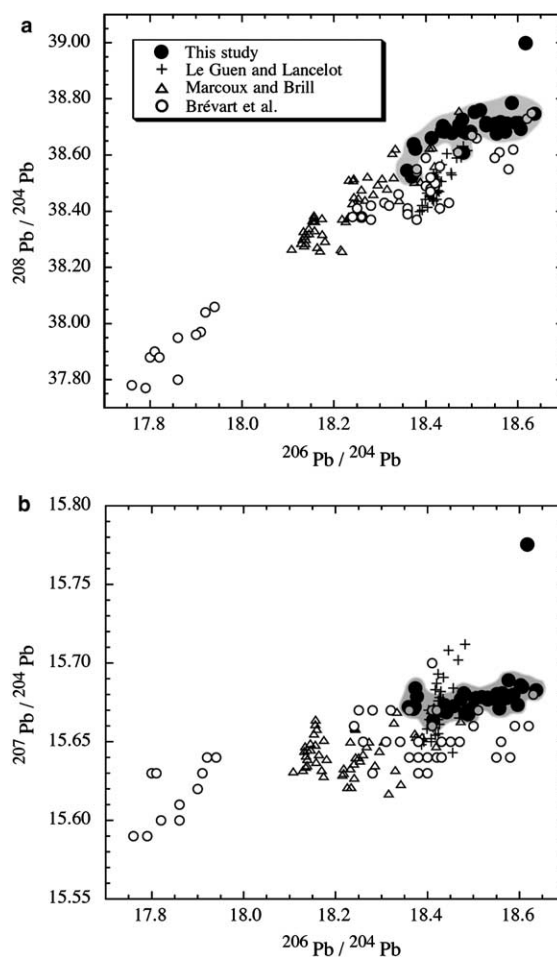


Fig. 3.  $^{208}\text{Pb}/^{204}\text{Pb}$  (a) and  $^{207}\text{Pb}/^{204}\text{Pb}$  (b) vs  $^{206}\text{Pb}/^{204}\text{Pb}$  diagrams showing the field of composition of galena from this study (black dots) along with those from other areas near the ML: (i) North (Margeride Massif, Marcoux and Brill, 1986), (ii) South of Cévennes (LeGuen and Lancelot, 1989), East (Montagne Noire, Brévar et al., 1982). Except for one sample from the Allenc-Beyrac area, galena samples from the ML define a restricted and distinct compositional field in comparison to other mineralised areas.

for both TIMS and MC-ICP-MS measurement techniques and are therefore considered as real.

Two phases (1 and 2) have been reported for the ores of the Margeride massif. The first, which results from a single mineralisation event, is more homogeneous than the second, which may result from the mixing of different sources (Marcoux and Brill, 1986). Brévar et al. (1982) have also reported two populations of Pb mineralisation. The first, located in the Montagne Noire massif, is very homogeneous and the least radiogenic so far found in the whole Cévennes massif. The second population comprises

Table 4  
Lead isotopic compositions of slags from different metallurgical sites

Number site	$^{208}\text{Pb}/^{206}\text{Pb}$	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{206}\text{Pb}/^{204}\text{Pb}$
2'	2.09309	1.17941	0.84788	38.691	15.673	18.485
3-1 <sup>b</sup>	2.09218	1.18042	0.84716	38.776	15.701	18.534
3-2 <sup>b</sup>	2.09318	1.17485	0.85117	38.655	15.663	18.467
3-3 <sup>b</sup>	2.08981	1.18099	0.84675	38.670	15.668	18.504
5	2.09395	1.18208	0.84597	38.735	15.686	18.498
5''	2.09372	1.17903	0.84816	38.681	15.669	18.475
7	2.09453	1.17956	0.84870	38.660	15.665	18.458
8	2.09385	1.17893	0.84822	38.682	15.670	18.474
Ores 8	2.09232	1.17988	0.84754	38.680	15.668	18.487
12	2.09426	1.17727	0.84942	38.642	15.673	18.451
13 (SO 42)	2.09488	1.17821	0.84874	38.672	15.668	18.460
(2sd) $n = 3^a$	0.00036	0.00006	0.00006	0.020	0.008	0.008
14	2.09064	1.18051	0.84709	38.680	15.672	18.502
16'	2.09387	1.17892	0.84824	38.677	15.668	18.472
18-A	2.09118	1.18038	0.84719	38.658	15.661	18.486
18-B	2.09032	1.18049	0.84710	38.668	15.670	18.499
19	2.09560	1.17755	0.84922	38.651	15.663	18.444
22	2.09382	1.17894	0.84822	38.680	15.669	18.473
Ores 22	2.09388	1.17884	0.84829	38.669	15.666	18.467
23	2.09389	1.17874	0.84836	38.670	15.668	18.468
24	2.09557	1.17780	0.84904	38.670	15.668	18.453
26 B	2.09398	1.17890	0.84824	38.678	15.668	18.471
27	2.09242	1.17974	0.84765	38.682	15.670	18.487
28	2.09397	1.17862	0.84845	38.656	15.663	18.460
30	2.09450	1.17721	0.84947	38.643	15.672	18.450
35	2.09436	1.17858	0.84848	38.674	15.668	18.466
36-1 <sup>b</sup>	2.09402	1.17889	0.84826	38.685	15.671	18.474
36-2 <sup>b</sup>	2.09408	1.17884	0.84829	38.684	15.670	18.473
36-3 <sup>b</sup>	2.09408	1.17873	0.84837	38.669	15.666	18.466
41	2.09396	1.17861	0.84846	38.663	15.666	18.464
42	2.09360	1.17914	0.84808	38.686	15.671	18.478
45	2.09578	1.17778	0.84905	38.672	15.667	18.453
46	2.09052	1.18074	0.84693	38.685	15.672	18.505
48	2.09461	1.17853	0.84851	38.682	15.670	18.467
60	2.09383	1.17894	0.84822	38.673	15.666	18.470
62-1 <sup>b</sup>	2.09354	1.17690	0.84969	38.615	15.673	18.445
62-2 <sup>b</sup>	2.09313	1.17709	0.84955	38.603	15.668	18.443
62-3 <sup>b</sup>	2.09328	1.17707	0.84957	38.608	15.669	18.444

<sup>a</sup> Three solid aliquots of the SO 42 sample (isotopic homogeneity of slag).

<sup>b</sup> Measures of different slag samples on the same site.

mineralisations from different areas of the Cévennes and is more heterogeneous and radiogenic. The new Pb isotope data on galena from the ML confirm the distinct and restricted sources of these Pb mineralisations. This observation is essential for the tracing of the ores that have supplied the medieval metallurgical activities.

#### 4.3. Isotopic composition of slag

The Pb isotopic compositions of more than 30 slag samples were measured (Table 4). The total range in Pb isotopic composition of nearly all of the samples is fairly restricted and is included in

the field of galena from the ML area. A slag from Site 3 and the whole Site 5 yielded a Pb isotopic composition outside the field of composition and will be omitted from the discussion.

Although this range is larger than the analytical uncertainty, the slags may be considered isotopically more homogeneous than the galena from the surrounding ore deposits. Further measurements were done in order to verify the isotopic homogeneity of a given site. For this, two or three different Pb balls from each of sites 3, 18, 36 and 62 were analysed. Samples from sites 36, 62 and 18 are isotopically homogeneous for all Pb isotope ratios whereas samples from Site 3 showed isotope variations well



outside the analytical precision. The three samples from Site 3 yielded three isotopic compositions that cover almost 2/3 of the whole range of composition measured in the slag samples. This suggests that a given smelting site might have been supplied by more than one mine or by a heterogeneous ore from a single mine. The latter case applies to all the mines studied except for Vialas and Le Tournel, for which different galena samples have relatively homogeneous isotopic compositions.

On the other hand, galena samples collected on site 8 and site 22 yielded a very similar isotopic composition to the related slag samples, suggesting that some sites were supplied by homogeneous materials. There is no simple relationship between the composition of the slag and its geographic position. Indeed, more and less radiogenic samples are found throughout the entire studied area. The only exception seems to be site 62, the northernmost location, for which all three samples are isotopically homogeneous with significantly lower  $^{208}\text{Pb}/^{204}\text{Pb}$  ratios than those of the other sites. All the other samples form relatively well-defined linear arrays in the Pb isotope diagrams (Fig. 4(a)–(c)).

#### 4.4. Tracing the sources of feeding ores

Very few studies have been carried out on ancient techniques of Pb smelting (Hetherington, 1980). Hetherington used a simple, charcoal fired, forced draft, bowl furnace for the direct reduction of galena at a temperature of ca. 1300 °C. This produced a liquid slag, but combined weights reported for the slags and Pb products were 20–50% less than the total material charged. The author could not separate metal from slag products and observed a very large weight loss during smelting, suggesting that much of the Pb volatilised as smoke or a gas phase. Another experiment on ancient Pb smelting also revealed extensive Pb-loss of up to 50% of the total charge (Baron, 2005). According to Budd et al. (1995), there is no isotopic fractionation during the extraction of Pb using ancient metallurgical techniques. The preliminary results also indicate no significant isotopic fractionation during metallurgical processes (Baron, 2005).

The composition of all the slag samples is presented in the various Pb–Pb diagrams of Fig. 4(a)–(c), along with the composition of the galena. The slag samples have a compositional range more restricted than measured in galenas. However, the composition of slag is included in the field defined

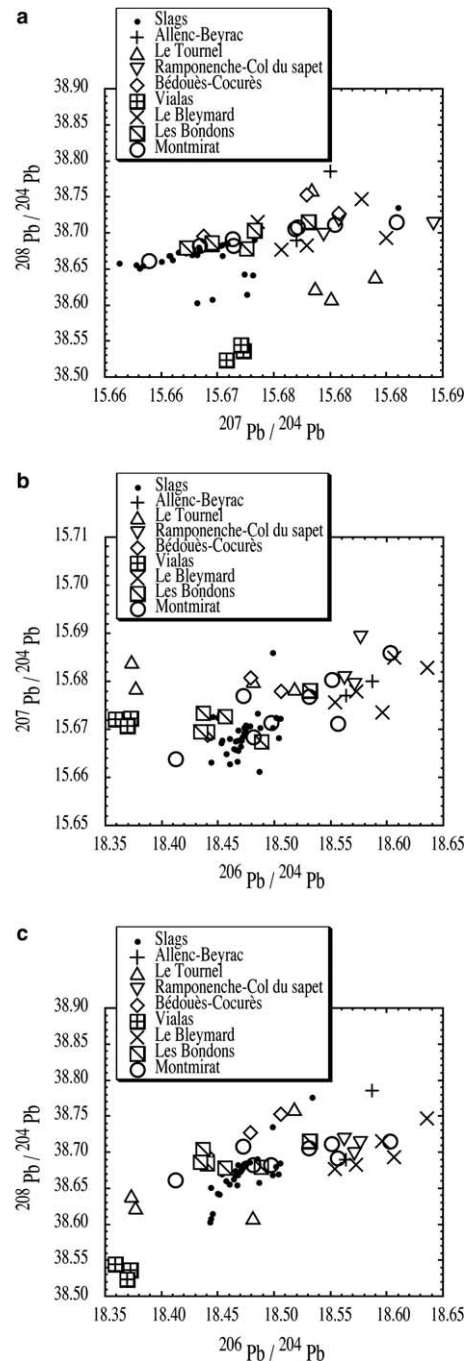


Fig. 4. Three different Pb–Pb isotope diagrams showing the relationship between slags and the sampled galena ores around the ML Massif. The “Eygas” vein (Allenc-Beyrac sector) and Slag 3 are excluded from all of the diagrams, in order to allow an appropriate scale for clarity.

by galena in most Pb isotope diagrams. In order to represent a potential source of ore, the composition of galena must be included, at least in part, in

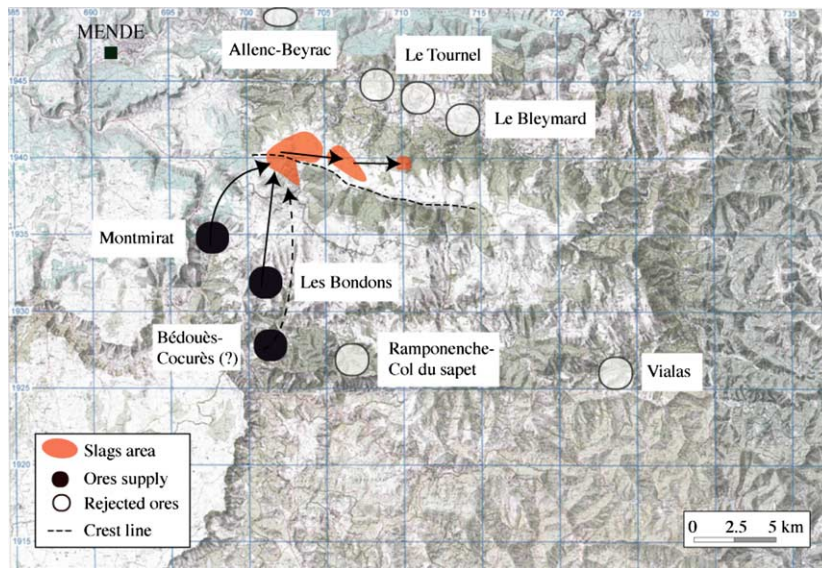


Fig. 5. Map showing the spatial relationship between the possible ore suppliers of the ancient metallurgical sites. Based on Pb isotopes, the Montmirat and Les Bondons sectors in the southern area correspond to the most probable ore sources with a possible contribution from the Bédouès-Cocurès sector.

the field defined by the slag in all the Pb–Pb spaces. According to these criteria, some ore sectors are excluded as suppliers. These are Allenc-Beyrac, Ramponche/Col du Sapet, Le Tournel, Bédouès-Cocurès, Vialas and Le Bleynard. Only galena from Les Bondons and Montmirat sectors would fit the composition of slag in all Pb isotope diagrams of Fig. 4, except that of sites 3 and 62 for which no galena fits the composition of the slags. From these two sectors, Ferrier and Malaval 1 (Les Bondons) and Le Devois and Les Combettes (South-Eastern of Montmirat) are the best candidates for suppliers of Pb ore corresponding to the slag analysed on the ML (Fig. 5). The Pb isotopic compositions of galena from other mines of the Les Bondons and Montmirat areas, such as Malaval 2, Lonjagnes, Le Montet and La Louve, partly overlap the field defined by the slag. It is difficult to exclude these definitively on the bases of only one galena analysed for each mine. Indeed, isotopic heterogeneity might occur within a single mine not only within a given mine area. Furthermore, the three mentioned mines from Montmirat may include the veins that are most enriched in Ag (Bouladon, 1960), an important consideration for the ore quality exploited for coinage.

#### 4.5. Historical considerations

According to the isotopic composition of slag and galena, mines from the near southern area

seem to be the most likely sources of ore for the medieval Pb metallurgy (Fig. 5). Indeed, the topography of the northern side of the ML massif is rougher and steeper than that of the southern side. The latter is often smooth, rising progressively to the top. Nevertheless, it is surprising that the northern sites were fed by the southern ores. The metallurgists must have had other reasons than topography to install their smelting activities on a high plateau away from the mines. One explanation might be that they needed water (most sites are close to peat bogs) or, more probably, a given type of wood as fuel for their furnaces. Indeed, site locations might correspond to the ancient beech boundary, as 99% of the charcoals related to slags found in excavations were made of beech. All the workshops were located within the same altitudinal range: 1360–1430 m. According to palynological records, this range may reflect the medieval limit of beech growth on the ML massif. Furthermore, archaeometallurgists believe that it was easier to transport ore materials toward forest than charcoal to mining areas, particularly if numerous small ore deposits were mined, as suggested by Pb isotopes and by surveys.

A second point concerns the fact that ore deposits closer to the metallurgical sites can be excluded as suppliers based on Pb isotopes. A simple explanation for this surprising observation

might be a difference in timing between the two activities, mining (the northern ores) and smelting. However it is more probably due to a question of land property. Indeed, the metallurgists probably had to do the ore smelting on the property of the Lord owning the mines, for example the Bishop of Mende, the Grèzes Viscount or the King of France. Up to now, no ancient document has confirmed the existence of different landlords in this particular area for this period of the medieval age. According to archaeologists, in medieval times, the monetary system was exclusively founded on a systematic and organised search for Pb (and Ag) ore deposits. In this case, geographical proximity between mines and smelters might not have been the most important constraint. The location of metallurgical sites on the ML massif might have been directly related to the medieval historical context in France and/or in all of Western Europe.

## 5. Conclusions

The lack of ancient documents on mining and metallurgical activities on the Mont-Lozère massif has prevented the determination of the spatial and temporal relationships between these two activities. The use of radiocarbon dating and Pb isotopes provides new information about the timing of smelting activities (Medieval Age: 985–1280 AD cal.), and allows identification of the likely suppliers among the numerous ore deposits surrounding the Mont-Lozère massif. Based on the Pb isotopic composition of slags and galena, the most probable ore sources are the mines located in the southern area, Montmirat and Les Bondons. The geographic locations of the sites suggest that the “medieval metallurgists” were constrained to perform their smelting activities at considerable distances from the supplier mines, so as to be closer to the type of trees/forests needed as charcoal for their furnaces and/or to water sources. Most charcoal samples found in association with the slags were beech wood, now almost absent from the area. The limited range of altitude (1340–1430 m) in which all the archeological sites were found may indeed represent the beech tree limit at the time. In addition, further constraints, probably related to land ownership, were also important, as shown by the fact that northern ore deposits closer to the smelting sites can be excluded as sources of Pb ore on the basis of Pb isotopes.

## Acknowledgements

This study was funded by the French Environmental Agency (ADEME) and by Languedoc-Roussillon Region. All the analyses were performed at the CRPG and SARM (CNRS), in Nancy. We thank the CERL of Mende and the National Park of Cévennes for their assistance. Thanks to the “Saint-Etienne du Vadonnez” community and its mayor; Claude Feybesse, for his technical support during fieldwork and his warm reception. Special thanks to Jean Peytavin. We also thank the SRA (Regional Service of Archaeology) for supporting the “Programme Collectif de Recherche” (PCR) entitled “Plomb ancien du Mont-Lozère”. This work is included in this PCR, all of whose members contribute to provide a multidisciplinary approach.

Thanks to Laurie for English corrections. CRGP Contribution No. 1789.

## References

- Alfonso, S., Grousset, F., Massé, L., Tastet, J.P., 2001. A European lead isotope signal recorded from 6000 to 300 years BP in coastal marches (SW France). *Atmos. Environ.* 35, 3595–3605.
- Allée, Ph., 2003. Dynamiques hydrosédimentaires actuelles et holocènes dans les systèmes fluviaux de moyenne montagne (Limousin, Hautes Cévennes, Maures). Habilitation à diriger des Recherches, Université de Limoges.
- Bailly-Maitre, M.C., 2002. L'argent: du minerai au pouvoir dans la France médiévale. A.&J. Picard, Paris.
- Baron, S., 2005. Traçabilité et évolution d'une pollution métallurgique médiévale de Plomb Argentifère sur le Mont-Lozère. Ph.D. Thesis, Univ. Montpellier II.
- Bouladon, J., 1960. Sur les minéralisations en Pb/Zn et Sb de la périphérie de Mont-Lozère. *Bull. Soc. Géol. France* 7, tome II, 7ème série, pp. 906–914.
- Brévart, O., Dupré, B., Allègre, C., 1982. Metallogenic provinces and the remobilisation process studied by lead isotopes: lead–zinc ore deposits from the southern Massif Central, France. *Econ. Geol.* 77, 564–574.
- Budd, P., Pollard, A.M., Scaife, B., Thomas, R.G., 1995. The possible fractionation of lead isotopes in ancient metallurgical processes. *Archaeometry* 37, 143–150.
- Ettler, V., Mihaljevic, M., Komárek, M., 2004. ICP-MS measurements of lead isotopic ratios in soils heavily contaminated by lead smelting: tracing the sources of pollution. *Anal. Bioanal. Chem.* 378, 311–317.
- Farmer, J.G., Eades, L.J., Mackenzie, A.B., Kirika, A., Bailey-Watts, T.E., 1996. Stable lead isotope record of sediments since 1630 AD. *Environ. Sci. Technol.* 30, 3080–3083.
- Hetherington, R., 1980. In: Oddy, W.A. (Eds.), *Aspects of Early Metallurgy*. Brit. Mus. Occas. Pap. 48, London, pp. 27–40.
- Laurent, S., 2005. Mines et métallurgie du plomb argentifère sur le Mont-Lozère (XI–XV<sup>èmes</sup> Siècles). Master memory. Université de Lyon II, France.

- LeGuen, M., Lancelot, J.R., 1989. Origine du Pb/Zn des minéralisations du Bathonien Sud-Cévenol. Apport de la géochimie isotopique comparée du plomb des galènes, de leur encaissant et du socle. *Chron. Rech. Min.* 495, 31–36.
- Marcoux, E., 1986. Isotopes du plomb et paragenèses métalliques, traceurs de l'histoire des gîtes minéraux. Ph.D. Thesis, Univ. Clermont-Ferrand, France, BRGM.
- Marcoux, E., Brill, H., 1986. Héritage et sources des métaux d'après la géochimie isotopique du plomb. *Mineral Deposita* 21, 35–43.
- 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.
- Monna, F., Hamer, K., Lévêque, J., Sauer, M., 2000. Pb isotope as a reliable marker of early mining and smelting in the Northern Harz province (Lower Saxony, Germany). *J. Geochem. Explor.* 68, 201–210.
- Niederschlag, E., Pernicka, E., Seifert, T.H., Bartelheim, M., 2003. The determination of lead isotope ratios by multiple multicollector ICP-MS: a case study of early bronze age artefacts and their possible relation with ore deposits of the Erzgebirge. *Archeometry* 45, 61–100.
- Nieminem, T.M., Ukonmaanaho, L., Shotyk, W., 2002. Enrichment of Cu, Ni, Zn, Pb and As in an ombrotrophic peat bog near a Cu–Ni smelter in southwest Finland. *Sci. Total Environ.* 292, 81–89.
- 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. *Archaeometallurgy in Europe, Milan, Italy*, vol. I, pp. 635–644.
- Rosman, K.J.R., Chisholm, W., Boutron, C.F., Candelone, J.P., Patterson, C.C., 1994. Anthropogenic lead isotopes in Antarctica. *Geophys. Res. Lett.* 21, 2669–2672.
- Rosman, K.R., Chisholm, W., Hong, J., Candelone, J.P., Boutron, C.F., 1997. Lead from Carthaginian and Roman Spanish mines isotopically identified in Greenland ice dated from 600 BC to 300 AD. *Environ. Sci. Technol.* 31, 3413–3416.
- Routhier, P., 1963. Les gisements métallifères: Géologie et principes de recherches, vol. 1. Masson, Paris, p. 342.
- Shotyk, W., Cheburkin, A.K., Appleby, P.G., Fankhauser, A., Kramers, J.D., 1996. Two thousand years of atmospheric arsenic, antimony, and lead deposition recorded in an ombrotrophic peat bog profile, Jura Mountains, Switzerland. *Earth Planet Sci. Lett.* 145, E1–E7.
- Shotyk, W., Weiss, D., Appleby, P.G., Cherburkin, A.K., Frei, R., Gloor, M., Kramers, J.D., Reese, S., Van Der Knaap, W.O., 1998. History of atmospheric lead deposition since 12,370 <sup>14</sup>C yr BP from peat bog, Jura Mountains, Switzerland. *Science* 281, 1635–1640.
- Strabon, 64 BC–23 AD. *Etudes Géographiques. Livre IV, 2.2.*
- Stuiver, M., Reimer, P.J., Bard, E., Beck, J.W., Burr, G.S., Hudhen, K.A., Kromer, B., McCormac, F.G., Plicht, J., Spurk, M., 1998. INT CAL 98 radiocarbon age calibration, 24,000–0 cal BP. *Radiocarbon* 40, 1041–1083.
- Thirlwall, M.F., 2002. Multicollector ICP-MS analysis of Pb isotopes using a <sup>207</sup>Pb–<sup>204</sup>Pb double spike demonstrates up to 400 ppm/amu systematic errors in Tl-normalization. *Chem. Geol.* 184, 255–279.
- Weiss, D., Shotyk, W., Appleby, P.G., Kramers, J.D., Cherburkin, A.K., 1999. Atmospheric Pb deposition since the industrial revolution recorded by five Swiss peat profiles: enrichment factors, fluxes, isotopic composition, and sources. *Environ. Sci. Technol.* 33, 1340–1352.
- White, W.M., Albarède, F., Télouk, P., 2000. High-precision analysis of Pb isotope ratios by multi-collector ICP-MS. *Chem. Geol.* 167, 257–270.