

High-temporal resolution landscape changes related to anthropogenic activities over the past millennium in the Vosges Mountains (France)

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Abstract Iron mining activities in the Bruche valley (Vosges Mountains, France) date historically from the Roman period to the mid-nineteenth century. The geochemical and palynological study of a core from the peat bog of Le Champ du Feu allows highlighting impacts of these activities over the past millennium. Trace metal contamination is recorded for lead (Pb), arsenic, zinc, and antimony during the Middle Ages, the sixteenth century, and from cal. AD 1750–1900, with several sources distinguished by Pb isotope analyses. Forest exploitation is attested by the palynological analysis of the core, with exploitation of *Fagus* for smelting processes and cutting of *Abies* for agro-pastoralism. This approach highlights several patterns of contamination, corresponding to the mixing sources and the contamination intensity, which can be linked to the pollen assemblage zones. Hence, anthropogenic activities such as mining and farming led to long-term modification of the landscape composition in this mountainous area.

Keywords Lead isotopes · Mines · Peat bog · Pollen · Vegetation dynamics

INTRODUCTION

For the last two millennia, several phases of increasing trace metal (TM) atmospheric pollution due to mines, smelters, waste incinerators, coal, leaded gasoline, or industrial emissions have been registered worldwide (Nriagu 1996). Besides being a major source of

contamination, metal production impacted the agro-pastoral and ecological landscape over time, as it has been observed by palaeo-environmental studies from former mining areas (Jouffroy-Bapicot et al. 2007; Bindler and Rydberg 2015). As an example, in Austria, Viehweider et al. (2015) observed a decrease of *Abies* in palynological record in the vicinity of former ore exploitation dated at 1000 BC. Deforestations, which can be observed during mining, are often related to a high consumption of wood for the construction of galleries and smelting and refinery processes with their charcoal needs (Jouffroy-Bapicot et al. 2007). In Sweden, iron (Fe) exploitation during the Middle Ages was linked to an increase of ruderal taxa indicating the creation of pastures and an increase of land use pressure to support population of miners from the area (Karlsson et al. 2015). These results are consistent with other research on the topic that showed that anthropogenic impact on the landscape varied function of the (i) intensity of mining, (ii) type of ore exploited, (iii) local vegetation, and (iv) climate (Breitenlechner et al. 2013; Servera Vives et al. 2014; Mighall et al. 2017). Hence, the impact of mining and other anthropogenic activities cannot be generalized and needs precise investigations to understand induced long-term changes.

Among the most active former mining sites in Europe, the Vosges Mountains, which are particularly rich in Fe and non-ferrous ores, have been intensively exploited over the last millennium with the main activity between the sixteenth and eighteenth centuries (Fluck and Ancel 1989; Leypold 1996). Previous study interesting on landscape changes during mining showed that no major deforestations were recorded near the district of Sainte-Marie-aux-Mines, the biggest former European lead (Pb)-silver mining in the fifteenth century (Mariet et al. 2016).

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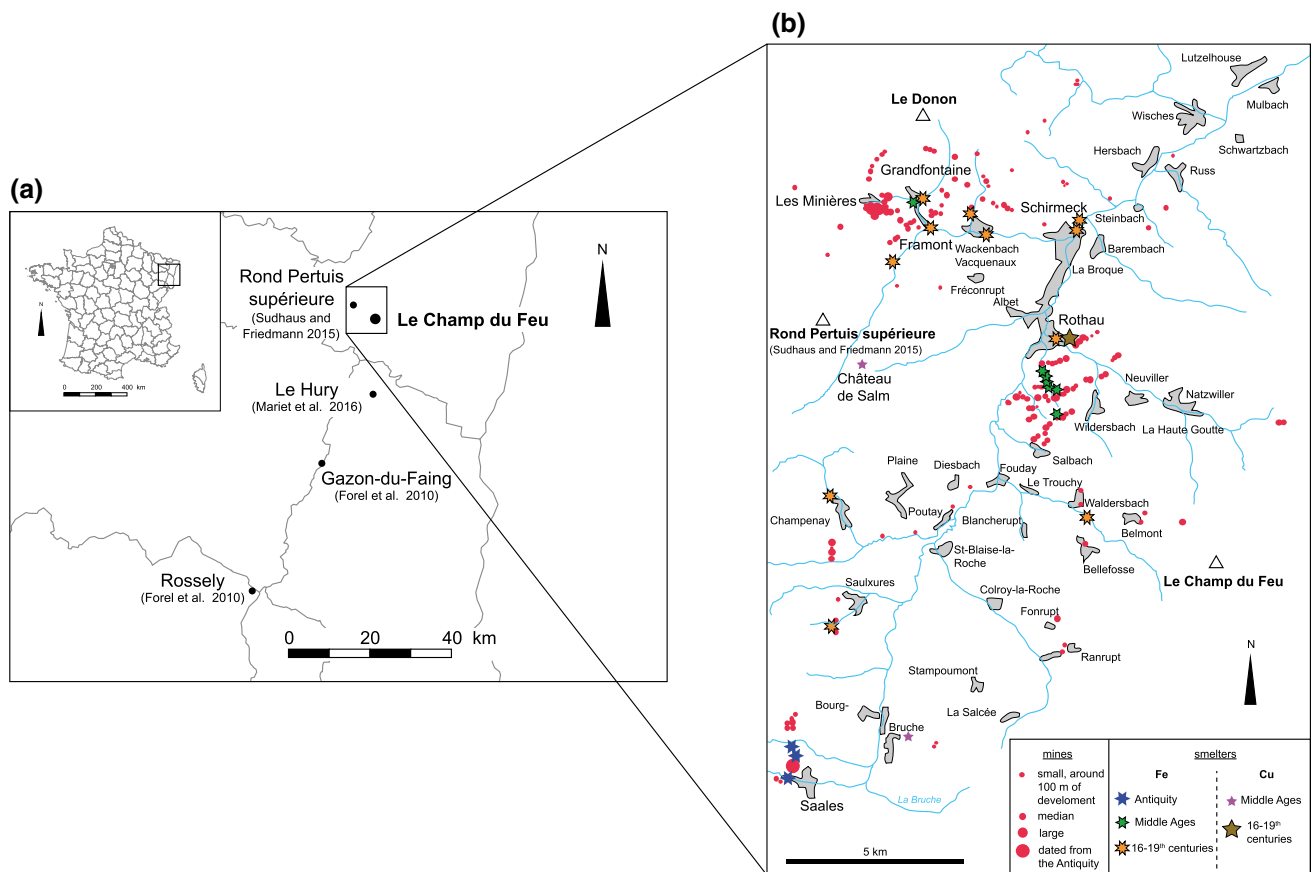


Fig. 1 **a** Map of the Le Champ du Feu peat bog and other studied sites in the Vosges Mountains for trace metals. **b** Mining map of the Bruche valley, modified according to Leybold (1996). Triangles indicate crests and correspond to peat bogs for Le Champ du Feu and Rond Pertuis supérieure (Sudhaus and Friedmann 2015)

However, historical archives indicated that charcoal was considered the limiting factor for Fe exploitation in the seventeenth century in the Bruche valley, at 15 km northward from Sainte-Marie-aux-Mines, because of the decrease in forest resources and the increasing price of wood or charcoal (Leybold 1996). The Bruche valley was known to be an important district of Fe exploitation which has been documented since the Roman period but with a main activity during the fifteenth–sixteenth centuries (Leybold 1996). Hence, although historical sources testify to occasionally drastic landscape modifications, the quantification of this impact remains a question. Were the landscapes in this valley totally deforested for mining activities? Or did some management strategies exist for ensuring the turnover of exploited forested areas? To answer these questions, palynological studies coupled with the geochemistry of TMs in environmental archives are an efficient tool for detecting phases of anthropogenic activities and associated landscape changes (Ejarque et al. 2009; Breitenlechner et al. 2013). When available, the historical and archaeological data bring help for the interpretation of the geochemical signal.

The objectives of this study are to reconstruct the changes in landscape related to anthropogenic activities in the Northern Vosges Mountains, focusing on the last millennium, when the mining activities were at their highest level in the region. A multi-proxy approach with a high time resolution was developed, combining palynological analyses to assess changes in the local vegetation and land use, and TM analyses and Pb isotopes to reveal the intensity and source of atmospherically deposited TM.

MATERIALS AND METHODS

Study site

The study site is located in the Bruche valley (North of the Vosges Mountains, eastern France), where many past Fe mining sites are documented (Fig. 1a, b). The geological background is composed of granites, granodiorites, and diorites, which form the domain of Champ du Feu (von Eller et al. 1970). The altitudinal ranges from 600 m a.s.l. in the valley to 1090 m a.s.l. at the summit of Le Champ du Feu.

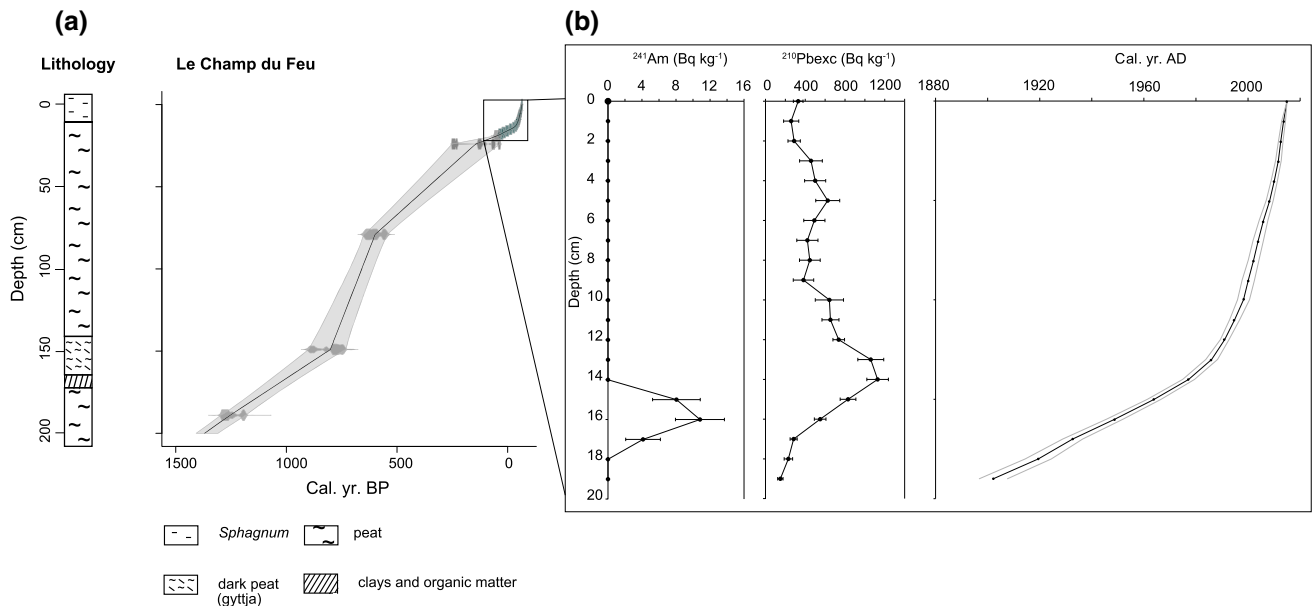


Fig. 2 **a** Age–depth model of the Le Champ du Feu core with four ^{14}C dates and lithology. **b** Activity of ^{241}Am , ^{210}Pb in excess and age–depth model associated with the upper 20 cm of the core

The vegetation is distributed approximately as follows: mixed forest from 600 to 1000 m a.s.l., coniferous forest from 900 to 1040 m a.s.l., and meadows, dwarf shrub heathland up to the summit. The site is an ombrotrophic peat bog called “Le Champ du Feu” (N48°23.971', E007°15.490', 1049 m a.s.l.) consisting of 3.6 ha of active peat situated in a crest. The surrounding environment is currently composed of a mixed beech, fir, spruce forest in the west and sub-alpine meadows, and dwarf shrub heathland in the east. The local vegetation is mainly composed of *Betula pubescens*, *Pinus* sp., *Vaccinium oxycoccos*, *Sphagnum* sp., *Calluna* sp., *Carex* sp. The core was collected in the center of the peat bog with a Russian GYP-type corer, after exploring the thickness of the complete peat deposit with an avalanche probe. The core was 200 cm depth (Fig. 2a) and was packed and stored in a dark cooling chamber (4 °C) until analyses.

Age–depth model

The core was dated with four ^{14}C dates (Table 1, Fig. 2a) on bulk samples using Accelerator Mass Spectrometry (AMS, Poznan Radiocarbon Laboratory, Poland). The youngest part of the core was dated by measuring ^{210}Pb and ^{241}Am activities. For this, the uppermost 20 cm was divided into contiguous samples of 1 cm thickness, and the samples were dried at 60 °C for 72 h. The ^{210}Pb and ^{241}Am activities were measured by gamma spectrometry using well-type Germanium detectors in the Modane underground laboratory (LSM/Radionuclides Unit, Chrono-Environment). The measurement of ^{210}Pb activity was done after 3 weeks of equilibration in a container sealed. The

Table 1 ^{14}C dates of the Le Champ du Feu core

Lab. code	Depth (cm)	Material	Uncalibrated ^{14}C age BP	Calibrated year AD/BC (2 σ)
Poz-76144	25	Bulk	101 ± 0.35 pMC	AD 1951–1959
Poz-76145	80	Bulk	600 ± 30 BP	AD 1297–1409
Poz-76146	150	Bulk	880 ± 30 BP	AD 1042–1105
Poz-76146				AD 1117–1222
Poz-76147	190	Bulk	1325 ± 30 BP	AD 650–722
Poz-76147				AD 740–768

chronology of ^{210}Pb in excess, obtained by removing ^{226}Ra to measured ^{210}Pb activity, was calculated using the Constant Rate of Supply (CRS) model (Appleby and Oldfield 1978) (Fig. 2b). Radiocarbon dates were calibrated using the IntCal09. ^{14}C calibration curve. The reliability of the age–depth model was checked using ^{241}Am contamination records with a peak corresponding to the maximum fallout intensity of atmospheric nuclear weapon tests (AD 1963) (Kreiser et al. 1992). The age–depth model was then run as a linear interpolation using the Clam program developed by Blaauw (2010) (Fig. 2), and sedimentation rates were calculated according to the age–depth model.

Palynological analyses

Sampling was conducted every two cm. Sub-samples (1 g fresh matter) were prepared using the standard method established by Faegri and Iversen (1989) after the addition of exotic pollen grains of *Lycopodium* to estimate pollen

accumulation rates. Sub-samples were filtered to 200 µm and then treated with HCl 10%, HF 40%, NaOH 10%, and acetolysis. A minimum of 1000 pollen grains were counted on each level at ×400 magnification and identified using the standard identification keys of the Central European pollen flora (Beug 1961; Punt 1976; Punt and Clarke 1980, 1981, 1984; Punt et al. 1988; Faegri and Iversen 1989; Moore et al. 1991; Reille 1992, 1995) and the reference collection of the Chrono-Environment laboratory.

The calculation of the pollen diagram was performed using the program TILIA 1.5.12 (Grimm 1991). The pollen sum was calculated from the arboreal and non-arboreal pollen count; water plants, i.e., *Nuphar*, *Callitriche*, *Sagittaria*, *Potamogeton*, *Hottonia palustris*, *Rumex aquaticus*, and *Typha*, hygrophilous taxa, and spores were excluded from the sum. The pollen accumulation rate (10^3 grains cm^{-2} year^{-1}) was calculated according to the wet bulk density of the sample, the *Lycopodium* counts and the sedimentation rate. Pollen data were divided into Pollen Assemblage Zones (PAZs) by constrained incremental sums of squares cluster analysis (CONISS) of the relative abundance of pollen taxa (Grimm 1987).

Trace metal and Pb isotope analyses

Trace metal and Pb isotopic measures were performed at the “Service d’Analyse des Roches et des Minéraux” (SARM; CRPG-CNRS, Nancy, France).

Trace metal analyses

Trace element concentrations were determined by an Inductively Coupled Plasma Mass Spectrometer (ICP-MS Thermo Elemental X7). Samples were prepared and measured following the procedure of Carignan et al. (2001). Briefly, samples were mixed with LiBO_2 and melted (alkaline fusion). The fusion products were further dissolved in diluted nitric acid before measurements (Table 2; see the SARM website at <http://www.crpm.cnrs-nancy.fr/SARM/>).

Table 2 Analytical accuracy of As, Pb, Sb, and Zn analyses with the limit of detection (LoD, $\mu\text{g g}^{-1}$) and error associated depending on concentration measured (higher than 1 and 50 $\mu\text{g g}^{-1}$). These data were obtained according to 5 certified reference materials (CRMs, $n = 150$ per CRM) that were routinely used for 6–12 months

	As	Pb	Sb	Zn
LoD ($\mu\text{g g}^{-1}$)	0.20	0.35	0.05	5.0
Error on LoD for concentration > 1 $\mu\text{g g}^{-1}$	< 20%	< 20%	< 10%	> 25%
Error on LoD for concentration > 50 $\mu\text{g g}^{-1}$	< 5%	< 10%	–	< 10%

Lead isotope analyses

Approximately 100 mg of each sample was weighted, mixed with three acids (HNO_3 , HCl, and HF) and put on a hot plate at 120 °C. Once fully digested, Pb was extracted from the matrix using ion exchange chromatography. Isolation was performed using a chromatographic column containing AG1-X8 (Cloquet et al. 2006). After being fixed in HBr 0.8 M, Pb was recovered in HCl 6 M (Manhès et al. 1980). After dissolution in 0.3 M HNO_3 , isotopic analyses were performed using a Multi-Collector Inductively Coupled Plasma Mass Spectrometer (Thermo Scientific Neptune Plus) at CRPG, Nancy. International standard solution SRM 981 with the addition of TI SRM 997 was measured to correct for instrumental mass bias using both external normalization and the standard-sample bracketing technique, as described earlier (White et al. 2000; De Muynck et al. 2007) using DS TIMS values (Thirlwall 2002). In addition, accuracy and long-term reproducibility were ensured using GSD 10 (river sediment) and BCR 482 (lichen) reference materials (Cloquet et al. 2015). The total Pb procedural blanks obtained along the course of the study were stable at approximately 300 pg.

Calculation of accumulation rates and enrichment factors of TMs

The accumulation rates (ARs) of TMs were calculated using the following equation (Eq. 1).

$$\text{AR} = \text{concentration} \times \text{sedimentation rate} \times \text{bulk density}, \quad (1)$$

where AR is in $\mu\text{g cm}^{-2} \text{year}^{-1}$, the concentration of total TM is in $\mu\text{g g}^{-1}$, the sedimentation rate is in cm year^{-1} , and the dry bulk density is in g cm^{-3} .

Enrichment factors (EFs) were calculated for each TM following Eq. 2 (Weiss et al. 1999).

$$\text{EF} = \left(\frac{\text{TM}_{\text{meas}}}{\text{Al}_{\text{meas}}} \right) / \left(\frac{\text{TM}_{\text{UCC}}}{\text{Al}_{\text{UCC}}} \right), \quad (2)$$

where TM_{meas} is the measured concentration of TM in $\mu\text{g g}^{-1}$, TM_{UCC} is the concentration of this element in the upper continental crust (UCC; Wedepohl 1995), Al_{meas} is the concentration of aluminum (Al) measured in $\mu\text{g g}^{-1}$, and Al_{UCC} is the concentration of Al in the UCC (i.e., 77 440 $\mu\text{g g}^{-1}$; Wedepohl 1995).

Chemical and physical characterization

The dry bulk density (g cm^{-3}) was measured on freeze-dried samples in terms of water content ($\%\text{H}_2\text{O}$). This measure was realized by weighing samples before and after freeze-drying to obtain the water content (Table 3).

Table 3 Sedimentation rate (cm year⁻¹), dry bulk density (g cm⁻³), %H₂O, ash content (%), %H₂O, ash content (%), total concentrations of As, Pb, Sb, and Zn (μg g⁻¹), and Pb isotope ratios (the errors are given at a 95% confidence level). < LoD: lower than limit of detection

Cal. year AD	Sedimentation rate (cm year ⁻¹)	Dry bulk density (g cm ⁻³)	%H ₂ O	Ash content (%)	As	Pb	Sb	Zn	²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁷ Pb/ ²⁰⁴ Pb	²⁰⁸ Pb/ ²⁰⁴ Pb	²⁰⁶ Pb/ ²⁰⁷ Pb	²⁰⁸ Pb/ ²⁰⁶ Pb
1991	0.20	0.119	0.84	95.7	5.57	180.2	3.07	136.06	17.948 ± 0.004	15.605 ± 0.004	37.899 ± 0.010	1.151 ± 0.000	2.112 ± 0.000
1963	0.07	0.113	0.85	93.0	7.15	158.9	4.12	71.74	18.138 ± 0.002	15.610 ± 0.002	38.123 ± 0.007	1.162 ± 0.000	2.102 ± 0.000
1932	0.08	0.113	0.86	94.2	6.74	104.0	2.58	51.32	18.322 ± 0.001	15.628 ± 0.001	38.345 ± 0.003	1.172 ± 0.000	2.093 ± 0.000
1902	0.05	0.102	0.88	97.2	4.21	78.29	1.62	51.32	18.370 ± 0.001	15.629 ± 0.001	38.387 ± 0.004	1.175 ± 0.000	2.090 ± 0.000
1864	0.05	0.067	0.89	98.3	3.10	66.84	0.91	55.27	18.448 ± 0.001	15.632 ± 0.001	38.455 ± 0.078	1.180 ± 0.000	2.085 ± 0.004
1825	0.05	0.079	0.90	97.7	3.243	58.68	0.76	56.31	18.505 ± 0.001	15.633 ± 0.001	38.493 ± 0.003	1.184 ± 0.000	2.080 ± 0.000
1797	0.12	0.066	0.91	98.9	2.263	38.04	0.43	53.87	18.639 ± 0.001	15.636 ± 0.001	38.604 ± 0.003	1.192 ± 0.001	2.071 ± 0.000
1781	0.12	0.063	0.91	98.6	2.551	33.87	0.42	48.24	18.680 ± 0.001	15.638 ± 0.001	38.636 ± 0.004	1.194 ± 0.000	2.068 ± 0.000
1764	0.12	0.066	0.92	99.2	1.923	25.89	0.38	40.48	18.669 ± 0.001	15.640 ± 0.001	38.632 ± 0.004	1.194 ± 0.000	2.069 ± 0.000
1748	0.12	0.046	0.92	98.8	2.165	21.59	0.28	38.08	18.563 ± 0.001	15.636 ± 0.002	38.544 ± 0.004	1.187 ± 0.000	2.076 ± 0.000
1723	0.12	0.055	0.92	98.1	2.382	21.79	0.63	30.19	18.460 ± 0.001	15.633 ± 0.001	38.483 ± 0.004	1.181 ± 0.000	2.085 ± 0.000
1698	0.12	0.047	0.92	98.4	1.671	29.95	0.40	24.99	18.423 ± 0.001	15.631 ± 0.001	38.444 ± 0.003	1.179 ± 0.000	2.087 ± 0.000
1674	0.12	0.047	0.93	99.4	1.413	37.99	0.26	22.53	18.474 ± 0.001	15.636 ± 0.001	38.491 ± 0.002	1.182 ± 0.000	2.084 ± 0.000
1640	0.12	0.059	0.92	98.8	1.734	28.92	0.42	20.99	18.524 ± 0.001	15.637 ± 0.001	38.522 ± 0.003	1.185 ± 0.0005	2.080 ± 0.000
1607	0.12	0.052	0.93	98.8	1.394	32.53	0.32	14.48	18.473 ± 0.001	15.636 ± 0.001	38.498 ± 0.003	1.181 ± 0.000	2.084 ± 0.000
1583	0.12	0.052	0.93	98.6	1.274	28.59	0.28	10.76	18.400 ± 0.001	15.635 ± 0.001	38.429 ± 0.003	1.177 ± 0.000	2.089 ± 0.000
1550	0.12	0.058	0.93	99.1	0.968	16.23	0.31	8.88	18.370 ± 0.001	15.639 ± 0.001	38.413 ± 0.003	1.175 ± 0.000	2.091 ± 0.000
1525	0.12	0.042	0.93	98.8	0.778	12.03	0.17	6.24	18.400 ± 0.001	15.635 ± 0.001	38.429 ± 0.003	1.177 ± 0.000	2.089 ± 0.000
1500	0.12	0.053	0.93	98.8	1.147	7.74	0.29	6.89	18.370 ± 0.001	15.639 ± 0.001	38.413 ± 0.003	1.175 ± 0.000	2.091 ± 0.000
1475	0.12	0.044	0.93	98.8	0.944	7.54	0.18	4.77	18.400 ± 0.001	15.635 ± 0.001	38.429 ± 0.003	1.177 ± 0.000	2.089 ± 0.000
1442	0.12	0.045	0.93	99.3	0.895	9.32	0.10	4.92	18.370 ± 0.001	15.639 ± 0.001	38.413 ± 0.003	1.175 ± 0.000	2.091 ± 0.000
1409	0.12	0.045	0.94	98.7	0.868	9.54	0.13	3.91	18.400 ± 0.001	15.635 ± 0.001	38.429 ± 0.003	1.177 ± 0.000	2.089 ± 0.000
1376	0.12	0.039	0.94	99.1	0.848	8.25	0.08	4.29	18.370 ± 0.001	15.639 ± 0.001	38.413 ± 0.003	1.175 ± 0.000	2.091 ± 0.000
1348	0.35	0.038	0.94	98.7	0.648	14.54	0.11	3.19	18.400 ± 0.001	15.635 ± 0.001	38.429 ± 0.003	1.177 ± 0.000	2.089 ± 0.000
1337	0.35	0.047	0.93	98.5	0.771	14.28	0.13	3.98	18.370 ± 0.001	15.639 ± 0.001	38.413 ± 0.003	1.175 ± 0.000	2.091 ± 0.000
1325	0.35	0.048	0.92	93.0	1.327	13.24	0.17	8.27	18.400 ± 0.001	15.635 ± 0.001	38.429 ± 0.003	1.177 ± 0.000	2.089 ± 0.000
1314	0.35	0.040	0.93	99.2	0.611	13.23	0.14	3.43	18.370 ± 0.001	15.639 ± 0.001	38.413 ± 0.003	1.175 ± 0.000	2.091 ± 0.000
1302	0.35	0.056	0.92	97.5	0.739	11.85	0.33	3.27	18.400 ± 0.001	15.635 ± 0.001	38.429 ± 0.003	1.177 ± 0.000	2.089 ± 0.000
1291	0.35	0.049	0.93	97.5	1.751	39.70	0.67	35.32	18.370 ± 0.001	15.639 ± 0.001	38.413 ± 0.003	1.175 ± 0.000	2.091 ± 0.000
1279	0.35	0.040	0.94	98.6	0.569	11.96	0.22	4.92	18.400 ± 0.001	15.635 ± 0.001	38.429 ± 0.003	1.177 ± 0.000	2.089 ± 0.000
1267	0.35	0.048	0.94	99.3	0.509	17.09	0.16	4.52	18.370 ± 0.001	15.639 ± 0.001	38.413 ± 0.003	1.175 ± 0.000	2.091 ± 0.000
1256	0.35	0.037	0.94	99.2	0.353	14.73	0.14	3.11	18.400 ± 0.001	15.635 ± 0.001	38.429 ± 0.003	1.177 ± 0.000	2.089 ± 0.000

Table 3 continued

Cal. year AD	Sedimentation rate (cm year ⁻¹)	Dry bulk density (g cm ⁻³)	%H ₂ O	Ash content (%)	As	Pb	Sb	Zn	²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁷ Pb/ ²⁰⁴ Pb	²⁰⁸ Pb/ ²⁰⁴ Pb	²⁰⁶ Pb/ ²⁰⁷ Pb	²⁰⁸ Pb/ ²⁰⁶ Pb
1244	0.35	0.044	0.94	99.5	0.407	17.18	0.09	3.55					
1233	0.35	0.043	0.94	99.1	0.311	10.69	0.10	3.78	18.372 ± 0.001	15.637 ± 0.001	38.384 ± 0.004	1.175 ± 0.000	2.089 ± 0.000
1221	0.35	0.040	0.94	99.6	0.328	11.99	0.07	3.94					
1210	0.35	0.042	0.94	99.3	0.280	10.59	0.08	2.77	18.435 ± 0.001	15.631 ± 0.001	38.412 ± 0.003	1.179 ± 0.000	2.084 ± 0.000
1195	0.35	0.039	0.94	99.7	0.349	13.23	0.07	3.14					
1181	0.35	0.022	0.97	99.5	0.301	13.71	0.09	2.84	18.549 ± 0.001	15.635 ± 0.001	38.524 ± 0.003	1.186 ± 0.000	2.077 ± 0.000
1166	0.35	0.043	0.94	99.4	0.625	13.63	0.15	2.96					
1152	0.35	0.039	0.94	99.2	0.605	12.93	0.18	3.01	18.621 ± 0.001	15.637 ± 0.001	38.592 ± 0.003	1.191 ± 0.000	2.072 ± 0.000
1104	0.09	0.035	0.95	99.0	0.625	14.77	0.17	3.06					
1047	0.09	0.093	0.90	95.1	0.764	8.39	0.28	3.29	18.618 ± 0.001	15.643 ± 0.001	38.629 ± 0.003	1.191 ± 0.000	2.075 ± 0.000
990	0.09	0.075	0.91	99.5	0.379	3.47	0.09	3.59					
934	0.09	0.041	0.94	99.5	0.249	2.18	0.12	< LoD	18.549 ± 0.004	15.643 ± 0.003	38.577 ± 0.007	1.186 ± 0.000	2.080 ± 0.000
877	0.09	0.050	0.94	99.2	0.376	1.86	0.05	2.84					
821	0.09	0.036	0.95	99.0	0.233	2.09	0.05	< LoD	18.521 ± 0.003	15.649 ± 0.002	38.562 ± 0.0056	1.184 ± 0.000	2.082 ± 0.000
764	0.09	0.027	0.95	99.2	0.326	1.96	0.05	3.13					
707	0.09	0.035	0.95	99.3	0.229	1.90	0.06	< LoD	18.550 ± 0.002	15.651 ± 0.002	38.581 ± 0.006	1.185 ± 0.000	2.080 ± 0.000
654	0.10	0.032	0.96	99.7	0.226	1.18	0.04	2.62					
612	0.10	0.030	0.95	99.0	0.171	9.17	0.06	< LoD	18.588 ± 0.003	15.649 ± 0.003	38.592 ± 0.008	1.188 ± 0.000	2.076 ± 0.000

Ash content was determined as follows: after drying at 105 °C for 20 h, the samples were weighted and burned at 550 °C for 4 h (Heiri et al. 2001). The loss of mass represents the ash content (Table 3).

Carbon (C) and nitrogen (N) contents were determined by a VarioMAX CNS analyzer (Elementar) on dried sub-samples (Fig. S1). Two measurements were performed on the sample every ten measurements to check the analyses.

Statistical analyses

Pollen diversity (Fig. S1) was estimated by rarefaction analysis (Birks and Line 1992) using the “vegan” R package (Oksanen et al. 2012). This method standardizes sample size and does not consider the abundance of different pollen types. Statistical analyses were performed using the R (ver 3.2.2) statistical software (R Core Team 2014).

RESULTS

Chronology and core characteristics

The 200-cm-long sequence covered approximately the past 1300 years (Table 1, Fig. 2a, b). The high-temporal resolution used allows covering from 5 to 20 years with a sample, according to the sedimentation rate (Table 3). The lithology is composed of active *Sphagnum* peat on the 15 upper cm and decomposed peat until 150 cm, where gyttja (dark peat) is present until 165 cm. Then, a clayish layer is observed on 8 cm. Decomposed peat forms the deeper 27 cm. Samples were highly organic, with ash contents ranging from 93 to 99.7% (Table 3).

Palynological diagram

Three major PAZs were defined, and some supplementary sub-zones were added by visual inspection of the diagram.

PAZ 1 was composed of two sub-zones (Fig. 3). PAZ 1a from cal. AD 592–800 had dominance of tree taxa at 90% with *Fagus*, *Alnus*, *Abies*, and *Carpinus* as major taxa. Some crop indicators were present with *Vitis*, *Cerealia* type and *Cannabis/Humulus*, as well as ruderal taxa, e.g., *Plantago lanceolata*, *Rumex*, or *Artemisia* (Fig. 3). The main change in PAZ 1b, from cal. AD 800–1000, was an increase of *Abies* up to 30%.

PAZ 2 was composed of five sub-zones. PAZ 2a, from cal. AD 1000–1150, was characterized by an increase in pollen accumulation rate from 5000 to 20 000 grains cm⁻² year⁻¹. Tree taxa slightly decreased at 70% due to *Abies*, *Alnus*, and *Carpinus*, but *Fagus* increased (Fig. 3). Herb taxa, crop

indicators, and ruderal taxa increased with the appearance of *Centaurea cyanus*. Ericaceae showed a brief peak up to 15%.

During PAZ 2b, from cal. AD 1150–1450, *Carpinus* and *Abies* decreased to its minimum value, lower than 5% representation, whereas *Betula* and *Corylus* increased. Tree taxa were in average at 65%. *Vitis* is continuously recorded during this zone. The pollen accumulation rate decreased and was in average 7000 grains cm⁻² year⁻¹. Ericaceae and *Sphagnum* reached high values.

PAZ 2c, from cal. AD 1450–1600, showed an increase of *Carpinus* and *Betula*, whereas *Fagus* decreased. However, the representation of tree and herb taxa remained stable. *Centaurea jacea* and *Vitis* disappeared and monolet spores decreased (Fig. 3).

PAZ 2d, from cal. AD 1600–1650, was marked by an increase of *Fagus* and a decrease of *Betula* and *Corylus*. The percent of tree taxa remained stable. Ruderal taxa increased with *Rumex* and *P. lanceolata*.

PAZ 2e, from cal. AD 1650–1850, showed the general decrease of arboreal taxa until cal. AD 1750 from 70 to 55% representation. Decreasing rates of *Fagus* (from 60 to 20%) were followed by the rise of *Quercus* and *Pinus* up to 10% representation. *Abies* slightly increased up to 10% representation. Tree taxa recovered up to 70% representation from cal. AD 1750–1850. Peaks of *Cannabis/Humulus* were noted, as the increase of ruderal taxa, e.g., *Rumex*, *P. lanceolata*, or Urticaceae.

PAZ 3 could be separated in two sub-zones. PAZ 3a, from cal. AD 1850–1950, was characterized by the decrease of *Fagus* to 10% representation and of arboreal taxa until 50%, whereas *Picea* and *Fraxinus* significantly increased (Fig. 3). *Cannabis/Humulus* sharply decreased while *Cerealia* type increased, as *P. lanceolata* or *Rumex* (Fig. 3). A peak of Cyperaceae was noted, corresponding to a sharp increase of the pollen accumulation rate, whereas trilete spores decreased.

The last sub-zone, PAZ 3b from cal. AD 1950 to present days, showed an increase of arboreal taxa at 85% principally with *Carpinus*, *Picea*, *Fraxinus*, and a last increase of *Fagus* up to 20% representation (Fig. 3). Crop indicators disappeared and herb and ruderal taxa decreased (Fig. S1).

Geochemical analyses

Trace metal analyses: Concentrations, ARs, and EFs

Due to its role as a major element, Fe could not be chosen to trace past mining activities in the Bruche valley, so four TMs, arsenic (As), Pb, antimony (Sb), and zinc (Zn), were chosen according to their presence in numerous exploited ores. Concentrations varied from 0.17 to 7.15 µg g⁻¹ for As, from 1.18 to 180 µg g⁻¹ for Pb, from 0.04 to 4.12 µg g⁻¹ for Sb, and they were up to 136 µg g⁻¹ for Zn (Table 3).

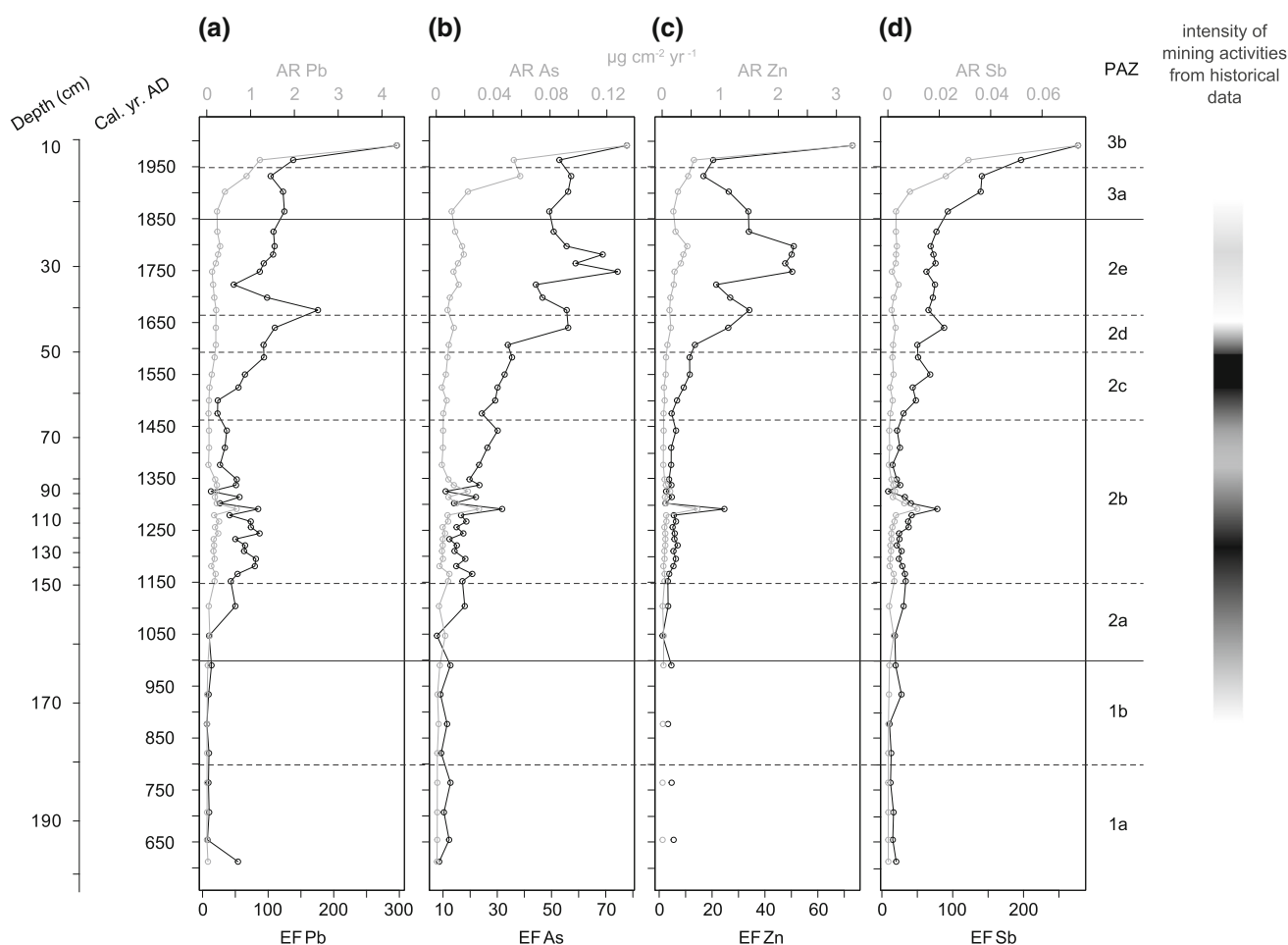


Fig. 4 Accumulation rates (ARs, gray lines, $\mu\text{g cm}^{-2} \text{ year}^{-1}$) and enrichment factors (EFs, black lines) of **a** Pb, **b** As, **c** Zn, and **d** Sb. Pollen assemblage zones (PAZs) defined in the palynological diagram are reported, as the intensity of local mining activities from historical data (Leybold 1996): black color means high intensity and white color means absence of mining

The ARs for the four chosen TMs had similar pattern until cal. AD 1400 (Fig. 4). One point dated from cal. AD 1300 had higher ARs for the four TMs. Concerning Pb, the ARs were stable between cal. AD 1400 and cal. AD 1550 at $0.04 \mu\text{g cm}^{-2} \text{ year}^{-1}$ and then increased at $0.2 \mu\text{g}_{\text{Pb}} \text{ cm}^{-2} \text{ year}^{-1}$ until cal. AD 1650 (Fig. 4a). Lead ARs then decreased until cal. AD 1750. A sharp increase was measured to the top of the sequence at $2.6 \mu\text{g}_{\text{Pb}} \text{ cm}^{-2} \text{ year}^{-1}$ (Fig. 4a). For the three other TMs, As (Fig. 4b), Zn (Fig. 4c), and Sb (Fig. 4d), the increase of the ARs was more progressive at cal. AD 1500–1550 with no decrease in cal. AD 1650.

Lead and Sb EFs were in the same range along the core, i.e., between 5 and 300, whereas those of As and Zn were comprised between 0 and 80 (Fig. 4). Enrichment factors remained low and stable for the four TMs from cal. AD 600–1000 and then increased until cal. AD 1300 at approximately 80 for Pb, 40 for Sb, 20 for As, and 6 for Zn (Fig. 4). After cal. AD 1300, a progressive increase was

noted up to 70 and 300 for As and Pb, respectively (Fig. 4). Arsenic and Zn had the same pattern of EFs: an increase from cal. AD 1400–1800, followed by a decrease and a sharp increase for the more recent point analyzed at cal. AD 1991 (Fig. 4).

Lead isotope analyses

Lead emitted by mining and smelting activities from the Vosges Mountains is considered to come from the three types of ores already known to be exploited in the mountains, namely “A”, corresponding to high-temperature deposits ($^{206}\text{Pb}/^{207}\text{Pb} \sim 1.1625 \pm 0.0034$), “B” consisting in F/Ba and Ag/Pb veins and presenting the most radiogenic isotopic compositions ($^{206}\text{Pb}/^{207}\text{Pb} \sim 1.200 \pm 0.0108$), and the Lusse type, which is intermediate between the two previous ones ($^{206}\text{Pb}/^{207}\text{Pb} \sim 1.171$; Marcoux 1987).

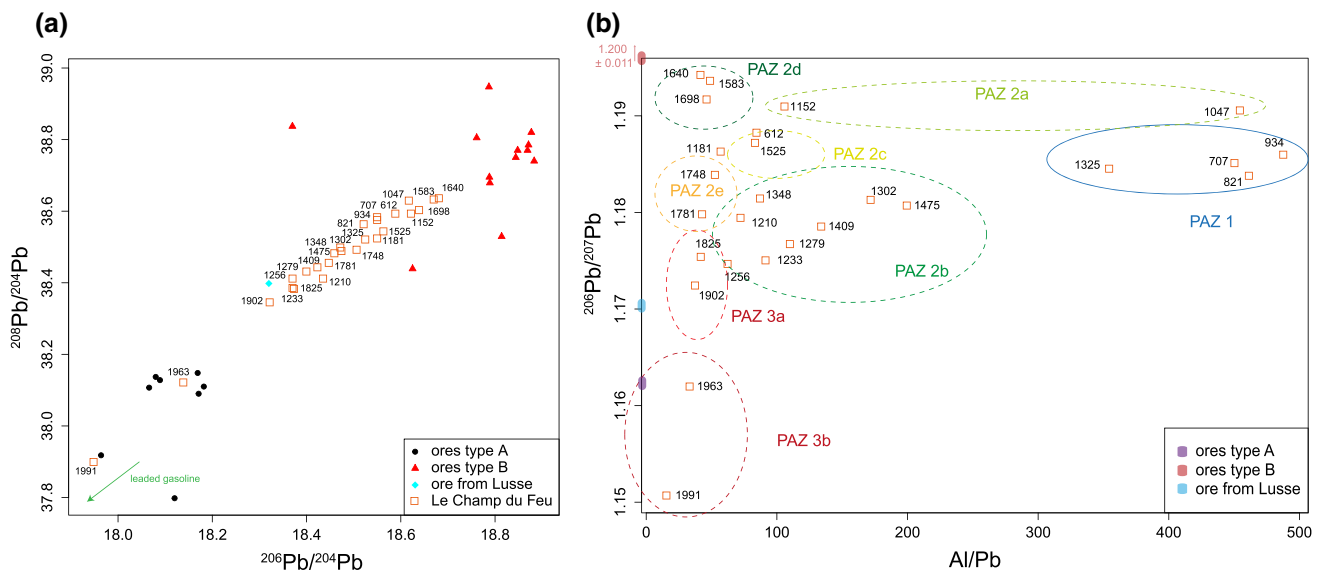


Fig. 5 **a** Biplot of $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$. Lead isotopic composition of the three types of ores are given by Forel et al. (2010). Numbers represent the calibrated years AD. **b** $^{206}\text{Pb}/^{207}\text{Pb}$ versus Al/Pb mixing diagram. Numbers represent the calibrated years AD. Pollen assemblage zones (PAZs) defined in the palynological diagram are reported by colored circles

The $^{206}\text{Pb}/^{207}\text{Pb}$ ratio varied from 1.188 to 1.190 between cal. AD 600–1100 and then decreased until cal. AD 1200 at 1.175 (Table 3, Fig. 3). An increasing peak was noted between cal. AD 1200 and 1400 at 1.185. The isotope ratio increased newly after cal. AD 1400 at 1.194 until cal. AD 1650, at which point, a sharp decrease is noted until present days at 1.150 (Table 3, Fig. 3).

Biplot of $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ showed that the samples, except the two most recent, have a Pb isotopic composition between those of two types of Pb ores known in the Vosges Mountains (ores of types A and B; Fig. 5a). Samples dated from cal. AD 1963 and 1991 had less radiogenic ratios, approaching those of leaded gasoline (Fig. 5a). The biplot of $^{206}\text{Pb}/^{207}\text{Pb}$ versus Al/Pb highlights that the PAZs established in the palynological diagram correspond to different patterns of Pb contamination: almost three different groups of similar isotopic compositions could be identified (Fig. 5b). Pollen assemblage zones 1, 2a, 2c, and 2d had an isotopic composition corresponding to a mixing of sources with a dominance of ores of type B (Fig. 5b). The group of PAZs 2b, 2e, and 3a had an isotopic composition corresponding to a mixing with a dominance of ore from Lusse (Fig. 5b). PAZ 3b corresponded to the dominance of an isotopic composition of leaded gasoline and industrial activities, with $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of 1.0839 ± 0.0096 and 1.1495 ± 0.0050 , respectively (Monna et al. 1997) (Fig. 5a).

DISCUSSION

From cal. AD 600–1000: Low human impact on ecosystem

The landscape is composed by a mixed forest: the pollen assemblage is part of the regional palynostratigraphic zone composed by *Fagus*, *Abies*, *Carpinus*, *Juglans*, and *Castanea* (de Klerk 2014). The core studied by Sudhaus and Friedmann (2015) in the Rond Pertuis supérieure, a peat bog situated at 12 km in the west of the Le Champ du Feu (Fig. 1b), highlights a similar landscape dominated by *Fagus* and *Abies* and a low representation of crop indicators. This time period, called the Migration Period at the transition of the Roman Times and the beginning of the Middle Ages, is defined by low human occupation and politic instability in this region (Fluck 2000). Trace metal emissions were low and crop activities were scarce, but there were the dominant activities of local populations, who were primarily farmers (Leypold 1996). Since cal. AD 800, the increase of *Abies* and the decline of herb taxa observed could traduce a forest recovery on the summits potentially due to a lowered human exploitation and a decline of pastoralism.

Compared to the two sequences from ombrotrophic peat bogs that are available in the Vosges Mountains (Gazon-du-Faing and Rossely; Forel et al. 2010; Fig. 1a), the

concentrations of Pb are similar, i.e., between 1 and 3 $\mu\text{g g}^{-1}$. The $^{206}\text{Pb}/^{207}\text{Pb}$ ratios presented the same pattern and similar values as in Gazon-du-Faing and Rossely; thus, the regional TM record is similar between the north and the south of the Vosges Mountains between the seventh and the eleventh centuries, confirming the low global industrial activity in the region (Fluck 2000).

From cal. AD 1000–1150: Increase of crop activities and TM contamination

The small increase of TM ARs, which corresponds to a high increase of EFs particularly for Pb, attests to the onset of industrial activities at the regional scale, as showed also by Forel et al. (2010). The corresponding increase of $^{206}\text{Pb}/^{207}\text{Pb}$ ratio was also registered in Gazon-du-Faing with similar Pb isotopic compositions ($^{206}\text{Pb}/^{207}\text{Pb} \approx 1.18\text{--}1.19$). This could be due to change in the mixing sources and the higher input of Pb from ores of type B. Indeed, from the study of a nearby minerotrophic marsh at Le Hury site (Fig. 1a), Mariet et al. (2016) attested that mining activities began around cal. AD 900 in the former mining district of Sainte-Marie-aux-Mines, where this type of ore was exploited (Fluck 2000).

This time period corresponds to an abrupt decrease of *Abies*, never recovering the high values recorded before cal. AD 1000. This is certainly due to a common practice of slash-and-burn in large areas (Garnier 2000), which contributed to the extinction of *Abies* at this altitudinal stage and to the peak of Ericaceae, known to be favored after burning. *Fagus* was not concerned by this deforestation for farming in lower altitudes. Moreover, human pressure is also indicated by the substantial increase of crop indicators, particularly *Cerealia* type and also by the presence of *Vitis* and *C. cyanus*, the latter indicating very local crops. This opening could be explained by (i) the development of crop areas for the food needs of increasing population, and (ii) considerable wood consumption for poly-metallic mining exploitation during the twelfth century, known as a renewal period for mining activities (Leybold 1996). The Rond Pertuis supérieure record showed an opposite pattern with a definitive decline of *Fagus* at around AD 1000, whereas *Abies* presented a temporary decline at around AD 1150 (Sudhaus and Friedmann 2015). The two closed peat bogs of Le Champ du Feu and Rond Pertuis supérieure were situated at 1049 and 690 m a.s.l., respectively. The clearing of the landscape is obvious around the two peat bogs because of mining and crop activities, but the species affected by the deforestation are not the same. This is due to a different local composition of woodland, which is a function of the altitudinal gradient.

From cal. AD 1150–1450: A changing period during the Middle Ages

A sharp decrease of *Fagus* was registered after cal. AD 1150, while an increase of pioneer taxa, such as *Betula* and *Corylus*, is noted. This openness of the landscape in the Bruche valley corresponds to the decrease of *Abies* registered in the Rond Pertuis supérieure peat bog for the same period (Sudhaus and Friedmann 2015). Trace metal emissions increased during cal. AD 1000–1350 and the impact of mining seems to be higher since cal. AD 1150 when the landscape was opening for high needs of wood. The development of Fe mining in the Bruche valley since the thirteenth century, as attested by the documentation of the first blast furnace (Fig. 1b; Leybold 1996), most likely contributed to these events. In addition to mining activities, increasing rates of *Cannabis/Humulus* could be related to the development of textile industry, as identified by Sudhaus and Friedmann (2015) near the Bruche valley. Since cal. AD 1300, the decrease of TM contamination, coupled with the recovery of *Fagus*, was observed in other peat bogs at a regional scale and is certainly due to the Black Plague, successive famines, and the Hundred Year's War (Fluck 2000; Forel et al. 2010). The palynological picture of the landscape also reflects the forest management with certain slash-and-burn on small surfaces in summits, contributing to the several peaks of Ericaceae. This indicates pasture woodland, with constant values of ruderal indicators, while crops certainly decreased in high altitude. In Sweden, Fe mining was related to increase of crops and ruderal taxa also due to the presence of pasture woodlands during the same time period (Karlsson et al. 2016).

Mixing sources of Pb changed several times during the Middle Ages, with shifts between contribution of ores of type A and Lusse, and those of ores of type B when TM contamination is the highest (Fig. 5). It highlights the highly changing period with an alternation of decline and recovery of industrial activities because of epidemics and wars (Fluck 2000). These events have also contributed to an alternative exploitation of different ore types. This regional disorganization of industrial activities was also detectable in Rossely with similar isotopic pattern (Forel et al. 2010).

From cal. AD 1450–1600: Major phase of Fe mining activities

Contamination by TMs, particularly As, Pb, and Zn, increased sharply during the sixteenth century, when the peak of Fe mining activities was reached in the Bruche valley (Fig. 1b; Leybold 1996). The more radiogenic Pb composition of samples belonging to this phase (Fig. 5b) is probably

due to the increased exploitation of ores of type B. In Gazon-du-Faing and Rossely sites, the Pb isotopic composition became less radiogenic (Forel et al. 2010). This difference between Le Champ du Feu and the two other peat bogs highlights a change in mixing TM sources over this period in the Vosges Mountains between the north and the south.

The decrease of *Fagus* has to be linked to its increasing use in blast furnaces because of the intensification of local mining (Leypold 1996). Indeed, mainly *Fagus*, *Quercus*, and *Betula* charcoals were used for blast furnaces, whereas mainly *Abies* charcoals were used for Fe refining and shaping in forges (Leypold 1996). Moreover, *Fagus* was the main taxa found in charcoal kilns in the Vosges Mountains and was widely used due to its high combustion temperature for smelting process (Nölken 2005). The pollen record showed a cutting of *Fagus* in the valley but the impact of mining activities on the forest cover was less than expected, as already shown in this region in the former mining district of Sainte-Marie-aux-Mines (Mariet et al. 2016). This could be due to the unequal distribution of forest plots between mining concessions according to their fuel needs. The absence of large deforestation was also noted in other sequences in Europe during phases of mining. In Austria, Viehweider et al. (2015) explained the slightest impact of mining on forest cover by forest management, sufficient supply of wood for smelting, or wood import. Even if it was lowest than presumed, the decrease of tree taxa is recognized during mining and has been demonstrated in other historical mining sites in the Cévennes (Baron et al. 2005) or in the Morvan (Jouffroy-Bapicot et al. 2007) in France with selective cutting of *Fagus* and *Betula*, while Karlsson et al. (2015) do not show selection of trees for mining in Sweden. A forest succession is observed in Le Champ du Feu during this period by the increasing representation of *Betula* and *Corylus*, as heliophilous and pioneer taxa, indicating the potential forest management of exploited areas for forest turnover (Garnier 2000). However, the landscape seems to have homogenized by the decrease of pollen diversity due to a high pressure on the forested ecosystem.

From cal. AD 1600–1650: The impact of the Thirty Years War

Trace metal emissions still increase after a slight plateau around cal. AD 1600, reaching a peak at the end of the zone, with more radiogenic Pb showing the increasing exploitation of, certainly, ores of type B. A lack of wood in AD 1609 near Schirmeck was described in the literature that contributed to the stop of the blast furnace (Leypold 1996), whereas the pollen arboreal taxa were higher than 70% representation, highlighting the presence of forested areas in the valley. During this short time period, a new change

in forest composition is noted with the recovery of *Fagus* instead of *Betula*. Compared to the previous period, the change in forest composition highlights the recovery of the forest while TM contamination is increasing. This difference of landscape could be explained by regional and/or extra-regional mining that lead to increase TM atmospheric contamination, while the area around Le Champ du Feu is not exploited for wood or farming due to the sharp decline of the population. Indeed, this period is marked by the Thirty Years' War (1618–1648) which was certainly the cause of the decline of mining and crop activities in the Bruche valley (Leypold 1996), observed by the decrease of crop indicators and the disappearance of *C. cyanus* as a proxy of local crops.

From cal. AD 1650–1850: Increasing global anthropogenic pressure

The decrease of TM contamination for Pb, As, and Zn along this phase corresponded to the stop of mining activities in the Vosges Mountains at the end of the seventeenth century due to a regional war called “la guerre des évêques” (Leypold 1996). During this PAZ, variations of ARs were registered but the Pb isotopic composition became less radiogenic (Figs. 4, 5). It indicates a change in sources of TMs with probably the abandonment of exploitation of ores of type B and the increasing contribution of coal combustion in regional industrial activities. The landscape opened until cal. AD 1750 and crops were present in the vicinity of the peat bog with *Cerealialia* type and textile crops with *Cannabis/Humulus*. Indeed, mining activities are replaced by agro-pastoralism and the textile industry in the valley (Leypold 1996). This development of several industrial activities and farming in former mining area during this time period has been also shown in the Pyrenees by Ejarque et al. (2009) where the impact of anthropogenic activities was at their highest level. A change in forest management occurred after the Thirty Years' War due to the establishment of a new law by Colbert in 1669 which wanted to increase wood production for navy yards (Garnier 2000). This law led to the intense cutting of large forested areas which disadvantaged *Fagus* for the benefit of *Quercus* in low altitudes, as shown in the pollen record of Le Champ du Feu. The signal of decreasing local mining activities is perfectly synchronous to the signal of the former mining district of Sainte-Marie-aux-Mines from cal. AD 1650–1750, highlighting the decrease of mining activities at the regional scale (Leypold 1996; Mariet et al. 2016).

After this period of regional decrease of mining, Fe exploitation quickly restarted in the mid-eighteenth century (Leypold 1996) and corresponded to the rapid increase of

TM contamination recorded after cal. AD 1750 in the Le Champ du Feu sequence. Concerning the landscape, *Fagus* continues to decrease slightly, as a result of wood exploitation for mining. The increase of arboreal taxa is due to *Pinus* and *Quercus*, which is recognized as a regional palynological signal in several sequences (Kalis 1984a, b). Indeed, forest management changed and favored species for construction wood rather than for charcoal production. Hence, the expansion of *Pinus* was proven to begin in cal. AD 1700 in the Vosges Mountains due to plantations in valleys (Kalis 1984b).

From cal. AD 1850 to present days: Modern Times

Iron mining activities were stopped in the Bruche valley around AD 1850 because of the impoverishment of ores and lack of competitiveness (Leypold 1996). The first part of this time period, from cal. AD 1850–1950, was marked by a sharp increase of TM emissions due to the chemical industry based on manganese during the nineteenth century in the Bruche valley (Leypold 1996) and by the openness of the landscape. The replacement of *Fagus* by *Picea* and *Pinus* highlights the increase of forestry exploitation with plantations for the production of construction wood. Anthropogenic pressure continued to increase locally with ruderal taxa (*P. lanceolata* and *Rumex*) in expansion related to pastoralism in high altitudes and an increase of human occupation in the valley due to the sharp development of textile industry.

From cal. AD 1950 to the present, a high decrease of anthropogenic pressure on the vegetation was attested, with the abandonment of agro-pastoralism and the increase of forest cover, as characterized by the increase of *Fagus*, *Picea*, and *Pinus* in detriment of *Abies*. This landscape is partly due to plantations of *Pinus* and *Picea* for wood production, which was the first economic resource in the region. Emissions of TMs were recorded until cal. AD 1991, and hence the recent decrease of TMs highlighted in other archives in Europe has not been shown. This decrease, observed at the European scale, corresponds to the end of the Industrial Revolution and the phasing out of leaded gasoline (Renberg et al. 2001).

CONCLUSIONS

The high time resolution of the multi-proxy geochemistry/pollen analysis of the Le Champ du Feu peat bog allows us to identify short phases of local mining compared to other peat records in the region. Indeed, differences in TM emissions and sources are highlighted, showing changes in the mixing sources of TMs over time, which differ from the north to the south, particularly during the main period of Fe

mining activities in the sixteenth century. The influence of several anthropogenic activities is highlighted in the landscape with the chronological contribution first of mining activities and agro-pastoralism until the seventeenth century, then of textile industry, and, finally, of forestry since the nineteenth century. While mining led mainly to *Fagus* cutting in low altitudes, agro-pastoralism led to *Abies* deforestation and contributed to its erasure around the tenth century in high altitudes. A local impact of mining on the landscape could be identified with (i) forest management for forest recovery and (ii) the homogenization of the landscape because of the high anthropogenic pressure.

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REFERENCES

- Appleby, P.G., and F. Oldfield. 1978. The calculation of lead-210 dates assuming a constant rate of supply of unsupported ^{210}Pb to the sediment. *CATENA* 5: 1–8. [https://doi.org/10.1016/S0341-8162\(78\)80002-2](https://doi.org/10.1016/S0341-8162(78)80002-2).
- Baron, S., M. Lavoie, A. Ploquin, J. Carignan, M. Pulido, and J.-L. de Beaulieu. 2005. Record of metal workshops in peat deposits: History and environmental impact on the Mont Lozère Massif, France. *Environmental Science and Technology* 39: 5131–5140.
- Beug, H.-J. 1961. Leitfaden der Pollenbestimmung für Mitteleuropa und angrenzende Gebiete (in German).
- Bindler, R., and J. Rydberg. 2015. Revisiting key sedimentary archives yields evidence of a rapid onset of mining in the mid-13th century at the Great Copper Mountain, Falun, Sweden: Mining at Great Copper Mountain, Falun, Sweden. *Archaeometry* 58: 642–658. <https://doi.org/10.1111/arc.12192>.
- Birks, H.J.B., and J.M. Line. 1992. The use of rarefaction analysis for estimating palynological richness from quaternary pollen-analytical data. *The Holocene* 2: 1–10. <https://doi.org/10.1177/095968369200200101>.
- Blaauw, M. 2010. Methods and code for “classical” age-modelling of radiocarbon sequences. *Quaternary Geochronology* 5: 512–518. <https://doi.org/10.1016/j.quageo.2010.01.002>.
- Breitenlechner, E., G. Goldenberg, J. Lutz, and K. Oeggl. 2013. The impact of prehistoric mining activities on the environment: a multidisciplinary study at the fen Schwarzenbergmoos (Brixlegg, Tyrol, Austria). *Vegetation History and Archaeobotany* 22: 351–366. <https://doi.org/10.1007/s00334-012-0379-6>.
- Carignan, J., P. Hild, and G. Mevelle. 2001. Routine analyses of trace elements in geological samples using flow injection and low pressure on-line liquid chromatography coupled to ICP-MS: A study of geochemical reference materials. *Geostandards Newsletter* 25: 187–198.
- Cloquet, C., J. Carignan, and G. Libourel. 2006. Atmospheric pollutant dispersion around an urban area using trace metal concentrations and Pb isotopic compositions in epiphytic

- lichens. *Atmospheric Environment* 40: 574–587. <https://doi.org/10.1016/j.atmosenv.2005.09.073>.
- Cloquet, C., N. Estrade, and J. Carignan. 2015. Ten years of elemental atmospheric metal fallout and Pb isotopic composition monitoring using lichens in northeastern France. *Comptes Rendus Geoscience* 347: 257–266. <https://doi.org/10.1016/j.crte.2015.04.003>.
- de Klerk, P. 2014. Palynological research of the Vosges Mountains (NE France): A historical overview. *Carolinea* 72: 15–39.
- De Muynck, D., C. Cloquet, E. Smits, F.A. de Wolff, G. Quitté, L. Moens, and F. Vanhaecke. 2007. Lead isotopic analysis of infant bone tissue dating from the Roman era via multicollector ICP–mass spectrometry. *Analytical and Bioanalytical Chemistry* 390: 477–486. <https://doi.org/10.1007/s00216-007-1679-z>.
- Ejarque, A., R. Julià, S. Riera, J.M. Palet, H.A. Orenge, Y. Miras, and C. Gascón. 2009. Tracing the history of highland human management in the eastern Pre-Pyrenees: an interdisciplinary palaeoenvironmental study at the Pradell fen, Spain. *The Holocene* 19: 1241–1255. <https://doi.org/10.1177/0959683609345084>.
- Faegri, K., and J. Iversen. 1989. *Textbook of pollen analysis*. IV edition by K. Faegri, PE Kaland & K. Chichester: Krzywinski. Wiley.
- Fluck, P. 2000. *Sainte-Marie-aux-Mines ou Les mines du rêve. Une monographie des mines d'argent*. Soultz: Les Editions du Patrimoine Minier (in French).
- Fluck, P., and B. Ancel. 1989. Le paysage minier des sites métalliques des Vosges et de la Forêt-Noire. *Annales de Bretagne et des Pays de l'Ouest* 96: 183–201. <https://doi.org/10.3406/abpo.1989.3323> (in French).
- Forel, B., F. Monna, C. Petit, O. Bruguier, R. Losno, P. Fluck, C. Begeot, H. Richard, et al. 2010. Historical mining and smelting in the Vosges Mountains (France) recorded in two ombrotrophic peat bogs. *Journal of Geochemical Exploration* 107: 9–20. <https://doi.org/10.1016/j.gexplo.2010.05.004>.
- Garnier, E. 2000. Les forêts vosgiennes à l'épreuve des tempêtes sous l'Ancien Régime (XVIIe et XVIIIe siècles). *Revue Géographique de l'Est* 40 (in French).
- Grimm, E.C. 1987. CONISS: a FORTRAN 77 program for stratigraphically constrained cluster analysis by the method of incremental sum of squares. *Computers & Geosciences* 13: 13–35. [https://doi.org/10.1016/0098-3004\(87\)90022-7](https://doi.org/10.1016/0098-3004(87)90022-7).
- Grimm, E.C. 1991. *TILIA and TILIA*GRAPH*.
- Heiri, O., A.F. Lotter, and G. Lemcke. 2001. Loss on ignition as a method for estimating organic and carbonate content in sediments: Reproducibility and comparability of results. *Journal of Paleolimnology* 25: 101–110. <https://doi.org/10.1023/A:1008119611481>.
- Jouffroy-Bapicot, I., M. Pulido, S. Baron, D. Galop, F. Monna, M. Lavoie, A. Ploquin, C. Petit, et al. 2007. Environmental impact of early palaeometallurgy: Pollen and geochemical analysis. *Vegetation History and Archaeobotany* 16: 251–258. <https://doi.org/10.1007/s00334-006-0039-9>.
- Kalis, A.J. 1984a. *Forêt de la Bresse, (Vogesen), végétatiekundige en pollenanalytische onderzakingen naar de bosgeschiedenis van een centraal-europees middelgebergte*.
- Kalis, A.J. 1984b. Un miroir éloigné : les défrichements anthropogènes dans les zones de basse altitude, réfléchis dans des diagrammes polliniques montagnards. *CNRS Centre de Recherches Archéologiques NOTES Monographiques Techniques N°17* (in French).
- Karlsson, J., J. Rydberg, U. Segerström, E.-V. Nordström, P. Thöle, H. Biester, and R. Bindler. 2016. Tracing a bog-iron bloomery furnace in an adjacent lake-sediment record in Angersjö, central Sweden, using pollen and geochemical signals. *Vegetation History and Archaeobotany* 25: 569–581. <https://doi.org/10.1007/s00334-016-0567-x>.
- Karlsson, J., U. Segerström, A. Berg, N. Mattielli, and R. Bindler. 2015. Tracing modern environmental conditions to their roots in early mining, metallurgy, and settlement in Gladhammar, southeast Sweden: Vegetation and pollution history outside the traditional Bergslagen mining region. *The Holocene* 25: 944–955. <https://doi.org/10.1177/0959683615574586>.
- Kreiser, A.M., N.J. Anderson, P.G. Appleby, R.W. Battarbee, S.T. Patrick, B. Rippey, and N.L. Rose. 1992. *A paleolimnological study of water quality of lakes in Vosges Mountains of France*. Report to the University of Bordeaux by ENSIS Ltd, London.
- Leybold, D. 1996. *La métallurgie du fer dans le massif vosgien. La vallée de la Bruche de l'antiquité au XIXe siècle*. Collection “Recherches et documents.” Société Savante d'Alsace (in French).
- Manhès, G., C.J. Allègre, B. Dupré, and B. Hamelin. 1980. Lead isotope study of basic-ultrabasic layered complexes: Speculations about the age of the Earth and primitive mantle characteristics. *Earth and Planetary Science Letters* 47: 370–382.
- Marcoux, E. 1987. *Isotopes du plomb et paragenèses métalliques. Traceurs de l'histoire des gîtes minéraux*. Document du BRGM, No. 117 (in French).
- Mariet, A.-L., C. Bégeot, F. Gimbert, J. Gauthier, P. Fluck, and A.-V. Walter-Simonnet. 2016. Past mining activities in the Vosges Mountains (eastern France): Impact on vegetation and metal contamination over the past millennium. *The Holocene* 26: 1225–1236. <https://doi.org/10.1177/0959683616638419>.
- Mighall, T., S. Timberlake, A. Martínez-Cortizas, N. Silva-Sánchez, and I.D.L. Foster. 2017. Did prehistoric and Roman mining and metallurgy have a significant impact on vegetation? *Journal of Archaeological Science* 11: 613–625.
- Monna, F., J. Lancelot, I.W. Croudace, A.B. Cundy, and J.T. Lewis. 1997. Pb isotopic composition of airborne particulate material from France and the southern United Kingdom: Implications for Pb pollution sources in urban areas. *Environmental Science and Technology* 31: 2277–2286.
- Moore, P.D., J.A. Webb, and M.E. Collinson. 1991. *Pollen analysis*, 2nd ed. Oxford: Blackwell.
- Nölken, W. 2005. *Holzkohleanalytische Untersuchungen zur Waldgeschichte der Vogesen*. Dissertation zur Erlangung der Doktorwürde der Fakultät für Biologie der Albert-Ludwigs-Universität Freiburg i. Br (in German).
- Nriagu, J.O. 1996. History of global metal pollution. *Science* 272: 223.
- Oksanen, J., G. Blanchet, R. Kindt, P. Legendre, R. O'Hara, G. Simpson, P. Solymos, H. Stevens, et al. 2012. *Vegan: Community ecology package*. R package version 1.17-11.
- Punt, W. 1976. *Northwest European pollen flora*, vol. I. Amsterdam: Elsevier.
- Punt, W., S. Blackmore, and G.C.S. Clarke. 1988. *Northwest European pollen flora*, vol. V. Amsterdam: Elsevier.
- Punt, W., and G.C.S. Clarke. 1980. *Northwest European pollen flora*, vol. II. Amsterdam: Elsevier.
- Punt, W., and G.C.S. Clarke. 1981. *Northwest European pollen flora*, vol. III. Amsterdam: Elsevier.
- Punt, W., and G.C.S. Clarke. 1984. *Northwest European pollen flora*, vol. IV. Amsterdam: Elsevier.
- R Core Team. 2014. R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. <http://www.Rproject.org>.
- Reille, M. 1992. *Pollen et spores d'Europe et d'Afrique du Nord*. Laboratoire de botanique historique et palynologie, URA CNRS 1152.
- Reille, M. 1995. *Pollen et spores d'Europe et d'Afrique du Nord: supplément I*. Marseille: Laboratoire de Botanique Historique et Palynologie.

- Renberg, I., R. Bindler, and M.-L. Brännvall. 2001. Using the historical atmospheric lead-deposition record as a chronological marker in sediment deposits in Europe. *The Holocene* 11: 511–516. <https://doi.org/10.1191/095968301680223468>.
- Servera Vives, G., Y. Miras, S. Riera, R. Julià, P. Allée, H. Orengo, S. Paradis-Grenouillet, and J. Maria Palet. 2014. Tracing the land use history and vegetation dynamics in the Mont Lozère (Massif Central, France) during the last 2000 years: The interdisciplinary study case of Countrasts peat bog. *Quaternary International* 353: 123–139.
- Sudhaus, D., and A. Friedmann. 2015. Holocene vegetation and land use history in the northern Vosges (France). *Quaternary Science Journal* 64: 55–66.
- Thirlwall, M.F. 2002. Multicollector ICP-MS analysis of Pb isotopes using a ^{207}Pb - ^{204}Pb double spike demonstrates up to 400 ppm/amu systematic errors in Tl-normalization. *Chemical Geology* 184: 255–279. [https://doi.org/10.1016/S0009-2541\(01\)00365-5](https://doi.org/10.1016/S0009-2541(01)00365-5).
- Viehweider, B., J. Lutz, and K. Oeggl. 2015. Late-Holocene land use changes caused by exploitation in the mining region of Kitzbühel (Tyrol, Austria). *Vegetation History and Archaeobotany* 24: 711–729. <https://doi.org/10.1007/s00334-015-0527-x>.
- von Eller, J.P., J.G. Blanalt, and P. Ham. 1970. Carte et notice géologiques de la France à 1/50 000, n°307 Sélestat. Edition du BRGM (in French).
- Wedepohl, K.H. 1995. The composition of the continental crust. *Geochimica et Cosmochimica Acta* 59: 1217–1232. [https://doi.org/10.1016/0016-7037\(95\)00038-2](https://doi.org/10.1016/0016-7037(95)00038-2).
- Weiss, D., W. Shotyk, P.G. Appleby, J.D. Kramers, and A.K. Cheburkin. 1999. Atmospheric Pb deposition since the industrial revolution recorded by five swiss peat profiles: Enrichment factors, fluxes, isotopic composition, and sources. *Environmental Science and Technology* 33: 1340–1352. <https://doi.org/10.1021/es980882q>.
- White, W.M., F. Albarède, and P. Télouk. 2000. High-precision analysis of Pb isotope ratios by multi-collector ICP-MS. *Chemical Geology* 167: 257–270. [https://doi.org/10.1016/S0009-2541\(99\)00182-5](https://doi.org/10.1016/S0009-2541(99)00182-5).
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