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Geochemical and Documentary Topography of a Medieval Silver Valley: Detection of Workshops and Identification of Their Function

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ABSTRACT

This paper presents the interdisciplinary investigation (archaeology, geochemistry, history) of a medieval silver and lead production site located in southern France, in the Minier valley (Occitanie, Aveyron, Le-Viala-du-Tarn). In order to identify the production sites, in situ geochemical surveys were carried out using a portable X-ray fluorescence spectrometer and differential GPS, guided on the analysis of medieval archival sources. The cartographic representation of the metal concentrations in the surface horizons shows significant enrichment of zinc and lead in the vicinity of the mines. This first type of enrichment makes it possible to highlight the activities of separation of sphalerite and silver-bearing galena. The galena thus isolated on the hillsides is then transported to the vicinity of watercourses, where it is crushed, washed, and smelted. These secondary activities result in a last type of enrichment in which only lead is found in large quantities. The cross-referencing of the information made it possible to overcome the challenges related to the location of the mineral processing workshops, which were often invisible on the surface. The medieval workshops have been located and a function suggested, outlining the first trends in the spatial and social division of labour and providing a solid corpus for future archaeological excavations. Finally, this study highlights the persistence of significant metal contamination in the soils of a rural valley and encourages the consideration of former mining areas when examining the environmental impact of metal production.

1 | Introduction

The identification of mineral processing sites, whether in the ore preparation phase or the smelting phase, is often a challenge for those working on ancient metal production. Although mines can be located through geological contexts and indicators, topographical anomalies, or the tailings they produce, mineral and metallurgical workshops that progressively transform ores into metals are sometimes discreet or even invisible on the surface (Stöllner 2014). Locating those sites is nevertheless crucial to

understanding the organization of mining production and documenting the processes used to sort, crush, and also smelt the ore extracted. The discovery of these sites enables in-depth archaeological studies, whether focusing on production techniques or work organization, material tracing, or measuring metallic contamination of the environment (Hrubý 2021; Tolksdorf et al. 2018; Benvenuti et al. 2014; Ploquin et al. 2010).

The aim of this paper is to present and evaluate the advantages of an interdisciplinary approach that allows an efficient

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identification of metal production sites, not only geographically but also functionally and even socially. This approach, which combines geochemistry and history around an archaeological question, has been applied to the Minier valley in southern France (Aveyron, commune of Viala-du-Tarn—Figure 1). During the Central Middle Ages, at least between the 12th and 15th centuries, silver-bearing deposits were exploited to varying degrees for the production of lead and silver (Dossat 1975; Johans 2000; Belmon 2003; Garrigou Grandchamp, Mazeran, and Galès 2013; Bernat 2018). Since 2019, collective research has been carried out in Le Minier valley to shed light on the work of the companies that shared the exploitation of the lead– silver deposits and the riverbanks, which probably led to the establishment of a small settlement in the centre of the valley, supplying the regional metal market and subject to the control and support of the local public authorities (Minvielle Larousse et al. 2019a) (Programme Collectif de Recherche [PCR] of the French Ministry of Culture [DRAC Occitanie]: [https://zenodo.](https://zenodo.org/communities/pcr_minier) [org/communities/pcr_minier](https://zenodo.org/communities/pcr_minier)).

During our surveys, we encountered difficulties in locating the mines tailings and the mineral processing and metallurgy workshops: Some mines were identified, but the tailings were largely covered by vegetation, and no workshops were visible in the field. Neither pedestrian surveys nor the DTM recorded by LIDAR were able to provide any significant clues. However, we knew from medieval documents that this valley contained a large proportion of the workshops necessary for metal production. In principle, the medieval lead–silver production process was divided into several stages. The ore was first extracted from the mines, near which the main taillings (rock and gangue) was deposited. Sufficiently mineralized blocks were recovered to be crushed and sorted in mineral processing workshops (Bailly-Maître 2002; Téreygeol 2019). The aim of this operation is to isolate the silver-bearing minerals and reject the non–silverbearing minerals. Once the silver-bearing minerals had been isolated, they were finely crushed using rock anvils and hammers, then grounded in hydraulic mills (Minvielle Larousse 2019), and finally subjected to hydrogravimetric sorting in basins (Hrubý 2011, 102–129). The ore concentrate obtained could be smelted in metallurgical workshops (Killick 2014). The result of this stage was lead-bearing slag, matte, and lead ingots, in which the silver is concentrated (Baron et al. 2009). This lead was finally treated by cupellation to separate the lead and silver (Téreygeol and Guirado 2012).

The workshops that can be found in a medieval mining area are therefore numerous, especially because they could be duplicated: sorting areas, crushing workshops, mills, washing plants, and foundries (at least for the production of lead ingots). Their common feature is that they produced mineralized wastes that locally contaminated the soil with metallic elements. In order to identify them, geochemical studies based on the in situ use of a pXRF were carried out, combined with a careful reading of an Digital Terrain Model (DTM) recorded by LIDAR and a close commentary on the archival sources.

2 | Historical, Geological, and Geographical Background

2.1 | Production Sites in Archival Sources

In most cases, the topography of a medieval silver production can be partially reconstructed using information from archival sources (Figure 2). The corpus on Le Minier currently contains 114 original, copied, or analysed documents dating from 1150 to 1460. These documents come from the charters of the co-lords

FIGURE 1 | Location of the study area (GIS—N. Minvielle Larousse).

FIGURE 2 | Workshop mentioned in the medieval archives and their function (Data—J. Belmon; GIS—N. Minvielle Larousse).

of Le Minier—the successive counts of Rodez, the count of Toulouse, Alphonse de Poitiers and his successors, and the kings of France—as well as from notarial registers. In addition to its exceptional quantitative importance for a single production area, the corpus has the advantage of covering a very wide typological spectrum. There are princely charters, legal documents, administrative correspondence, administrative acts (surveys, lists, terriers, accounts), and private transactions (Belmon 2003; Minvielle Larousse et al. 2019a).

These documents therefore mention and locate mines, almost all of which are located at the bottom of the western slope of the Minier valley. From north to south, these are the mines of Orzals, Sompa, and Socca, located near the Voltes thanks to the toponyms of the terriers and the land registers; the mine of Roucadou, located near a ravine that still bears this name; the mine of Saliège, located in the Pradal ravine, one of the plots of which still bears its medieval name in the old land register (19th century); the mine of Cantamerle, located to the north of the village and opening onto a cliff of the same name (Vaissière 2011). However, other mines have not yet been precisely located, such as Doulsac, Grand Minier, or a mine exploited in 1452 near a vineyard belonging to Jean Robi.

The texts also mention equipment related to mining production, namely, mills, whose millstones could be used to grind ore or slag. However, it is rare for the texts to explain their role in the silver production process: There is only one reference, from 1311, to the "wheel of the mine mill" to describe one of them. A connection between the mine and certain mills can also be inferred from the fact that some of these mills belonged to individuals involved in mining activities, such as the Count of Rodez, his representative Géraud de Luzençon in the 1270s and 1280s, and the Ferrier brothers, masters of the Orzals mine in the 1260s and 1270s. All these mills were located on the banks of the valley's main river, the Amalou. Only a small number have survived to the present day; in the absence of any material traces, many of them have been located by the persistence of toponymy; for a few, particularly where the potential area for implantation could correspond to an important zone, the location has proved imprecise. However, although mills are present in the written records, mining documents do not mention the location of smelters or ore washing facilities. This lack of documentation is perhaps due to the ephemeral nature of these installations: Furnaces were short-lived facilities that could be set up in a variety of locations, whereas mills were more limited in location, and their multifunctionality gave them greater durability over time. The absence of any textual information on the location of the smelting or washing plants, and the imprecision of the location of certain mills over relatively large areas, made it necessary to carry out geochemical studies in order to try to locate the missing equipment.

2.2 | A Permian and Anthropized Valley

This narrow valley, exploited by medieval miners, opens onto an extension of the Permian basin of Saint-Affrique, then in contact with the edge of the Palaeozoic dome of Lévézou to the north and the edge of the Mesozoic Grands-Causses to the east

FIGURE 3 | Geological map of the valley showing veins identified by BRGM (Data—BRGM; GIS—N. Minvielle Larousse).

(Figure 3). The various sulphide veins, mainly lead and zinc, are embedded in the Permian formations, with the exception of those of Saint-Symphorien and Orzals, which are embedded in the Lévézou basement. These are mainly quartz and/or baryte veins of rather modest dimensions, both in extension (a few tens of metres) and in thickness (2 to 3m) (BRGM 1984; Cachau 1961; Goloubinoff 1984; Hübner, Körner, and Schneider 2011). The veins are clearly of hydrothermal origin, with highly brecciated zones. The ores present in the veins are mainly composed of assemblages of argentiferous galena (lead sulphides) and sphalerite (zinc sulphides), supplemented in the Pradal vein by rare argentiferous tetrahedrite (copper sulphosalts) finely associated with the galena. These assemblages give rise to polymetallic metallurgy producing silver, lead and possibly some copper (no mention of copper has yet been found, but the smelting of some tetrahedrites has been noted at La Rode; Tomczyk and Minvielle Larousse 2023). No supergene alteration layers have been observed in this mid-mountain region, which has been glaciated recently.

The valley is structured by its main river, the Amalou, its main tributaries, the Laurette (formerly the Oulette) to the north-west and the Douzillenque to the north-east, and by several ravines that cut into its slopes (Figure 4).

These ravines are important landmarks in its topography: They determine part of the cadastre, the toponymy, and sometimes expose the rocky substrate. This is how the veins were discovered and their exploitation began. Today, the bottom of the valley is occupied by the village of Le Minier in the centre and then by gardens and fields. The slopes have some cultivated fields but are mainly covered by dense forest (Figure 5).

However, this landscape is relatively recent. Until the 1950s, there were no forests or scrubland. Except perhaps in a few places, the slopes were entirely cultivated or used for sheep grazing. The banks of the streams were also exploited, both for fields and gardens and for the use of hydraulic energy in several mills (Bernat 2021). Due to the steepness of the valley, the crops were distributed in a dense system of plots built on terraces. They are still very visible on the left bank of the Amalou or near the Pradal ravine, whereas they disappear on the right bank, for example, towards the Roucadou ravine. One sector may have partially remained or become more ancient heathland or woodland: the Voltes. These terraces and, more generally, all the anthropic developments that marked the valley before the advance of the forest have, of course, had important consequences for its sedimentary dynamics. It will therefore be necessary to interpret the results of the geochemical surveys in the light of this long occupation, which limits access to the soils and medieval remains.

3 | Material and Methods

3.1 | Geochemical Prospection

3.1.1 | Prospected Parcels

The parcels to be prospected were selected on the basis of information from documentary sources, in particular toponyms characterizing relatively large areas known to have housed equipment that has now disappeared, but without allowing their exact location to be determined (Figure 2). The bottom of the Minier valley and the lower parts of its western slope thus

FIGURE 4 | Satellite and LIDAR view of the valley and the surveyed area (Data—IGN; GIS—N. Minvielle Larousse).

formed the epicentre of the prospections. From there, extensions were made to the north and south, and tests were carried out at the base of the eastern slope. Finally, the plots in the northeast of the valley, at Doulsac—where medieval works are mentioned—and at La Roubière, were added to the list. The area occupied by the village and some inaccessible plots (fences, blackberry bushes, etc.) had to be excluded from the survey. A total of 0.16km2 was covered, from Les Voltes in the north to Le Moulinet in the south, including part of the fields of La Roubière and Doulsac (Figure 6).

3.1.2 | **Portable X-Ray Fluorescence Measurements**

There is a wide array of instruments, methods, and practices in the implementation of geochemical measurements of soils and sediments to study the impact of human activities (Aston, Martin, and Jackson 2015; Bintliff and Degryse 2022; Hrubý et al. 2012; Pastor et al. 2016). Mass spectrometry is often used (e.g., Camizuli et al. 2018; Degryse et al. 2003; Horák and Hejcman 2016; Martín et al. 2014; Maulana et al. 2019), but it is expensive to set up and it is difficult to cover large areas

FIGURE 5 | View of the Minier valley (photo—N. Minvielle Larousse).

with a dense grid. Although it is still often used in the laboratory, portable X-ray fluorescence has an important advantage: it can be used in situ. Concentrations can then be read directly and prospections can be oriented in real time (Carey and Moles 2017; Janovský and Horák 2018; Kennedy and Kelloway 2021; Mohammadi et al. 2023; Ravansari, Wilson, and Tighe 2020; Save et al. 2020; Shugar 2013; Téreygeol et al. 2010; Volpi, Dallai, and Donati 2019). This second option was chosen for this study due to the large area to be prospected and the difficulty of assuming the location of the production workshops.

The geochemical dosages were carried out using a handheld XRF, model Tracer 5i, acquired in May 2021 by the Quai Branly consortium, ArScAn, and AoRoC laboratories as part of the funding provided by the Île-de-France region (Dim Matériaux). The model is the latest from the supplier Bruker. It allows the precise quantification of light elements up to magnesium (Mg). It has three calibrations: Alloys, Precious Metals, and Mudrock. The Mudrock calibration, designed for the study of soils, was chosen. It allows the quantification of its main elements (Figure 7). Duplicate analyses were carried out in cases where the concentrations appeared particularly anomalous (which can be explained by the presence of a rock fragment or minerals in the soil analysis window).

It should be noted that certain elements, such as silver (Ag) or antimony (Sb), which are of interest in the context of our work, are not measured by this calibration because they are not fixed in the soils. Indeed, the fixation or not of certain chemical elements by the soils depends on several factors, such as their acidity or the conditions of oxidoreduction (Förstner 1985). Thus, copper (Cu) and zinc (Zn) are poorly fixed in acidic soils (which are abundant in the study area and result from the alteration of siliceous rocks), whereas arsenic (As), whose presence is generally associated with the oxidation of sulphides, is easily fixed there (Table 1). A chemical element, on the other hand, is a valuable marker for tracing ancient mining, mineralogical, and metallurgical activities: lead (Pb). In fact, lead has very low mobility in acidic soils and is very insensitive to variations in oxidation reduction caused by the oxidation of sulphides discarded in the production process. It is also associated with silver in the extracted galena and all the way down to the smelting. Lead is therefore favoured for the location of all metal production sites, from mines to foundries.

The parameters of the handheld XRF make it possible to choose the acquisition times for the measurement of heavy elements and then light elements (the light/heavy elements limit is set by the machine from manganese (Mn)). The longer the acquisition time, the better the precision of the data. We have therefore chosen a particularly long acquisition time for the heavy elements (60 s) in order to accurately quantify the elements, especially lead (Pb) (Table 2).

On the other hand, the acquisition time for the light elements (Table 3) was chosen to be short (15s) because, apart from sulphur (S), these are mainly markers of soil types and animal presence (Barnett et al. 2016; Laenger et al. 2022; Williams, Errickson, and Taylor 2021) and are therefore of little relevance in the context of our study.

Finally, some of the elements measured by the calibration are systematically absent or below the detection limit. These include chlorine (Cl), cobalt (Co), molybdenum (Mo), and uranium (U).

3.1.3 | **Prospecting and Recording Protocol**

During the archaeological campaigns of August 2021 and 2022, a team of two to four people was mobilized to carry out these surveys, which enabled 1303 points to be measured. The measurements were made by direct contact with the ground, taking care to remove vegetation by scraping with a trowel. The surveys were not carried out on days with heavy rainfall, as high soil moisture (>25%) can affect the quality of measurements with this type of portable instrument (Laperche 2005). The analyses were carried out using an 8-mm collimator protected by a polypropylene film. The choice of an 8-mm

FIGURE 6 | Location of surface pXRF analyses (Data—C. Tomczyk; GIS—N. Minvielle Larousse).

collimator, rather than a 3 mm one, is based on the need to obtain the widest possible observation window, avoiding possible "nugget effects" that could be related to the presence of large soil aggregates (it should be noted that taking a sample that can be finely crushed before analysis helps to avoid these aggregate effects and to obtain more accurate values, as the soil is then homogenized. Although this practice is useful for obtaining very fine signatures from very homogeneous soils, it is not essential for prospecting when the aim is to highlight extremely marked differences in concentration)

or millimetre-sized mineralized fragments. However, we checked for their absence before each measurement.

Each chemical analysis was accompanied by a set of coordinates obtained using a differential GPS provided by LA3M (University of Aix-Marseille, CNRS), operating in RTK mode with an *x*,*y*,*z* accuracy of about 15 cm in open terrain and about 1.5 m in wooded areas—bearing in mind that the *x*,*y* accuracy of the measurement then remained in the order of 30 cm. The measuring points were spaced about 5 m apart, but the inability

图			Non-measured elements													z
Ħ			Elements measured													He
SECTION 灘 з Li Be 18122 63843											в	œ	At Liquid æ N	COCKSCREEN 81 \circ	191 F	390 30 Ne
5001011 magnesium 12 m Na Mg 24.305 22,862											aluminium 13 Al 26,982	sticon 14 Si 39,096	phosphorus 15 P 30.974	sulfur 16 S 32,065	chlorine 17 СI 35.453	800 18 Ar 338,3568
calcium potassium 20 19 κ Cа 40.078 39.098	BORNING $21 -$ Sc.	titanium 22 Ti 47,867	vanadium 23 ٧ 50.942	chromium 24 Cr 51,996	manganese 25 Mn 54,938	Iron 26 Fe 55 845	cobalt 27 Co 58,933	ricke! 28 Ni 58,693	copper 29 Cu 63,546	zne 30 Zn 65.39	gallum 31 Ga 69.723	chanki 32 Ge BOOK	arsenic 33 As 74.922	selenium 34 Se 78.96	Stockling 35 Br 69,004	Krypton 36 Kr
rubidium strontium 38 37 Rb Sr 87.62	yttrium 39 Υ 88,906	ziroonium 40 Zr 91.224	micblum 41 Nb 92,906	molybdenur 42 Mo 95.94	43 Tc man	44 Ru 101.02	<i><u>housset</u></i> 45 Rh 192001031	21132917 46 Pd 30830	30100 47 Ag 1607187	48 Cd 310.31	39. In	50 Sn	aco recor 51 Sb 101078	52 Te 127,803	3509 53 126,05	54 Xe
barium 39331 55 57.70 56 Cs Ba b. 137.33	71 Lu 174.97	72 Hf 170.49	$73-$ Ta 480.94	73 W m		76 Os	$\overline{11}$ Ir 109-99	78 Pt 496-06	79 Au	80 Hg	83 T	lead. 82 Pb 207.2	83 Bi	SORMIDI 184 Po	STANDS 8 ⁶ At	7960 36 Rn
87 39-182 88 In I ING	103 u.	104 INTE	505 UD	10 ou		H B n 10	109 IVIII	110 UUR	111 B. B. B.	112 U U L		318 Uuo				
*Lanthanide series	157 La	58 Ce	59 Pr	60 Nd	61 Pm	82 Sm	163 Eu	64 Gd	65 Tb	66 Dy	Ho	68 Er	69 Tm	70 Yb		
** Actinide series	10000 89 Ac	thorium 90 Th 232.04	EXISTEN 91 Pa	KAA-DA uranium 92 υ 238.03	FGARE TEXTER UP 93 Np	350.96 12241917 94 Pu	188,88 STANDARD AND 95 Am	RAY ON 3500000 96 c_{m}	Higher BRSK8919 97 Bk	98 O1	99 British	100 Hm	KANCING 1980000 101 Md	178.84 1908091887 102 No		

FIGURE 7 | Table of elements quantified by pXRF.

TABLE 1 | Mobility of certain trace metals in soils (C. Tomczyk according to Förstner 1985).

	Ph		Redox potential					
Relative mobility	Neutral-alkaline	Acid	Oxidizing	Reducing				
High	As	Zn, Cd, Hg, Co, Ni, (Mn)	Mo, Se					
Medium	Mn	Cu, Al, Pb, Cr	Cu, Co, Hg, Ni, Zn, Cd	Mn				
Low	Pb, Fe, Zn, Cd, Tl	Fe (III), T1	Pb, Tl	Fe, Zn, Co, Ni, Tl				
Very low	Al, Cr, Hg, Cu, Ni, Co	Mo, Se, As	Al, Cr, Fe, Mn	Al, Cr, Hg, Cu, Se, B, Mo, Cd, Pb				

to obtain a GPS signal in some wooded areas, and the presence of many very overgrown areas with a lot of blackberry bushes in some of the plots surveyed, did not always allow us to respect this distance. Finally, as the XRF pistol displays all the quantifications for each element detected in the soil on its screen, it was possible to orientate the surveys in real time. As soon as a concentration higher than the natural geochemical background was detected, a tighter grid was used to verify the presence of an enrichment and define its contours.

3.2 | Chemical Elements Associated With Mining Activities

3.2.1 | Chemical Elements Represented

Based on the results of the measurements, the nature of the ore deposits, and the prospecting environment, we have chosen to present only lead and zinc. In fact, in the Minier Valley, these two elements are the only relevant markers for the presence of mining, mineral processing, and metallurgical activities. Several factors justify this.

Firstly, they are the two elements that are mainly present in the local deposits, in the form of silver-bearing galena and sphalerite. As lead is well fixed in the soil, it is not surprising that it shows significant variations (from none to around 20 000 ppm). Moreover, even if zinc is not well fixed in the soil and can be absorbed by plants, the surveys have shown that it is present in such quantities (5000 to nearly 27 000 ppm) in certain sectors that it allows the identification of tailings areas related to the processing of ores containing sphalerite. On the other hand, sulphur, although present in these minerals, has not been effectively preserved in soils. Its low detection (about 750 ppm ± 80 ppm on average) confirms its mobility. Furthermore, if tetrahedrites have also been identified in the veins, the low presence of copper in the soils $(95 ppm \pm 10 ppm$ on average) is difficult to interpret. Copper is easily absorbed by plants and is used in the form of Bordeaux mixture (a mixture of copper sulphates and lime) in orchards and vegetable gardens. Finally, the presence of arsenic in large quantities (often >270 ppm \pm 7 ppm) calls for caution. In fact, arsenic shares a peak (one of the lead rays [L alpha] and one of the arsenic rays [K alpha] are very close in energy, at around 10.55 KeV) with lead, and the arsenic levels seem to

TABLE 2 | Margin of error (%) provided by the pXRF (average of the 1303 analyses carried out for this study) for quantification of heavy elements detected (C. Tomczyk).

Element	Mn	Fe	Ni	Cu			Zn Ga As Se Rb Sr Y			Zr	Nb	Ba	P _b	Th
Average error $(\%)$	3.6 0.5 11 3.3 1.2 4.3 1.0						16 3.5	4.7	3.2	3.2	46	7.5	0.7	4.8

TABLE 3 | Margin of error (in %) provided by the pXRF (average of the 1303 analyses carried out for this study) for quantification of light elements detected (C. Tomczyk).

be explained by a failure to differentiate between these two elements in portable X-ray fluorescence (Arles 2009, 211; Laperche and Lemière 2020).

3.2.2 | **Natural Geochemical Background Variations Across the Valley**

In order to identify lead and zinc enrichments, it is first necessary to establish the natural geochemical background. Although there are national data that estimate local natural levels of total lead in surface horizons (0-30 cm) at over 200 ppm and zinc at over 300 ppm, these data are not very precise as they represent a very wide interval taken from few points (Gis Soil data: [https://](https://www.gissol.fr/donnees/cartes/les-teneurs-en-plomb-total-des-horizons-de-surface-0-30-cm-des-sols-de-france-2374) [www.gissol.fr/donnees/cartes/les-teneurs-en-plomb-total-des](https://www.gissol.fr/donnees/cartes/les-teneurs-en-plomb-total-des-horizons-de-surface-0-30-cm-des-sols-de-france-2374)[horizons-de-surface-0-30-cm-des-sols-de-france-2374](https://www.gissol.fr/donnees/cartes/les-teneurs-en-plomb-total-des-horizons-de-surface-0-30-cm-des-sols-de-france-2374)). Its purpose is to define a regional value, which is not well suited to local studies.

In the Minier valley, it was first important to distinguish the mineralized sectors from the others, because the deposits can naturally enrich the soils that cover them. Then we checked that there was no difference, even a slight one, between its northern part, rich in amphibolites, gneiss, and quartzite, and its southern part, composed of a Permian substrate of sandstone, conglomerate, and shale. Because the mineralization is associated with different veins, the question arose as to whether there might be a difference in lead and zinc enrichment between these sectors. We therefore sampled from several locations to define the natural background as accurately as possible (Table 4). We based this calculation on 15 surface analyses per sector. On the Voltes slope, where there is an abundance of tailings, we dug a 1m20 pit to ensure that we were measuring nonanthropogenic levels. The absence of anthropogenic spills was only verified by simple auger checks in the other sectors. Measurements in the valley bottom were taken on stabilized horizons and not on alluvium.

Soils naturally formed on areas rich in veins (and not anthropogenically modified) have comparable surface levels of lead and zinc, around 300ppm for lead and 460ppm for zinc. Soils at the bottom of the valley are richer near the village of Minier (about 330ppm for lead and zinc). Although special care was taken to select areas with no human activity, we cannot exclude the possibility that these soils have been remixed or introduced. However, the most likely hypothesis would be an accumulation linked to mining activities upstream or closer to the valley of Persignac. The values measured at high altitudes, outside the mineralization, and on soils located downstream (last two rows of the table) show much lower natural concentrations, around 230ppm for lead and 140ppm for zinc.

3.3 | Spatial Representations

The most direct way of representing point concentrations is the proportional circle. Although it is accurate and corresponds to continuous data, it is difficult to read when concentrations are close together and does not facilitate the identification of enrichments. For this reason, discretization of the concentrations is also useful. With an asymmetric positive distribution model (see below), the Jenks algorithm is recommended as it maximizes the interclass variance while minimizing the intraclass variance.

Finally, to obtain a continuous representation, among several possible interpolation methods, kriging was chosen (Chilès and Delfiner 2012, 147–238). This is a method that assumes that nearby measurements tend to have similar characteristics, which corresponds to the behaviour of metal contamination of soils, because the composition of the latter varies little at the valley scale (matrix effects are negligible at the scale of the study area [for more details, see in detail Huang et al. 2020; Kim et al. 2019; Li et al. 2022; Ravansari, Wilson, and Tighe 2020). An ordinary kriging was therefore carried out using the Arcgis software (Spatial Analyst Tools, Interpolation, Kriging), based on a spherical model of the semivariogram ([https://desktop.arcgis.com/fr/arcmap/10.3/tools/](https://desktop.arcgis.com/fr/arcmap/10.3/tools/3d-analyst-toolbox/understanding-interpolation-analysis.htm) [3d-analyst-toolbox/understanding-interpolation-analysis.htm;](https://desktop.arcgis.com/fr/arcmap/10.3/tools/3d-analyst-toolbox/understanding-interpolation-analysis.htm) [https://desktop.arcgis.com/fr/arcmap/10.3/tools/ 3d-analyst-toolb](https://desktop.arcgis.com/fr/arcmap/10.3/tools/3d-analyst-toolbox/how-kriging-works.htm) [ox/how-kriging-works.htm\)](https://desktop.arcgis.com/fr/arcmap/10.3/tools/3d-analyst-toolbox/how-kriging-works.htm). The resulting rasters were stretched to improve contrast, with a standard deviation set at 2.5 and histogram equalization. The first method (standard deviation) focuses on the main concentrations, whereas the second expands and refines the variations (histogram equalization).

Finally, the reading of geochemical maps, especially those that are interpolated, must take into account the relief. For this reason, they are superimposed on the DTM of the valley, obtained with a resolution of 0.25 m by a LIDAR survey (survey carried out as part of the research programme in 2020 by Nicolas Poirier and Carine Calastrenc [TRACES - CNRS, Université de Toulouse Jean-Jaurès], then post-processed in 2021 by Véronique Rinalducci and Jules Fleury [CEREGE and LA3M - CNRS, Université d'Aix-Marseille]. This survey

TABLE 4 | Average values of the natural background measured in 2021 in different sectors (average of around 15 measurements—C. Tomczyk).

will focus on the valley floor and its slopes. It will be supplemented by the HD LIDAR survey now available from IGN). The rasters were adapted to the archaeological analysis using the Blender algorithm of the Relief Visualization Toolbox with its default parameters (Štular et al. 2012).

4 | Results

4.1 | Pb and Zn Concentrations

The maps of the measurements and their statistical distribution show that a part of the detected lead and zinc levels exceed the natural background (Figures 8–10).

However, only 25% of the 1303 samples exceed 1000 ppm for zinc and 1300ppm for lead. Furthermore, only 10% exceed 2000ppm for zinc and 2300ppm for lead, despite tighter netting in areas with high concentrations. The maximum concentration quantified for lead is 9169ppm (0.9%), whereas that for zinc is 27385ppm (or 2.7%). These exceptionally high levels are not unusual. They have been observed on several occasions in areas of mines tailings (see below) with almost no cover, where fragments of minerals, particularly sphalerite, are scattered. However, they do affect the averages, which reach 950 ppm for lead and 925 ppm for zinc. However, the median, which is little influenced by very high values, shows that slightly less than half of the lead and zinc concentrations measured are within the natural levels of the valley.

4.2 | Metal Enrichments: Scatter Plot

To better define the areas where lead and zinc are present, the lead and zinc levels are discretized into five classes using the Jenks algorithm—recommended in the case of asymmetric (Figure 11).

Considering the geochemical background and the measured values, it can be assumed that there is a second class of concentration, starting from 600-ppm lead and 800-ppm zinc. This second class corresponds to values between the median and the third quartile. It marks the presence of weak anomalies or is on the edge of more important concentrations grouped in the three upper classes corresponding to the last deciles. The resulting maps (Figures 12 and 13) thus highlight the metal concentrations. Cartographically, the darkest points belong to the statistical classes with the highest lead and zinc values. The centre of the various concentrations generally reaches 3000–5000ppm for lead (i.e., more than 10 times the geochemical background value)

and the edges of the concentrations exceed 1000 ppm. Zinc enrichments exceed 1000-2000 ppm and often reach 5000 ppm. In the valley floor, however, it is rare for the centre of concentrations to exceed 600-1000 ppm (which is still well above the geochemical background).

4.3 | Geochemical Concentrations: Continuous Representation

The geochemical concentrations represent in a punctual form an information that is continuous in space. Restoring this continuity is therefore the challenge of mapping. The grids obtained by ordinary kriging can be visualized in different ways, depending on the questions asked. Here, we use two representations: one based on the standard deviation (Figures 14 and 15), that is, the measure of the dispersion of the values around the mean, and the other based on the equalization of the histogram (Figures 16 and 17), designed to make the distribution as uniform as possible. These two visualizations of the same grid are complementary. The first highlights the areas of high variability, whereas the second is useful when the distribution of lead and zinc estimated by ordinary kriging is characterized by the presence of particularly high or low values.

These maps effectively target the places where metal concentrations are highest, while allowing a finer reading of soil contamination. The soils of the valley are thus characterized by more than a dozen lead-contaminated sites. The enrichments form particularly large areas on the slopes, at Les Voltes and La Saliège. In the valley, they are limited to a few tens of metres in diameter. Zinc contamination is rarer, but particularly high and widespread on the same slopes of Les Voltes and La Saliège. The location of the enrichments and the comparison of lead and zinc contamination are therefore the two geochemical data that will be discussed and cross-commented with topographical information and documentary sources.

5 | Discussion

5.1 | The Technical and Spatial Organization of the Production Process

The first contribution of these studies is on a valley scale. It is based on the observation that high concentrations of leadzinc are distributed on the slopes, whereas on the banks of the Amalou, the concentrations are mainly lead and little zinc.

FIGURE 8 | Lead content represented by proportional circles (Data—C. Tomczyk; GIS—N. Minvielle Larousse).

5.1.1 | **Identification of Ore Processing Workshops**

The high concentrations of lead, and even more so of zinc, which cover large areas on the slopes, are close to the mines. The zinc and lead enrichments therefore correspond to areas for sorting and rejecting ores considered sterile by the medieval workers, directly at the mine exits or near the mineral crushing workshops. The presence of numerous decimetric gangue blocks containing sphalerite suggests (as did Téreygeol et al. 2010) that zinc sulphides were not valued

and were rejected during the initial processing of the ores. Of these taillings, only the one at Les Voltes was still mentioned in the 19th century (Boisse 1858, 387–392), just before it disappeared under the vegetation, like the one at La Saliège. The geochemical maps allow us to identify them, to draw them, and to assess the extent of the tailings, knowing that the materials have probably been marked by a process of dispersion over the centuries: anthropic, during road works or the construction of cultivation terraces, and sometimes natural (colluvium). The question remains, however, because if the spoil

FIGURE 9 | Zinc content represented by proportional circles (Data—C. Tomczyk; GIS—N. Minvielle Larousse).

heaps at Les Voltes and La Saliège are similar in composition and size, those at Roucadou and Roubière are different, being poor in zinc and limited in area. This difference could be explained by a different mineralogy of the deposits, by different places of dumping and treatment of the ores, or by the reuse of the tailings.

At the bottom of the valley, it is mainly lead concentrations that are observed, forming several areas with surfaces much

smaller than those of zinc. The materials present in these places are therefore mainly galena, treated in workshops using water from the Amalou. These could be the ore mills mentioned in the documentary sources. However, the grinding of the ore cannot be an important source of tailings, because the ground ore produced, except in the case of accidents or losses, were intended to be enriched in washing plants. It is only after the ore have been hydrogravimetrically sorted that the materials considered sterile are discarded. Furthermore, although several foundries

FIGURE 10 | Statistical distribution (boxplot and data summary table) of lead (Pb) and zinc (Zn) levels detected. Number of individuals: 1303 (Data—C. Tomczyk).

FIGURE 11 | Histogram of the distribution of lead (left) and zinc (right) levels (expressed as a %) and values bounding the discretized statistical classes (Data—C. Tomczyk; GIS—N. Minvielle Larousse).

could have been operating in the valley, we have so far only identified slags around the La Rode mill. We have already established that the enrichment identified is indeed due to these slags, remobilized in the fills of a cultivation terrace (Tomczyk and Minvielle Larousse 2023).

5.1.2 | **Objectives and Organization of the Work**

The aim of the workers was to separate the galena from the baryte and quartz gangue that contained it, as well as from the sphalerite. Sorting was carried out on leaving the mines, or even inside them, and was continued for some of the material by finer sorting carried out in nearby crushing workshops. As the valley floor concentrations remain relatively rich in zinc, this initial sorting was not perfect. Although the distinction between galena and sphalerite is visually easy for experienced workers, they can actually be intertwined on a microscopic scale in the veins. Identifying the zinc thresholds reached at each stage of the production process will therefore be a way of evaluating and comparing the technical efficiency of the workers, as well as questioning the consequences of a residual presence of zinc in the smelting process. Indeed, it has been shown that large quantities of zinc are detrimental to the separation of lead from silver (Chiarantini et al. 2021). However, it is possible that a very small amount of zinc minerals may have no effect on the metallurgical process (Anguilano, Timberlake, and Rehren 2010; Olovčić et al. 2022) or may even be slightly beneficial for the separation of lead and silver (Merkel et al. 2016). In the latter case, a certain amount of sphalerite, yet to be defined, may have been deliberately retained. Few studies currently address the question of the threshold above which zinc could affect (positively or negatively) the metallurgy of lead and silver. It therefore deserves to be documented: first by excavating the workshops, then by drawing up an experimental protocol.

Pending further studies, it can be seen that the enrichment of the ores at Minier was based on a double optimization: that of the sequence of manual and hydraulic preparation techniques, and that of the transport of materials (Figure 18). Most of the sorting and crushing took place in the immediate vicinity of the mines, in order to remove the maximum amount of tailings with the minimum amount of transport: sterile rock, gangue,

FIGURE 12 | Discretized lead content (Jenks) in five classes (Data—C. Tomczyk; GIS—N. Minvielle Larousse).

and sphalerite. Only the galena, together with the remaining sphalerite, was then transported to the bottom of the valley for further enrichment with river water. Preliminary calibrations could be carried out near the mills, with some additional tailings, then the ground ore were sorted by hydrogravimetric methods. The ore ready for smelting could finally be smelted on site or, more probably at the present stage of research, it could be transported to a foundry to the south, near La Rode, which could collect the materials from the companies in the valley.

The number of enrichment zones found between Deux-Aygues and the Minier suggests the presence of several workshops with similar functions, unless these are subsequent remobilizations. This co-presence could indicate chronological developments, or the presence of several neighbouring workshops designed to absorb the quantities of material extracted from the mines without delay, or even workshops dedicated to the processing of ores from different companies. In the latter case, spatial discontinuities would correlate with social discontinuities. In the Central Middle Ages, each company

FIGURE 13 | Discretized zinc content (Jenks) in five classes (Data—C. Tomczyk; GIS—N. Minvielle Larousse).

was indeed master of its production process and could build workshops for its own use (see Braunstein 2003; Minvielle Larousse 2023). Several parallel production processes could therefore take place in the valley, multiplying the number of workshops, regardless of the cumulative quantities of materials or other rationalities such as the reduction of transport times. This question could also be answered by excavating each of the sectors identified by the geochemical surveys.

5.2 | Locating the Workshops

The second contribution of the surveys is the ability to locate each potential workshop more precisely. The combined reading of the geochemical maps (point, discretized, and kriged) with the digital terrain model and the topography from documentary sources makes it possible to formulate hypotheses for each sector and thus to prepare excavation campaigns.

FIGURE 14 | Spatial interpolation (ordinary kriging) of lead levels, raster as a function of standard deviation at 2.5 (Data—C. Tomczyk; GIS—N. Minvielle Larousse).

5.2.1 | **Mining Works: Les Voltes, La Saliège, and La Roubière**

At Les Voltes (Figure 19), the terrain slopes negatively to the north. With the exception of the field to the south, the valley slope is currently covered with woods and coppices. Aerial photographs show a slight progression of the forest from the mid-20th century to the present, but this cover appears to be old, as no cultivation terraces are visible. Apart from the sedimentary dynamics associated with the slope and erosion, and the more punctual transport associated with the maintenance of the roads, the soils appear to be relatively well preserved. Within a large contaminated area, lead and zinc are concentrated mainly in two sectors: a northern sector (a) corresponding to mining remains (trenches and surface dumps) and a southern sector (b) upstream, in a field. A final concentration is observed between the two: in the immediate vicinity of another set of mining remains (c).

This sector is beginning to be known as excavations are underway (pending publication, access to the archaeological reports is

FIGURE 15 | Spatial interpolation (ordinary kriging) of lead levels, raster with an equalized histogram (Data—C. Tomczyk; GIS—N. Minvielle Larousse).

available on request; Minvielle Larousse et al. 2022). To the north and in the centre, the presence of workings and taillings has been confirmed, and a small group of workshops is being excavated in the field to the south. The contamination found on the surface is therefore of multiple origin: from the mines and workshops on the slope. However, several questions remain. It will indeed be necessary to distinguish the three mines mentioned in the texts, Orzals, which is the main one, La Sompa and Socca, which seem to be more ephemeral; to be able to delimit the group of workshops, especially towards the east; and to understand why the miners chose to move the material from downstream to upstream, when an arrangement of the banks of the river could have optimized the transport and processing of the ores, concentrating in one place the manual and hydraulic stages of ore preparation.

At La Saliège (Figure 20), the terrain has a very steep negative slope to the north, bordered by the ravine and the village. The ravine where the workings are located (a) is entirely terraced, now

FIGURE 16 | Spatial interpolation (ordinary kriging) of lead levels, raster with an equalized histogram (Data—C. Tomczyk; GIS—N. Minvielle Larousse).

abandoned and covered with brushwood. Upstream there is an open field to the west (b) and a stand of pine trees to the east (c). The plantations are recent, occupying a field that was still open in 1970. The northern boundary of these two fields is marked by the path, and higher up by some terraces, but the terrain here is not cultivated. Perhaps it has been cultivated? In any case, the main phenomenon that should structure the soil is this slope effect.

Two paradoxes characterize this sector. Firstly, the enrichments are again upstream of the mine, which would mean that the spoil heaps dumped downstream of the trench may have been remobilized, but that at least some of the material was taken up to be processed. Perhaps the mines were equipped with an ascending shaft to facilitate this transport? This would imply that mineral preparation workshops may have been located upstream of fields b and c. Secondly, it seems that the highest concentrations are found in the upper parts of these fields, despite the steep slope. A fairly homogeneous distribution is observed over a length of 100m and a width of 35m. It is therefore possible that the spoil heaps were contained by retaining walls, preventing the material

FIGURE 17 | Spatial interpolation (ordinary kriging) of zinc levels, raster with an equalized histogram (Data—C. Tomczyk; GIS—N. Minvielle Larousse).

from flowing towards the village. In addition, by comparing the maps of lead and zinc, it can be seen that the field to the northwest (b) seems to be mainly contaminated with lead, whereas the field to the south-east is more contaminated with zinc (c). It will be necessary to verify if this difference could be an echo of the mineral preparation, with the preservation of galena in the north-west and the rejection of sphalerite in the south-east.

At La Roubière (Figure 21), a large area is located at the edge of a forest and a path. The ground slopes steeply (around 10°) towards the west and the vegetation in this area is sparse compared with the wooded areas bordering this sloping area. This difference in vegetation could be linked to the presence of numerous blocks of quartz and baryte, mineralized with galena and rarer sphalerite, 5 to 10 cm in size, visible on the surface, leading us to interpret it as a spoil heap. It should be noted, however, that unlike Les Voltes and La Saliège, this tailing is only enriched in lead and not in zinc. Further studies are therefore required in this area before any excavation can be considered.

FIGURE 18 | Proposed modelling of the lead and silver production process in the Minier valley (C. Tomczyk).

5.2.2 | **Mining and Mineral Processing: Roucadou**

Around the Roucadou ravine (Figure 22), the terrain is varied. The river, which is deeply incised here, and the ravines are surrounded to the west by small cultivation terraces covered with coppice, whereas to the east, there is a platform 25 to 50m wide, also built with retaining walls on each side. It appears that a palaeochannel with a few blocks crosses its southern part, suggesting the presence of a hydraulic structure. Two geochemical enrichments have been observed: a main one in the centre of this platform, strongly marked by lead (a), and a secondary one on the other bank to the west, marked by lead and to a lesser extent zinc (b).

Documentary sources mention a mine, the Roucadou mine, whose ravine runs perpendicular to the vein, and a mill in the Théron terroir, called the wheel of Géraud de Luzençon (an officer who represented the Count of Rodez at Le Minier between at least 1276 and 1281). In 1311, the link between this mill and the mine is made explicit by its designation as the "wheel of the mine mill." It would therefore seem logical that this sector was both a mining site and, at the very least, a place for the preparation of minerals (crushing, grinding, and washing). To date, neither the mine nor the mill have been found. Topographical clues are rare and ambiguous, geochemical maps confirm the potential and provide some clues. If sphalerites were discarded during sorting and crushing, they would be found in area b, near the mill. Processing of galena (grinding and washing) would take place on platform a.

5.2.3 | **Hydraulic Workshops: From Deux-Aygues to La Rode**

The Deux-Aygues mill (Figure 23) is located at the confluence of two streams. The present mill is situated on a small platform surrounded by woods and pastures surrounded by dry stone walls. We did not detect any metal content in the ruin of the mill itself, but two concentrations were detected around ten metres. It is certain that this area is not mineralized and that the lead (zinc) contamination can only be anthropogenic. These two concentrations are nevertheless difficult to interpret because of the remobilization of the soil during the construction of the terraces. They have similar grades (of the order of 3000-ppm lead and around 1000-ppm zinc) and it is possible that these two enrichments reflect the remobilization of the tailings from the mill (which would explain the similarity of the two concentrations). The most that can be assumed from the text is that the mill, in its medieval state, could have been used to grind ore.

Further south, at the Arbus mill (Figure 24), there are the remains of a mill that was still active in the 19th century. It is situated on a terrace along the river. In fact, the whole of this sector consists of gardens and terraced fields. The cadastre divides small plots on this boundary and larger plots to the west, upstream of the road. The land is flat on all plots, but has a negative slope to the north-east, from the base of the slope to the river. The soils have probably been marked by tens

FIGURE 19 | Detailed maps of the Voltes (Data—C. Tomczyk, J. Bemon; GIS—N. Minvielle Larousse).

FIGURE 20 | Detailed maps of the Saliège (Data—C. Tomczyk, J. Bemon; GIS—N. Minvielle Larousse).

of years or more of ploughing and fertilizing. Moreover, the construction of these terraces, at an unknown time, undoubtedly marks a clear break in the sedimentary dynamics of this sector. In fact, the lead contamination is diffuse. They are observed over a length of 150 m and a maximum width of 50 m. However, it is likely that a medieval ore mill operated in this sector. The fact that these terraces are contaminated confirms this, unless it is a case of transporting mining tailings from elsewhere.

At the Raynal mill (Figure 25), a field runs along the river. It is a flat terrace over its length, with a slight slope to the south-west over its width. A mill is recorded here in the Middle Ages, although it is not known whether it was used for grinding ore. This overgrown field was certainly cultivated, so one might have expected an extensive concentration such as that observed at the Arbus mill. On the contrary, it is found to be confined to the lower part of the field, against the wall of the upper terrace, and its lead content is high: between 0.4 and 0.9%. The context of this field is both significant and complex. The field is located downstream of a mill, along the river, on whose banks a fragment of an ore millstone has been observed (Minvielle Larousse et al. 2021). However, the field is not far from the modern mines of Persignac, one of whose entrances is 100m further

FIGURE 21 | Detailed maps of the Roubière (Data—C. Tomczyk, J. Bemon; GIS—N. Minvielle Larousse).

FIGURE 22 | Detailed maps of the Roucadou (Data—C. Tomczyk, J. Bemon; GIS—N. Minvielle Larousse).

downstream. The other possibility would be to see a heap of recent tailings dumped in this field during or after the closure of the Persignac mine.

At La Rode Mill (Figure 26) there is a long and wide terrace that runs along the river. The mill, which was built in the centre, is in ruins but was in operation until the present day. The soil contamination is high and is located on the northern plot, upstream of the mill. It occupies the whole width of the field for 55m in length and forms distinct contours. We know that an ore mill was documented there as early as 1287. It was known as the Ferrier wheel, referring to Bertrand Ferrier or his brother

Raymond, lords of the Orzals mine from the 1260s. Lead-bearing slag was scattered throughout the site, suggesting the presence of a foundry. An archaeological study has already established that the metal contamination is due to the spread of this slag in the terraces (Tomczyk and Minvielle Larousse 2023). However, no metallurgical or mineral processing structure has yet been identified within the limits of the survey. Further trenching is therefore required.

At the Bousquet (Figure 27), further terraces built along the river structure the terrain. The metallic contamination identified, spread by the crops, is relatively faint and therefore of little

FIGURE 23 | Detailed maps of the Deux-Aygues (Data—C. Tomczyk, J. Bemon; GIS—N. Minvielle Larousse).

FIGURE 24 | Detailed maps of Arbus (Data—C. Tomczyk, J. Bemon; GIS—N. Minvielle Larousse).

significance. This could be due to short processing activities, the transport of materials during the construction of the terraces, or the erosion of a dump from contemporary mining in the valley, deposited above the terrace.

5.3 | Methodological Choices, Relevance and Limitations

At the end of these discussions, we propose some methodological considerations aimed at extending or improving the results. In fact, two deliberate choices have structured the geochemical surveys: the decision to carry out in situ measurements and the decision to base the survey on a generic grid of approximately 5m. This work has been carried out mainly by cross-reading documentary, geochemical and topographical sources.

5.3.1 | **Relevance of the Methods Used**

In situ measurements without sample preparation are less accurate than measurements taken in a plastic bag, in the field, or prepared in the laboratory, ex situ, for the quantification of light elements (Williams, Taylor, and Orr 2020). However, the gap narrows

FIGURE 25 | Detailed maps of Raynal (Data—C. Tomczyk, J. Bemon; GIS—N. Minvielle Larousse).

FIGURE 26 | Detailed maps of the Rode mill (Data—C. Tomczyk, J. Bemon; GIS—N. Minvielle Larousse).

for heavy elements such as lead (Horta et al. 2021; Hürkamp, Raab, and Völkel 2009; Lagerström, Norling, and Eklund 2016; Shuttleworth et al. 2014). Thus, in situ pXRF analyses remain relevant for the study of heavy metal contamination in soils and allow for efficient surveys (Carr et al. 2008; Ding et al. 2018; Higueras et al. 2012; Peinado et al. 2010; Qu et al. 2019; Sut-Lohmann et al. 2022; Weindorf, Paulette, and Man 2013).

In fact, the enrichments detected in this study have such high concentrations of lead and zinc that neither the analytical error margin of $\pm 0.7\%$ for lead and $\pm 1.2\%$ for zinc, nor the other parameters that may vary the elemental composition of the measurements (humidity, compaction, etc.) prevent the anomalies (whose edges have concentrations higher than 800 ppm) from being distinguished from the natural geochemical background, which is more than twice as low. This margin of error is even very small for the objective of these surveys. With the benefit of hindsight, it would have been possible to reduce the survey time to achieve an error margin of $\pm 10\%$ for lead and zinc and to cover the surface more quickly.

We then chose to distance each measurement by 5m whenever lead levels remained below 500ppm (considering these levels to be close to the natural geochemical background). The spacing

FIGURE 27 | Detailed maps of the Bousquet (Data—C. Tomczyk, J. Bemon; GIS—N. Minvielle Larousse).

was only reduced to 2m when lead levels exceeded 1000 ppm. In retrospect, this $2m \times 2m$ grid seems sufficient, as the concentration (including centres and edges) do not appear to be less than $4m²$. Given the shapes taken by medieval ore processing workshops (e.g., Belli, Francovich, and Grassi 2005; Flament, Téreygeol, and Sarah 2019; Hrubý et al. 2021; Minvielle Larousse et al. 2019b), even a single building on a slope would occupy an area of more than 5m2, even more so if the space for the disposal of tailings is included. Although smaller areas are always conceivable, they would probably not correspond to individual or clustered workshops, but rather to a remobilization of contaminated sediments. Of course, this observation applies to sedentary and relatively intensive production. For other periods or contexts, the question of the grid should be reconsidered.

5.3.2 | **Archaeological Contributions and Limitations**

From an archaeological point of view, geochemical maps provide more than just potential workshop locations. We have seen that variations in concentrations and surfaces allow functional hypotheses to be made which, when corroborated by the topographical environment and documentary information, can form a preliminary discourse on the organization of production at the scale of the prospected space. In the case of research on metal production, this prospecting method is therefore as easy to implement as it is useful. In other cases, it can be used to complement geophysical or thermal prospecting.

However, two difficulties remain. The first is knowing at what depth the remains—tailings or workshops—are located. Surface surveys should therefore be followed by auger boreholes to identify contamination levels, to provide evidence of the origin of this contamination and to provide elements of dating. The second difficulty is to know whether the contamination is from primary or secondary materials, and therefore from workshop remains, or just tailings. The distribution or concentration of contaminants can be a clue, but only in the context of soil formation. For example, when more diffuse concentrations were found on the surface of the terraces, we assumed that the remobilization of sediments and materials in the fills could explain this dispersion. The drilling carried out at the Rode mill confirmed this. On the other hand, where the soils appear to be less disturbed, as at Les Voltes, workshops have indeed appeared from the first drillings.

Thus, if we can reasonably expect to bring to light remains at the centre of concentrations reaching 3000–5000ppm, it will be necessary to implement more preliminary drillings in places where the concentrations are lower or in those characterized by important sedimentary dynamics.

5.3.3 | **The Interdisciplinary Approach**

Finally, we would like to underline once again that the approach taken in this study is interdisciplinary. If we had had to organize these surveys without the knowledge of documentary sources, the area studied would undoubtedly have been larger and the grid more widely spaced. In addition, the few mine tailings exploited in the 19th and 20th centuries on the eastern slope of the valley (Persignac) would also have been measured, which would have significantly modified the thresholds corresponding to the enrichments sought, those of medieval production (contemporary tailings have lead and zinc concentrations three times higher than medieval waste dumps). This pre-established temporal and spatial discrimination made the surveys more efficient and immediately usable. However, although it has been fruitful in terms of operational efficiency, keeping the geochemical surveys within an acceptable time frame and budget, this discrimination runs the risk

of leaving out areas of exploitation that are not covered by the documentation. It is therefore essential that a detailed knowledge of the terrain and the observation of its enrichment can correct this bias and also guide the geochemical surveys, as shown by the Roubière sector.

The main interest of the approach therefore lies in the interpretation of the results. Our understanding of some workshop sites and by knowing that the extraction took place on the slopes and the processing in the valley floor, we have been able to understand the distribution of the concentrations and to develop a discourse that needs to be refined, but which is already verified by the sounding of the plots. The isolated commentary of documentary sources suffers from certain gaps and spatial inaccuracies. Geochemistry alone can define enrichment areas, but it depends on sedimentary dynamics and its ability to interpret the origin of enrichments will be limited. Here, the LIDAR DTM was mainly characterized by the contemporary forms of occupation of the valley, so that traces of medieval soils and remains only appeared in exceptional

FIGURE 28 | Overview map. Geochemical and documentary topography of medieval production in the Minier valley (Data—C. Tomczyk, J. Bemon; GIS—N. Minvielle Larousse).

cases. By cross-referencing these three sources, identifications have been made more precise and complete, and interpretations have been broadened and consolidated. Because it is rare, even exceptional, to find a similar approach in the studies we have examined, we conclude with a plea in favour of linking sources and methods. Of course, the Minier valley is a particularly suitable case study for this purpose, but the tools needed to effectively locate the sites and identify their functions had to be put in place.

6 | Conclusion

At the end of this study, all the archaeological objectives had been achieved. After compiling the archival corpus of the valley and measuring 1303 points in situ with a pXRF at a distance of approximately 5m, the topography of the medieval production was actually drawn (Figure 28). Although the mines were located, their spoil heaps were no longer visible. Now, they had been demarcated. Although we did not know the location of the mineral processing workshops, the combination of their documentary references and the geochemical maps made it possible to draw up an inventory, at least representative, of the places where their remains can be found. A dozen sectors are listed. Uncertainties remain in terms of depth and, above all, preservation, but the locations are precise enough to plan and carry out coring with a drill, followed by archaeological excavations to fill in the gaps.

In addition to defining the location of these sites, a double discourse on silver production has been developed. The research has made it possible to outline part of the organization of the work, between mining sectors on the slopes (the Voltes, La Saliège), which seem to have been dedicated to the sorting of ores rich in galena and sphalerite, and other sectors in the valley bottom, mainly enriched in lead, which seem to have been dedicated to the rest of the process, probably grinding, washing, and metallurgy. The fact that several lead enrichments have been identified suggests that mineral processing was not centralized in space or permanent in time. As we know that several mining companies were active in the valley at the same time, several parallel production processes were in operation. This suggests a social division of labour as well as a technical sequence of workshops. One of the aims of future excavations at workshop level will therefore be to understand the economic choices and spatial practices of each company. In this respect, Géraud de Luzençon's wheel currently offers the best potential. In fact, we have a relatively precise site facing one of the most remarkable metallic concentrations on the left bank. Moreover, the fact that we can link a workshop to its tenant and, more generally, to its operating context, will enrich and consolidate the study.

More generally, the results provide food for thought in the field of methods and palaeopollution. In addition to feedback on the mesh and acquisition time of pXRF measurements, the application of geostatistics to the construction of geochemical maps has only been touched upon here. The dataset associated with our study could be remobilized in the future to refine the geochemical commentary (e.g., Mikołajczyk and Milek 2016; Trant et al. 2021). This will be all the more useful as we are already able to compare surface maps with waste scatters or the remains of the workshops that produced them. Finally, this study has also demonstrated the existence and persistence of metal contamination in the soils of a rural valley largely removed from contemporary industry. Even if they are localized, we have seen that the concentrations measured remain punctually high for several centuries after production has ceased. Old mining areas must therefore be taken into account in inventories and considerations of the environmental impact of metal production (Maus and Werner 2024). At Le Minier, the question of this impact—its knowledge and its management—arises both for the medieval community at its origin and for all those who have occupied and still occupy the valley (Geltner 2023; Walraven et al. 2016). More than an extension, it is the opening of a new avenue of research that this study makes possible, at the intersection of social and environmental sciences.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that supports the findings of this study are available in the supplementary material of this article.

References

Anguilano, L., S. Timberlake, and T. Rehren. 2010. "An Early Medieval Lead-Smelting Bole From Banc Tynddol, Cwmystwyth, Ceredigion." *Historical Metallurgy* 44, no. 2: 85–103.

Arles, A. 2009. *Entre monnayage officiel et faux-monnayage: la fabrication de la monnaie au marteau en France (XIIIe - XVIIe siècles): approche physico-chimique, expérimentale et historique*. Orléans: Université d'Orléans. [http://tel.archives-ouvertes.fr/tel-00418642/.](http://tel.archives-ouvertes.fr/tel-00418642/)

Aston, M. A., M. H. Martin, and A. W. Jackson. 2015. "The Potential for Heavy Metal Soil Analysis on low Status Archaeological Sites at Shapwick, Somerset." *Antiquity* 72, no. 278: 838–847. [https://doi.org/10.](https://doi.org/10.1017/S0003598X00087445) [1017/S0003598X00087445.](https://doi.org/10.1017/S0003598X00087445)

Bailly-Maître, M.-C. 2002. "Concasser et broyer sur un site minier des XIIe-XIVe siècles: Brandes-en Oisans (Huez, Isère). Première étude à partir des outils, des ateliers et des résidus." In *Moudre et broyer. L'interprétation fonctionnelle de l'outillage de mouture et de broyage dans la Préhistoire et l'Antiquité: II - Archéologie et histoire: du Paléolithique au Moyen-âge*, edited by H. Procopiou and R. Treuil, 213–228. Paris: CTHS.

Barnett, M. C., N. A. Forster, G. A. Ray, L. Li, C. N. Guppy, and R. S. Hegarty. 2016. "Using Portable X-ray Fluorescence (pXRF) to Determine Fecal Concentrations of Non-Absorbable Digesta Kinetic and Digestibility Markers in Sheep and Cattle." *Animal Feed Science and Technology* 212: 35–41. [https://doi.org/10.1016/j.anifeedsci.2015.](https://doi.org/10.1016/j.anifeedsci.2015.12.015) [12.015.](https://doi.org/10.1016/j.anifeedsci.2015.12.015)

Baron, S., C. Le-Carlier, J. Carignan, and A. Ploquin. 2009. "Archaeological Reconstruction of Medieval Lead Production: Implications for Ancient Metal Provenance Studies and Paleopollution Tracing by Pb Isotopes." *Applied Geochemistry* 24, no. 11: 2093–2101.

Belli, M., R. Francovich, and F. Grassi, eds. 2005. *Archeologia di un castello minerario: il sito di Cugnano (Monterotondo M.mo, GR)*. Firenze: Edizioni All'insegna del giglio.

Belmon, J. 2003. "La production de l'argent en Rouergue au Moyen Âge: première approche d'après les sources écrites." In *Rouergue, carrefour d'histoire et de nature*, 238–272. Rodez: Fédération Historique de Midi-Pyrénées, Société des lettres, sciences et arts de l'Aveyron. [http://www.](http://www.persee.fr/web/revues/home/prescript/article/numi_0484-8942_2003_num_6_159_2519) [persee.fr/web/revues/home/prescript/article/numi_0484-8942_2003_](http://www.persee.fr/web/revues/home/prescript/article/numi_0484-8942_2003_num_6_159_2519) [num_6_159_2519.](http://www.persee.fr/web/revues/home/prescript/article/numi_0484-8942_2003_num_6_159_2519)

Benvenuti, M., Bianchi, G., Bruttini, J., Buonicontri, M., Chiarantini, L., Dallai, L., et al. 2014. "Studying the Colline Metallifere Mining Area in Tuscany: An Interdisciplinary Approach." IES Yearbook, 260–287. [https://doi.org/10.13140/2.1.3270.1446.](https://doi.org/10.13140/2.1.3270.1446)

Bernat, A. 2018. "Les mines d'argent médiévales du Minier." *Cahiers d'archéologie Aveyronnaise* 31: 109–158.

Bernat, A. 2021. "Le moulin de Dosaygues (commune du Viala-du-Tarn) (XVe-XIXe siècle)." Etudes aveyronnaises, 301–324.

Bintliff, J., and P. Degryse. 2022. "A review of soil geochemistry in archaeology." *Journal of Archaeological Science: Reports* 43: 103419.

Boisse, A. 1858. "Recherches sur le gisement des minerais métalliques dans l'Aveyron." *Mémoires de la Société des lettres, sciences et arts de l'Aveyron* 8: 285–418.

Braunstein, P. 2003. *Travail et entreprise au Moyen Âge*. Bruxelles: De Boeck. Accessed January 23, 2013. <http://www.sudoc.fr/076311155>.

BRGM. 1984. *Les gisements de Pb-Zn français (situation en 1977)*. Orléans: BRGM.

Cachau, C. 1961. *Bassin permien de Saint-Affrique*. Orléans: BRGM - A1899.

Camizuli, E., R. Scheifler, S. Garnier, et al. 2018. "Trace Metals From Historical Mining Sites and Past Metallurgical Activity Remain Bioavailable to Wildlife Today." *Scientific Reports* 8, no. 1: 3436. [https://](https://doi.org/10.1038/s41598-018-20983-0) doi.org/10.1038/s41598-018-20983-0.

Carey, C. J., and N. R. Moles. 2017. "Geochemical Survey and Evaluation Excavations at Alderley Edge: Recognizing Anthropogenic Signatures Within a Mining Site-Scape." *Archaeological Prospection* 24, no. 3: 225– 244. [https://doi.org/10.1002/arp.1566.](https://doi.org/10.1002/arp.1566)

Carr, R., C. Zhang, N. Moles, and M. Harder. 2008. "Identification and Mapping of Heavy Metal Pollution in Soils of a Sports Ground in Galway City, Ireland, Using a Portable XRF Analyser and GIS." *Environmental Geochemistry and Health* 30, no. 1: 45–52. [https://doi.org/10.1007/s1065](https://doi.org/10.1007/s10653-007-9106-0) [3-007-9106-0.](https://doi.org/10.1007/s10653-007-9106-0)

Chiarantini, L., M. Benvenuti, G. Bianchi, L. Dallai, V. Volpi, and R. Manca. 2021. "Medieval Pb (Cu-Ag) Smelting in the Colline Metallifere District (Tuscany, Italy): Slag Heterogeneity as a Tracer of Ore Provenance and Technological Process." *Minerals* 11, no. 2: 97. [https://](https://doi.org/10.3390/min11020097) [doi.org/10.3390/min11020097.](https://doi.org/10.3390/min11020097)

Chilès, J.-P., and P. Delfiner. 2012. *Geostatistics: Modeling Spatial Uncertainty*. New York: Wiley-Interscience. [https://onlinelibrary.wiley.](https://onlinelibrary.wiley.com/doi/book/10.1002/9781118136188) [com/doi/book/10.1002/9781118136188.](https://onlinelibrary.wiley.com/doi/book/10.1002/9781118136188)

Degryse, P., P. Muchez, S. Six, and M. Waelkens. 2003. "Identification of ore Extraction and Metal Working in Ancient Times: A Case Study of Sagalassos (SW Turkey)." *Journal of Geochemical Exploration* 77, no. 1: 65–80. [https://doi.org/10.1016/S0375-6742\(02\)00270-4](https://doi.org/10.1016/S0375-6742(02)00270-4).

Ding, L., S. Wang, B. Cai, M. Zhang, and C. Qu. 2018. "Application of Portable X-Ray Fluorescence Spectrometry in Environmental Investigation of Heavy Metal-Contaminated Sites and Comparison With Laboratory Analysis." *IOP Conference Series: Earth and Environmental Science* 121, no. 3: 032031. <https://doi.org/10.1088/1755-1315/121/3/032031>.

Dossat, Y. 1975. "La mine d'argent d'Orzals en Rouergue pendant la seconde moitié du XIIIe siècle." In *Mines et métallurgie, XIIe-XVIe siècles: actes du 98e Congrès national des sociétés savantes, Saint-Étienne, 1973, Section de philologie et d'histoire jusqu'à 1610*, 81–95. Paris: Bibliothèque nationale. Accessed January 23, 2013. [http://babordplus.univ-borde](http://babordplus.univ-bordeaux.fr/notice.php?lang=es&q=id:585449) [aux.fr/notice.php?lang=es&q=id:585449](http://babordplus.univ-bordeaux.fr/notice.php?lang=es&q=id:585449).

Flament, J., F. Téreygeol, and G. Sarah. 2019. "La production du cuivre et de ses alliages à Castel-Minier (Ariège, France): opportunisme métallurgique et pragmatisme économique d'une fonderie de moyenne montagne au XVe¬ siècle." In *Les métaux précieux en Méditerranée médiévale. Exploitations, transformations, circulations: actes du colloque international d'Aix-en-Provence, 6–8 Octobre 2016*, edited by N. M. Larousse, M.-C. Bailly-Maître, and G. Bianchi. Aix-en-Provence: Centre Camille-Jullian/Presses Universitaires de Provence.

Förstner, U. 1985. "Chemical methods for assessing bio-available metals in sludges and soils." In *Chemical methods for assessing bio-available metals in sludges and soils*, edited by R. Leschber, R. D. Davis, and P. L'Hermite. London; New York: Elsevier Applied Science Publishers. <https://link.springer.com/book/9780853343592>.

Garrigou Grandchamp, P., F. Mazeran, and F. Galès. 2013. "Les maisons médiévales du Minier (le Viala)." In *Journée d'étude: La maison médiévale en Aveyron*, 12–14. Toulouse: Société Archéologique du Midi de la France.

Geltner, G. 2023. "Ecological Impacts and Environmental Perceptions of Mining in Europe, 1200–1550: Preliminary Notes." *Parergon* 40, no. 1: 157–180. [https://doi.org/10.1353/pgn.2023.a905418.](https://doi.org/10.1353/pgn.2023.a905418)

Goloubinoff, C. 1984. *Le permo-houiller du nord du bassin de Saint-Affrique, Aveyron*. Orléans: Editions du Bureau de recherches géologiques et minières, Service géologique national.

Higueras, P., R. Oyarzun, J. M. Iraizoz, S. Lorenzo, J. M. Esbrí, and A. Martínez-Coronado. 2012. "Low-Cost Geochemical Surveys for Environmental Studies in Developing Countries: Testing a Field Portable XRF Instrument Under Quasi-Realistic Conditions." *Journal of Geochemical Exploration* 113: 3–12. [https://doi.org/10.1016/j.gexplo.](https://doi.org/10.1016/j.gexplo.2011.02.005) [2011.02.005.](https://doi.org/10.1016/j.gexplo.2011.02.005)

Horák, J., and M. Hejcman. 2016. "800 Years of Mining and Smelting in Kutná Hora Region (The Czech Republic)—Spatial and Multivariate meta-Analysis of Contamination Studies." *Journal of Soils and Sediments* 16, no. 5: 1584–1598. <https://doi.org/10.1007/s11368-015-1328-7>.

Horta, A., L. Azevedo, J. Neves, A. Soares, and L. Pozza. 2021. "Integrating Portable X-Ray Fluorescence (pXRF) Measurement Uncertainty for Accurate Soil Contamination Mapping." *Geoderma* 382: 114712. [https://doi.org/10.1016/j.geoderma.2020.114712.](https://doi.org/10.1016/j.geoderma.2020.114712)

Hrubý, P. 2011. *Jihlava – Staré Hory. Archeologický výzkum středověkého důlního, úpravnického a obytného areálu v letech 2002–2006*. Prague: Univerzita Karlova v Praze.

Hrubý, P. 2021. *Erzbergbau und Edelmetallproduktion im böhmischen Königreich während des 13. Jhs. im Kontext der europäischen Montanarchäologie*. Dresden: Landesamt für Archäologie Sachsen.

Hrubý, P., P. Hejhal, A. Hoch, et al. 2012. "Středověký úpravnický a hornický areál Cvilínek u Černova na Pelhřimovsku." *Památky archeologické* 103, no. 1: 339–418.

Hrubý, P., M. Kmošek, R. Kočárová, et al. 2021. "Medieval Mining Centre of Buchberg in the Bohemian-Moravian Highlands. Metal Production in the Kingdom of Bohemia (13th–14th Centuries)." *Památky archeologické* 112: 333–384. [https://doi.org/10.35686/PA2021.7.](https://doi.org/10.35686/PA2021.7)

Huang, B., Z. Yuan, D. Li, M. Zheng, X. Nie, and Y. Liao. 2020. "Effects of Soil Particle Size on the Adsorption, Distribution, and Migration Behaviors of Heavy Metal (Loid)s in Soil: A Review." *Environmental Science: Processes & Impacts* 22, no. 8: 1596–1615. [https://doi.org/10.](https://doi.org/10.1039/D0EM00189A) [1039/D0EM00189A.](https://doi.org/10.1039/D0EM00189A)

Hübner, N., F. Körner, and J. Schneider. 2011. "Tectonics, Climate and Facies of the Saint Affrique Basin and Correlation With the Lodève Basin (Permian, Southern France)." *Zeitschrift der Deutschen Gesellschaft für Geowissenschaften* 162: 157–170. [https://doi.org/10.1127/1860-1804/](https://doi.org/10.1127/1860-1804/2011/0162-0157) [2011/0162-0157.](https://doi.org/10.1127/1860-1804/2011/0162-0157)

Hürkamp, K., T. Raab, and J. Völkel. 2009. "Two and Three-Dimensional Quantification of Lead Contamination in Alluvial Soils of a Historic Mining Area Using Field Portable X-Ray Fluorescence (FPXRF) Analysis." *Geomorphology* 110, no. 1: 28–36. [https://doi.org/10.1016/j.](https://doi.org/10.1016/j.geomorph.2008.12.021) [geomorph.2008.12.021.](https://doi.org/10.1016/j.geomorph.2008.12.021)

Janovský, M., and J. Horák. 2018. "Large Scale Geochemical Signatures Enable to Determine Landscape Use in the Deserted Medieval Villages." *Interdisciplinaria Archaeologica—Natural Sciences in Archaeology* IX, no. 1: 71–80. <https://doi.org/10.24916/iansa.2018.1.5>.

Johans, E. 2000. "Les mines d'argent du comté de Rodez. Etude de la charte de coutume du Minier-de-Montjaux (Aveyron)." *Revue du Rouergue*, no. 64: 553–573.

Kennedy, S. A., and S. J. Kelloway. 2021. "Heavy Metals in Archaeological Soils: The Application of Portable X-Ray Fluorescence (pXRF) Spectroscopy for Assessing Risk to Human Health at Industrial Sites." *Advances in Archaeological Practice* 9, no. 2: 145–159. [https://doi.](https://doi.org/10.1017/aap.2020.52) [org/10.1017/aap.2020.52](https://doi.org/10.1017/aap.2020.52).

Killick, D. 2014. "From Ores to Metals." In *Archaeometallurgy in Global Perspective: Methods and Syntheses*, edited by B. W. Roberts and C. P. Thornton, 11–45. New York: Springer. [https://doi.org/10.1007/978-1-](https://doi.org/10.1007/978-1-4614-9017-3_2) [4614-9017-3_2](https://doi.org/10.1007/978-1-4614-9017-3_2).

Kim, H.-R., K.-H. Kim, S. Yu, et al. 2019. "Better Assessment of the Distribution of As and Pb in Soils in a Former Smelting Area, Using Ordinary Co-Kriging and Sequential Gaussian Co-Simulation of Portable X-Ray Fluorescence (PXRF) and ICP-AES Data." *Geoderma* 341: 26–38. <https://doi.org/10.1016/j.geoderma.2019.01.031>.

Laenger, A., A. Martel, F. Boucher, et al. 2022. "Comparison of Geophysical Prospecting and Geochemical Prospecting at the Medieval and Modern Cistercian Abbey of Carnoët (Finistère, France)." *Archaeological Prospection* 29, no. 4: 597–606. [https://doi.org/10.1002/](https://doi.org/10.1002/arp.1875) [arp.1875](https://doi.org/10.1002/arp.1875).

Lagerström, M., M. Norling, and B. Eklund. 2016. "Metal Contamination at Recreational Boatyards Linked to the Use of Antifouling Paints— Investigation of Soil and Sediment With a Field Portable XRF." *Environmental Science and Pollution Research* 23, no. 10: 10146–10157. [https://doi.org/10.1007/s11356-016-6241-0.](https://doi.org/10.1007/s11356-016-6241-0)

Laperche, V. 2005. *Evaluation des performances du spectromètre portable de fluorescence X NITON XL723S (au laboratoire et sur le terrain) (No. RP-53377-FR) (p. 107)*. Orléans: BRGM.

Laperche, V., and B. Lemière. 2020. "Possible Pitfalls in the Analysis of Minerals and Loose Materials by Portable XRF, and How to Overcome Them." *Minerals* 11, no. 1: 33. <https://doi.org/10.3390/min11010033>.

Li, Q., Y. Wang, Y. Li, et al. 2022. "Speciation of Heavy Metals in Soils and Their Immobilization at Micro-Scale Interfaces Among Diverse Soil Components." *Science of the Total Environment* 825: 153862. [https://](https://doi.org/10.1016/j.scitotenv.2022.153862) doi.org/10.1016/j.scitotenv.2022.153862.

Martín, F., M. Simón, I. Garca, A. Romero, and V. González. 2014. "Pollution of Pb in Soils Affected by Pyrite Tailings: Influence of Soil Properties." In *Environmental Risk Assessment of Soil Contamination*,

edited by M. C. Hernandez Soriano. London, United Kingdom: Intech. <https://doi.org/10.5772/57270>.

Maulana, A. A., B. V. Tangahu, A. A. G. Kartika, et al. 2019. "Study of Lead (Pb) Distribution in Soil of Jetis District, Mojokerto Regency." *Journal of Civil Engineering and Environmental Sciences* 5, no. 2: 5–12.

Maus, V., and T. T. Werner. 2024. "Impacts for Half of the World's Mining Areas Are Undocumented." *Nature* 625, no. 7993: 26–29. [https://](https://doi.org/10.1038/d41586-023-04090-3) doi.org/10.1038/d41586-023-04090-3.

Merkel, S. W., A. Hauptmann, T. Kirnbauer, and F. Téreygeol. 2016. "Silver Production at al-Radrad: Archaeometallurgical Analysis of ore, Slag and Technical Ceramics From Early Medieval Yemen." *Arabian Archaology and Epigraphy* 27, no. 1: 107–126. [https://doi.org/10.1111/aae.12070.](https://doi.org/10.1111/aae.12070)

Mikołajczyk, Ł., and K. Milek. 2016. "Geostatistical Approach to Spatial, Multi-Elemental Dataset From an Archaeological Site in Vatnsfjörður, Iceland." *Journal of Archaeological Science: Reports* 9: 577–585. [https://](https://doi.org/10.1016/j.jasrep.2016.08.036) [doi.org/10.1016/j.jasrep.2016.08.036.](https://doi.org/10.1016/j.jasrep.2016.08.036)

Minvielle Larousse, N. 2019. "A 13th-Century Hydraulic Ore Mill at the Mining Site of Brandes (Isère), France." In *Tilting at Mills, the Archaeology and Geology of Mills and Milling, Proceedings of the Colloquium Held at the Museum of Archaeology of Almería, Spain, 5th-8th March, 2014*, edited by T. Anderson, 202–223. Southampton: Highfield Press.

Minvielle Larousse, N. 2023. *L'âge de l'argent. Mines, société et pouvoirs en Languedoc médiéval. Aix-en-Provence*. Rome: Presses Universitaires de Provence, Ecole française de Rome.

Minvielle Larousse, N., J. Belmon, A. Bernat, et al. 2021. *Le Minier: histoire et archéologie des entreprises argentifères médiévales. Rapport de PCR*, 186. Toulouse: Ecole française de Rome LA3M - UMR7298 AMU-CNRS. Accessed December 20,2021. [https://halshs.archives-ouvertes.](https://halshs.archives-ouvertes.fr/halshs-03495432) [fr/halshs-03495432.](https://halshs.archives-ouvertes.fr/halshs-03495432)

Minvielle Larousse, N., A. Bernat, J. Belmon, and F. Galès. 2019a. "Le Minier. Résultats de la campagne de prospection 2019." *Cahiers d'archéologie aveyronnaise* 32: 109–131.

Minvielle Larousse, N., L. Brevet, C. Denizeau, and C. Tomczyk. 2022. *Le Minier. Rapport de fouilles programmées 2022*. Ecole française de Rome: Laboratoire d'archéologie médiévale et moderne en Méditerranée. Accessed April 28, 2023. [https://shs.hal.science/halshs-04084883.](https://shs.hal.science/halshs-04084883)

Minvielle Larousse, N., I. Commandré, M. Fabre, et al. 2019b. "Les ateliers-maisons des argentières du Colombier. Travailler et vivre au XIe et XIIe siècles dans une exploitation minière cévenole." *Archéologie Médiévale* 49: 1–52. <https://doi.org/10.4000/archeomed.24762>.

Mohammadi, S. P., J. Horák, L. Lisá, et al. 2023. "Soils as an Environmental Record of Changes Between Iron age and Medieval Occupations at Chotěbuz-Podobora Hillfort." *Geoderma* 429: 116259. [https://doi.org/10.1016/j.geoderma.2022.116259.](https://doi.org/10.1016/j.geoderma.2022.116259)

Olovčić, A., M. Memić, A. Kevilj-Olovčić, and E. Ramić. 2022. "Medieval Slag From Gornji Potočari (Srebrenica Municipality, B&H): A Relationship Between Initial Ore and Metallurgical Processes." *Godišnjak Centra za balkanološka ispitivanja* 46: 215–224. [https://doi.](https://doi.org/10.5644/Godisnjak.CBI.ANUBiH-46.95) [org/10.5644/Godisnjak.CBI.ANUBiH-46.95.](https://doi.org/10.5644/Godisnjak.CBI.ANUBiH-46.95)

Pastor, A., G. Gallello, M. L. Cervera, and M. de la Guardia. 2016. "Mineral Soil Composition Interfacing Archaeology and Chemistry." *TrAC Trends in Analytical Chemistry* 78: 48–59. [https://doi.org/10.](https://doi.org/10.1016/j.trac.2015.07.019) [1016/j.trac.2015.07.019.](https://doi.org/10.1016/j.trac.2015.07.019)

Peinado, F. M., S. M. Ruano, M. G. B. González, and C. E. Molina. 2010. "A Rapid Field Procedure for Screening Trace Elements in Polluted Soil Using Portable X-Ray Fluorescence (PXRF)." *Geoderma* 159, no. 1: 76– 82. [https://doi.org/10.1016/j.geoderma.2010.06.019.](https://doi.org/10.1016/j.geoderma.2010.06.019)

Ploquin, A., M.-C. Bailly-Maître, P. Allée, et al. 2010. "Mines et métallurgies anciennes du plomb dans leurs environnements Apports des méthodes contribuant à leur étude." *ArchéoSciences* 34: 97–307.

Qu, M., J. Chen, W. Li, et al. 2019. "Correction of In-Situ Portable X-Ray Fluorescence (PXRF) Data of Soil Heavy Metal for Enhancing Spatial Prediction." *Environmental Pollution* 254: 112993. [https://doi.org/10.](https://doi.org/10.1016/j.envpol.2019.112993) [1016/j.envpol.2019.112993](https://doi.org/10.1016/j.envpol.2019.112993).

Ravansari, R., S. C. Wilson, and M. Tighe. 2020. "Portable X-Ray Fluorescence for Environmental Assessment of Soils: Not Just a Point and Shoot Method." *Environment International* 134: 105250. [https://doi.](https://doi.org/10.1016/j.envint.2019.105250) [org/10.1016/j.envint.2019.105250](https://doi.org/10.1016/j.envint.2019.105250).

Save, S., J. Kovacik, F. Demarly-Cresp, et al. 2020. "Large-Scale Geochemical Survey by pXRF Spectrometry of Archaeological Settlements and Features: New Perspectives on the Method." *Archaeological Prospection* 27, no. 3: 203–218. [https://doi.org/10.1002/](https://doi.org/10.1002/arp.1773) [arp.1773.](https://doi.org/10.1002/arp.1773)

Shugar, A. N. 2013. "Portable X-Ray Fluorescence and Archaeology: Limitations of the Instrument and Suggested Methods to Achieve Desired Results." In *Archaeological Chemistry VIII*, edited by R. A. Armitage and J. H. Burton, 173–193. New Orleans: American Chemical Society. [https://doi.org/10.1021/bk-2013-1147.ch010.](https://doi.org/10.1021/bk-2013-1147.ch010)

Shuttleworth, E. L., M. G. Evans, S. M. Hutchinson, and J. J. Rothwell. 2014. "Assessment of Lead Contamination in Peatlands Using Field Portable XRF." *Water, Air, & Soil Pollution* 225, no. 2: 1844. [https://doi.](https://doi.org/10.1007/s11270-013-1844-2) [org/10.1007/s11270-013-1844-2.](https://doi.org/10.1007/s11270-013-1844-2)

Stöllner, T. R. 2014. "Methods of Mining Archaeology (Montanarchäologie)." In *Archaeometallurgy in Global Perspective*, edited by B. W. Roberts and C. P. Thornton, 133–159. New York: Springer. [https://doi.org/10.1007/978-1-4614-9017-3_7.](https://doi.org/10.1007/978-1-4614-9017-3_7)

Štular, B., Ž. Kokalj, K. Oštir, and L. Nuninger. 2012. "Visualization of Lidar-Derived Relief Models for Detection of Archaeological Features." *Journal of Archaeological Science* 39, no. 11: 3354–3360. [https://doi.org/](https://doi.org/10.1016/j.jas.2012.05.029) [10.1016/j.jas.2012.05.029.](https://doi.org/10.1016/j.jas.2012.05.029)

Sut-Lohmann, M., S. Ramezany, F. Kästner, and T. Raab. 2022. "Feasibility of pXRF to Evaluate Chosen Heavy Metals in Soil Highly Influenced by Municipal Waste Disposal—A Monitoring Study of a Former Sewage Farm." *Land Degradation & Development* 33, no. 3: 439–451. <https://doi.org/10.1002/ldr.4147>.

Téreygeol, F. 2019. "La préparation des minerais argentifères au Moyen Âge: choix technique ou contrainte économique ?" In *Les métaux précieux en Méditerranée médiévale. Exploitations, transformations, circulations. Actes du colloque international d'Aix-en-Provence des 6, 7 et 8 octobre 2016*, edited by N. M. Larousse, M.-C. Bailly-Maître, and G. Bianchi. Aix-en-Provence: Presses universitaires de Provence.

Téreygeol, F., A. Arles, E. Foy, N. Florsch, and M. Llubes. 2010. "Dosages par fluorescence X portable d'ateliers médiévaux de production des métaux non-ferreux." *ArchéoSciences. Revue d'archéométrie* 34: 243–252.

Téreygeol, F., and M.-P. Guirado. 2012. "Affiner l'argent au four de coupellation: expérimentations autour du De Re Metallica d'Agricola." In *Comprendre les savoir-faire métallurgiques antiques et médiévaux*, edited by F. Téreygeol, 169–187. Paris: Errance.

Tolksdorf, J. F., M. Bertuch, C. Herbig, and H. Hönig. 2018. *Mittelalterlicher Bergbau und Umwelt im Erzgebirge: eine interdisziplinäre Untersuchung*. Dresden: Landesamt für Archäologie Sachsen.

Tomczyk, C., and N. Minvielle Larousse. 2023. "Efficiency of Portable X-Ray Fluorescence for Distinguishing Lead Slag." *Applied Spectroscopy* 78: 175–185. <https://doi.org/10.1177/00037028231216758>.

Trant, P. L. K., S. M. Kristiansen, A. V. Christiansen, B. Wouters, and S. M. Sindbæk. 2021. "Sampling Density and Spatial Analysis: A Methodological pXRF Study of the Geochemistry of a Viking-Age House in Ribe, Denmark." *Archaeological and Anthropological Sciences* 13, no. 1: 21.<https://doi.org/10.1007/s12520-020-01243-7>.

Vaissière, M. 2011. "Le château du Trépador: étude d'un ancien chef-lieu (2ème partie)." *Cahiers d'archéologie aveyronnaise* 24: 122–159.

Volpi, V., L. Dallai, and A. Donati. 2019. "L'uso di tecnologie ad elevate prestazioni, pXRF, per lo studio del distretto minerario delle Colline Metallifere (Toscana, Italia)." In *Les métaux précieux en Méditerranée médiévale. Exploitations, transformations, circulations: actes du colloque international d'Aix-en-Provence, 6–8 octobre 2016*, edited by N. M. Larousse, M.-C. Bailly-Maître, and G. Bianchi, 16. Aix-en-Provence: Centre Camille-Jullian/Presses Universitaires de Provence. [https://](https://books.openedition.org/pup/40360?lang=fr) books.openedition.org/pup/40360?lang=fr.

Walraven, N., M. Bakker, B. Van Os, G. Klaver, J. J. Middelburg, and G. Davies. 2016. "Pollution and Oral Bioaccessibility of Pb in Soils of Villages and Cities With a Long Habitation History." *International Journal of Environmental Research and Public Health* 13, no. 2: 221. [https://doi.org/10.3390/ijerph13020221.](https://doi.org/10.3390/ijerph13020221)

Weindorf, D. C., L. Paulette, and T. Man. 2013. "In-Situ Assessment of Metal Contamination via Portable X-Ray Fluorescence Spectroscopy: Zlatna, Romania." *Environmental Pollution* 182: 92–100. [https://doi.org/](https://doi.org/10.1016/j.envpol.2013.07.008) [10.1016/j.envpol.2013.07.008.](https://doi.org/10.1016/j.envpol.2013.07.008)

Williams, R., D. Errickson, and G. Taylor. 2021. "Mapping an Archaeological Site: Interpreting Portable X-Ray Fluorescence (pXRF) Soil Analysis at Boroughgate, Skelton, UK." *Journal of Archaeological Science: Reports* 38: 103109. [https://doi.org/10.1016/j.jasrep.2021.103109.](https://doi.org/10.1016/j.jasrep.2021.103109)

Williams, R., G. Taylor, and C. Orr. 2020. "pXRF Method Development for Elemental Analysis of Archaeological Soil." *Archaeometry* 62, no. 6: 1145–1163. [https://doi.org/10.1111/arcm.12583.](https://doi.org/10.1111/arcm.12583)

Supporting Information

Additional supporting information can be found online in the Supporting Information section.