Journal of Archaeological Science: Reports: Volume 42, April 2022, Article number 103366
DOI: 10.1016/j.jasrep.2022.103366

Tracking the source of lead of medieval glazed pottery of the Meuse valley (Belgium) through lead isotope analyses

The corrections made in this section will be reviewed and approved by a journal production editor.

Eric Goemaere[a,*], egoemaere@naturalsciences.be, Sophie Challe[b], Sylvie de Longueville[b], Thomas Delbey[c], Daniel Demaiffe[d]

[a]Geological Survey of Belgium, Royal Belgian Institute of Natural Sciences, Rue Vautier 29, 1000 Brussels, Belgium

[b]Direction Scientifique et Technique, Agence Wallonne du Patrimoine, Service public de Wallonie, Rue des Brigades d'Irlande 1, 5100 Jambes, Belgium

[c]Cranfield Forensic Institute, Cranfield University, Defence Academy of the United Kingdom, Shrivenham SN6 8LA, United Kingdom

[d]Laboratoire G-time, Département de Géologie (DGES, CP160/02), UniversitéLibre de Bruxelles (ULB), Avenue F. Roosevelt 50, 1050 Bruxelles, Belgium

*Corresponding author.

Abstract

Lead isotope analyses (by MC-ICP-MS) have been performed on lead-glazed pottery artefacts from several production and consumption sites in the Meuse basin (Belgium) spanning a long-time period from the 9th to the 16th century CE. Comparison of the lead isotope data of the glazes from three Mosan workshops with those of galenas from Palaeozoic (Variscan) Pb-Zn deposits from both Belgium and Western Germany points to a common Pb source that we identify as the regional Pb deposits hosted in Dinantian limestones of the Ardenno-Rhenish Massif, more specifically in the Namur and Verviers synclines in Belgium and in the Aachen-Stolberg mining district in Germany. The overall similarity of isotopic compositions between the medieval artefacts and the Variscan galenas implies that the Mosan medieval potters used accessible local Pb-Zn ores mined between Namur and Huy. On the consumption sites of Dinant, the slightly different isotopic compositions of some potteries suggest that other regional Pb sources were used to produce the glazes. A comparison with Roman lead objects discovered in north-western Europe (Northern Gaul) shows the very good correspondence of the Pb isotopic compositions with those of the Medieval artefacts which indicates a very long continuity of regional lead supply and consequently of lead ore mining.

Keywords:

Lead-glazed pottery, Middle age, Lead isotope analysis, Lead ores, Sourcing, Mosan valley, Belgium

Abbreviations

No keyword abbreviations are available

1 Introduction and aims

Glazed ceramics has been developed in the Middle East since the second millennium BCE but this technique remains for a long time confined to the East Mediterranean area. The earliest use of lead glazes in the Greco-Roman world seems to have occurred during the late Hellenistic period, in Anatolia, from about the first century BC onwards. Then, lead-glazed ceramics were found in the Western Mediterranean with workshops that date to the Augustan period (27 BC – 14 AD) identified in both Italy and near Lyon in Gaul (Walton and Tite, 2010). They were extensively used for both potteries and tiles throughout the Islamic and Byzantine worlds, and in medieval Europe. Such high-lead glazes have higher refractive indexes and hence greater brilliances than the alkali glazes (Tite et al., 1998). While this decorative technique continued around the Mediterranean (Spain, Italy, the Islamic world) during the first centuries of the Middle Ages, the use of glaze seems to have disappeared in north-western Europe during the 4th and 5th centuries (Hurst, 1969). The question of its reappearance in the 9th and 10th centuries is complex and not fully resolved (Verhaeghe, 1995; Husi, 2006).

In the Meuse valley in Belgium, the oldest productions of glazed ceramics were discovered in Haillot, where at least eight kilns were in use during the second half of the 10th and the beginning of the 11th century (de Longueville and Vanmechelen, 2017), and in Mozet, where three kilns dating from the first half of the 11th century were discovered (de Longueville and Plumier, 2007). It is in the agglomerations of Namur and Huy, however, that significantly older consumption contexts have revealed Mosan glazed ceramics (Giertz, 1996; de Longueville, 2006). The proportion of ceramics that were at least partially glazed increased until they represented nearly 90% of the production of the Huy potters' workshops from the beginning of the 14th century. Archaeological studies of medieval ceramics from the Meuse Valley most often focus on typological and technical aspects (Giertz, 1996; Challe and de Longueville, 2013; de Longueville, 2015; de Longueville and Vanmechelen, 2017; Challe et al., 2017). These approaches are sometimes complemented by petrographic analyses to characterise the production and identify the sources of the raw clays (Van Wersch et al., 2020).

The first chemical analyses (obtained by EDS) carried out on the Mosan glazes of Dinant have brought to light some interesting findings: the glaze mixture was applied to raw clay as well as to clay after a first firing; all the glazes analysed contain zinc, in small but significant quantities (0–2.4% ZnO) which appears to be a local or even regional specificity (Goemaere et al., 2015). The light yellow to orange transparent glazes are typical of a high lead type (42 to 63% PbO) with moderate contents of SiO_2 (28–42 %) and Al_2O_3 (5–12 %) and traces of Zn and Fe. Medieval recipes to produce the lead glazes in the Meuse valley are unknown. The nature of the Pb-bearing component applied to the ceramic body is this not known neither. Several possibilities can be mentioned: powdered galena, lead oxides, (PbO, Pb_3O_4), metallic lead (Pb^0), other minerals ($PbSO_4$, $PbCO_3$). The binding agent (flour, milk, water) has not been identified. Experimental studies are in progress. As lead is a heavy element (mass numbers of all stable isotopes > 200), the relative mass differences between isotopes are small: <1% for isotopic ratios $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ and < 2% for

$^{208}Pb/^{206}Pb$. So, whatever the process of turning galena into Pb-bearing glaze, this will not induce isotopic fractionation. Consequently, the Pb isotopic composition of the glaze is identical to that of the original galena and can thus be used as a tracer of the Pb source.

The aims of this paper are manyfold: 1) determine the lead isotopic signature of the Mosan medieval glazed ceramics; 2) compare the lead composition of the glazes found in the production workshops of Haillot, Andenne and Huy, as well as with the samples found in nearby consumption sites; 3) identify the source(s) of lead of the medieval pottery workshops; 4) establish whether the source(s) of the lead ores stays unchanged or varies during a time span of eight centuries; 5) compare the source of the lead used by medieval potters with the one used by Roman craftsmen.

We also had the opportunity to analyse a water supply pipe in lead from the "Li Bassinia" fountain. This water tank in Huy is dated from 1406 but the pipe could date from the 15th or 16th century CE (Peters, 2018). The issue here is to know if the lead used is of local or regional origin and if it can be compared to the glazing mixture made by medieval potters.

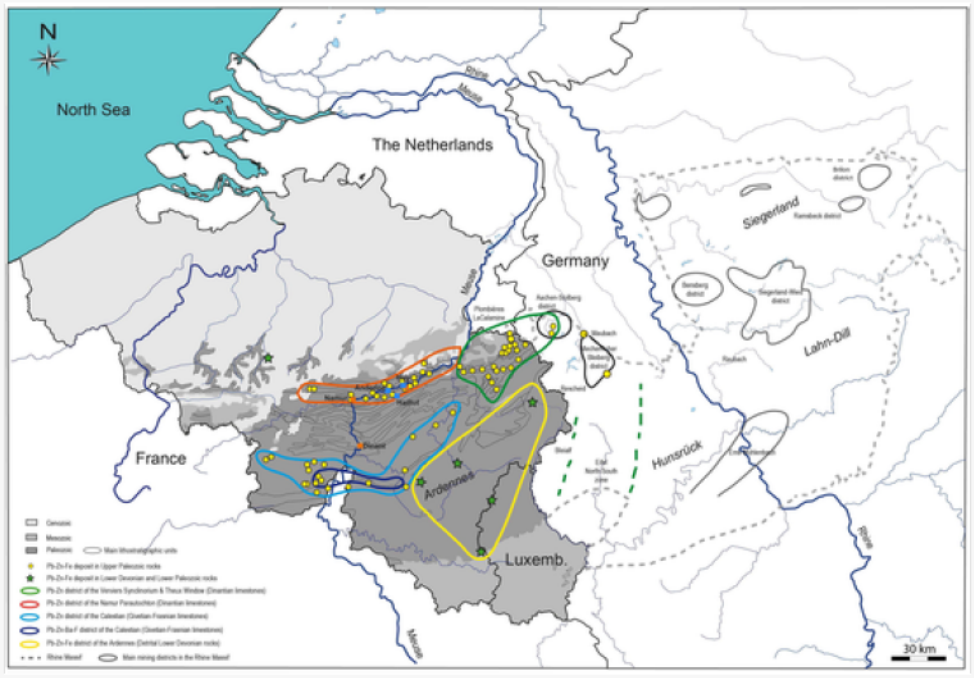
2 Samples and experimental procedures

2.1 Archaeological setting and ceramic artefacts

The 25 glazed medieval sherds analysed in this study come from Belgian mosan sites, located in the province of Namur and excavated by the Service public de Wallonie. They come from production contexts (Haillot, Huy, Andenne) and consumption contexts (Namur, Huy, Dinant) dated between the end of the 9th and the 16th century CE (Fig. 1, Fig. 2, Table 1).

Images are optimised for fast web viewing. Click on the image to view the original version.

Fig. 1



Geographical, geological and metallogenic sketch map of the area considered in this study. Blue and orange squares respectively represent the pottery workshops and the consumption sites with lead-glazed pottery. The Pb-Zn mining districts of Belgium and the location of geological samples are modified after Dejonghe (1998). The Pb-Zn metallogenic map of the Rhine Massif is modified after Bode et al. (2009).

Images are optimised for fast web viewing. Click on the image to view the original version.

Fig. 2

Mosan glazed pottery: a. Haillot (second half 10th c.- first half 11th c.); b. Andenne-résidence Noël (middle 11th c. - first quarter 12th c.); c. Andenne (first half 12th c.). Pictures : a) R. Gilles © AWaP; b) © Espace muséal d'Andenne, c) © Espace muséal d'Andenne.

Table 1

The table layout displayed in this section is not how it will appear in the final version. The representation below is solely purposed for providing corrections to the table. To preview the actual presentation of the table, please view the Proof.

Short description of the lead-glazed medieval ceramics objects of the Meuse valley.

Excavation site	Discovery setting	Chronology	Inventory number	Analytical Id.	Description
Andenne (Noël) - potter's workshop	Pottery wasters pit F006	first quarter 12th c.	AND13NOE.01.046.0123	AND-03	Carinated bowl. Mosan orange clay. Yellow-orange glaze
Andenne (Noël) - potter's workshop	Pottery wasters pit F015	13th c.	AND13NOE.01.061.0001	AND-07	Bowl ("terrine"). Mosan white clay. Yellow glaze
Andenne (Noël) - potter's workshop	Quadrangular potter's kiln F068	14th c.	AND15NOE.01.369.0002	AND-09	Bowl ("terrine"). Mosan white clay. Yellow glaze
Andenne (Noël) - potter's workshop	Quadrangular potter's kiln F068	14th c.	AND15NOE.01.369.0002	AND-09bis	Bowl ("terrine"). Mosan white clay. Yellow glaze
Dinant (Churchill) - settlement	Backfill before fire.	first half 15th c.	DIN07CHUR.01.132.0003	Di-003	Jug. Mosan white clay. Yellow glaze
Dinant (Churchill) - settlement	Backfill before fire.	first half 15th c.	DIN07CHUR.01.132.0007	Di-007	Tripod cooking pot. Mosan white or grey clay. Brown metallescent glaze
Dinant (Churchill) - settlement	Backfill of a cellar.	15th c.	DIN07CHUR.01.080.0010	Di-080	Globular pot with handles. Mosan white clay. Yellow glaze
Dinant (Filature) - settlement	Latrine backfill F48	14th - 16th c.	DIN03FIL.01.127.0013	Di-001	Large bowl ("tèle"). Mosan red clay. Orange glaze
Dinant (Filature) - settlement	Latrine backfill F48	14th - 16th c.	DIN03FIL.01.130.0010	Di-010	Basket-handle pot. Mosan white clay. Yellow glaze
Dinant (Filature) - settlement	Latrine backfill F48	14th - 16th c.	DIN03FIL.01.130.0011	Di-011	Globular pot with handles. Mosan white clay. Yellow glaze
Dinant (Filature) - settlement	Latrine backfill F48	14th - 16th c.	DIN03FIL.01.130.0012	Di-012	Large bowl ("tèle"). Mosan white clay. Green glaze
Dinant (Filature) - settlement	Latrine backfill F48	14th - 16th c.	DIN03FIL.01.127.0022	Di-022	Large bowl ("tèle"). Mosan red clay. Dark orange glaze
Dinant (Filature) - settlement	Foundation ditch backfill F25	until the end 16th c.	DIN03FIL.01.020	Di-020/1	Sherd of an indeterminate pot. Mosan white clay. bluish yellow glaze
Dinant (Filature) - settlement	Cellar backfill F20	until the end 16th c.	DIN03FIL.01.52	Di-052	Dish. Mosan white clay. Yellow-orange glaze with red barbotine decoration
Dinant (Filature) - settlement	Cellar backfill F20	until the end 16th c.	DIN03FIL.01.52	Di-052bis	Dish. Mosan white clay. Yellow-orange glaze with red barbotine decoration
Dinant (Filature) - settlement	Backfill of pit F146	end 15th c.	DIN03FIL.01.423	Di-425	Large bowl ("tèle"). Mosan red clay. Light yellow glaze
Haillot - potter's workshop	Backfill of potter's kiln F30	10th - beg. 11th c..	OHE05HAI.07.160.0001	EG-6	Bottom of an indeterminate pot. Mosan white clay. Light yellow glaze
Haillot - potter's workshop	Abandonment layer of potter's kilns F99	10th - beg. 11th c..	OHE05HAI.07.205.0001	EG-7	Sherd of a globular pot. Mosan white clay. Greenish yellow glaze

Haillot - potter's workshop	Abandonment layer of potter's kilns F99	10th - beg. 11th c..	OHE05HAI.07.205.0002	EG-8	Sherd of a globular pot. Mosan white clay. Yellow glaze
Huy (Aux Ruelles) - potter's workshop	Pottery wasters pit F60	first half 14th c.	HY05RU.01.274.374	EG-12	Sherd of a terrine. Mosan white clay. Yellow glaze
Huy (Aux Ruelles) - potter's workshop	Pottery wasters pit F60	first half 14th c.	HY05RU.01.274.378	EG-13	Cooking pot (sherd). Mosan red clay. Yellow glaze
Huy (Aux Ruelles) - potter's workshop	Pottery wasters pit F60	first half 14th c.	HY05RU.01.274.379	EG-14	Cooking pot (sherd). Mosan red clay. Orange brown and green glaze
Huy (Aux Ruelles) - settlement	Fill F132	end 9th - 10th c.	HY06RU.01.666.0001	EG-11	Handle of a pot. Mosan white clay. Dark yellow glaze
Huy (Aux Ruelles) - settlement	Backfill of pit F114	end 10 th - beg. 11th c.	HY06RU.01.608.0001	EG-9	Sherd of a globular pot. Mosan white clay. Yellow glaze
Namur (Grognon) - riverbank	Black earths F229	end 9th - mid. 10th c.	NRGRO2.17.765.0012	EG-16	Sherd of a globular pot. Mosan white clay. Yellow glaze
Huy - fountain “Le Bassinia”	Lead water pipe of a fountain	15th - 16th c.		EG-1	Lead water pipe. Pure metallic lead

In the dataset, the oldest vessels, dated between the end of the 9th and the end of the 10th century, are associated with layers from the banks of the Meuse River in Namur (Grognon: EG-16) and with a levelling layer of a domestic occupation in Huy (Aux Ruelles: EG-11; Challe et al., in press). Three sherds were taken from the production wastes of the Haillot workshop, which worked between the middle of the 10th and the middle of the 11th century (EG-6, EG-7, EG-8). Finally, glazed vessels were also selected from a pit dating from the end of the 10th or the beginning of the 11th century and linked to the settlement of Aux Ruelles street in Huy (EG-9, EG-10). These pre-Andenne lead glazes are applied as a liquid glazing mixture to white kaolinitic unfired vessels such as simple globular pots, globular pots with pouring spouts and/or handles, as well as to larger piriform pots or carinated bowls. The glaze may cover an underlying decoration printed with a wheel or with applied clay bands. The colour of the glaze is usually uniform, varying from light to dark yellow, but from the mid-11th century onwards it may be punctuated with brownish spots or dots.

Three glazed sherds were taken from three waste pits of a potter's workshop from Andenne, excavated in 2013 (Residence Noël site) (Challe et al., 2017): these sherd pits are dated to the first quarter of the 12th century (AND-03), the 13th century (AND-07) and the 14th century (AND-09, AND-09bis). Four other samples (EG-12, EG-13, EG-14, EG-15) originate from the Huy potters' workshop (Aux Ruelles street) whose production is dated to the second quarter of the 14th century. The last eleven glaze samples were taken from ceramics found in Dinant, Churchill Avenue (Verbeek and Danese, 2009; Verbeek and Siebrand, 2011), and Dinant/Bouvignes, Fourneau street, on the site of the old spinning mills (Challe, 2007), excavated in 2003, 2006 and 2009. They were found in the backfill levels of latrine pits, cellars or pits dug in the brass workshops, or in the adjoining gardens. They attest to the daily consumption of a middle-class population between the 13th and 16th centuries. These Mosan lead glazes cover ceramics of quite varied types (globular pot, tripod cooking pot, jug, basket-handled pot, dish and bowl) made from a white kaolinitic clay or richer in iron oxides. The glazes obtained have a wide range of colours: yellow, orange, and more rarely brown, sometimes purplish, metalescent or green.

2.2 Geological setting and reference geological material

Belgium is an old mining country, well-known for its zinc, lead and iron deposits. The exploitation of Zn-Pb deposits likely dates back to the Bronze age (unproven), followed by a Roman mining activity (assumed) and an intense exploitation during the Middle Age (documented by archives, Ladeuze et al., 1991). The apogee is reached during the second half of the 19th c., followed by continuous decline and the closing of the last mine in 1946 (Ladeuze et al., 1991). The mineralogy is simple with galena, sphalerite, pyrite or marcasite and their weathering products associated in various proportions. Pb-Zn ore deposits (>200 localities) are found in Devonian and Carboniferous rocks, mainly carbonates, which were intensely folded and faulted during the Variscan orogeny. The main economic Zn-Pb veins occur in faults, which are transverse to the Variscan fold axes. Rare veins also occur in siliciclastic rocks of Lower Devonian age or older (Dejonghe and Boni, 2004). Several ore deposit types are distinguished: syndiagenetic, vein and connected flats and paleokarstic types. The syndiagenetic deposits are made up of numerous disseminated-type deposits with low grades and small tonnages; they are linked to Upper Devonian reef facies carbonate formations. The largest exploited vein-type deposits are hosted in Lower Carboniferous carbonate rocks (Dejonghe et al., 1993; Dejonghe, 1998). In the Calamine area, close to the German border, the ore is dominated by the “Calamine-type” deposit, a non-sulphide Zn ore of supergene origin which is characterized by high Zn/Pb ratios. The “La Calamine” deposits were exploited at least since the 14th century (Dejonghe and Boni, 2004). Dejonghe (1998) distinguishes three lead–zinc districts (Fig. 1).

The Pb-Zn-(Ba) district of the Namur-Verviers Synclinoria: it is the largest belt (120 km long and 10–25 km wide) that extends towards Aachen area (Germany) to the east and along the Meuse and Sambre valleys to the west. The mineralisation is hosted in Dinantian limestones. In this paper, this large district is subdivided into the Pb-rich Mosan area (between Namur and Liège) corresponding to the Namur Parautochthon (in which studied medieval pottery workshops and consumption sites are all located) and the Zn-rich Verviers Synclinorium, east part of the Ardennes Allochthon. The NE lateral extension of this belt in Germany is the Rhenohercynian Zone, which includes most of the Ardenno-Rhenish Massif (Vogel et al., 1987), the Werra Anticline and the Harz. In the German Rhine Massif, Pb-Zn ore deposits occurred on both sides of the Rhine. The well-known Pb-Zn Aachen-Stolberg mining district (Walther, 1986) is located in the Inde Syncline (North Rhine-Westphalia, Germany) and is the NE prolongation of the Verviers Synclinorium. Near Stolberg, calamine has been mined since the 1st century CE (Dejonghe, 1998). The ores from the Brilon district are of epigenetic origin, the Bensberg and Aachen-Stolberg districts house hydrothermal Pb-Zn-veins and the ores of Mechernicher Bleiberg are mostly of submarine exhalative origin. Mining districts in Aachen-Stolberg district (Plombières-La Calamine), Maubach (mineralization in Triassic limestones, DE), in the Sauerland (Brilon district, North Rhine-Westphalia, DE) and in the Bergische Land (Bensberg district, DE), east of the river Rhine in North-Rhine Westphalia are reported on the metallogenic map of the Rhine Massif (Bode et al., 2009). The oldest known written references of lead ore mining activities between Namur and Huy (Mosan valley) date back to 1265, in the commune of Seilles, where lead mines were already described as 'old'. Between 1265 and 1522, other mentions (1265–1289: Seilles, 1265, 1371, 1375, 1352: Sclayn; <1278: Couthuin-Marsinnes; 1356: Ban of Andenne (Andenne and Sclayn), <1395: between Seilles and Landenne, XIV°: Moha (Wanze), 1395–1396: between Vezin (Namur) and Wartet (Namur); 1416–17, 1432, 1436–1438: Landenne and Seilles; <1432: Andenne) are numerous (Génicot 1964; Hasquin 1980; Brognet et al. 1993; Van de Roy 1996; Dejonghe 2010).

The Pb-Zn-Ba-F district of the Dinant Synclinorium: the mineralisation is associated to Givetian-Frasnian limestones and dolostones of the so-called Calestian Band (a narrow band in relief, 2 to 10 km wide and 130 km long). Fluorite and barite occur in the centre of this mining district.

The Pb-Zn district of the Ardennes: The mineralisation is located in Lower Devonian detrital rocks. Mines are rare and dispersed on a large territory.

Some rare and small Pb-Zn veins are sporadically found in Lower Palaeozoic, Eifelian and Namurian series.

2.3 Lead isotope analytical method

Lead isotope analysis is a very successful method to establish the geographical origin of lead present in ancient metals and other man-made materials (e.g. glass, glaze, paint, coins, alloys) and to trace the development of patterns of mining and trade routes. The isotopic composition of lead ores is variable and depends on a combination of factors, the age of the deposit and the geochemical features (U/Pb, Th/Pb and U/Th ratios) of the source-region of the metal (e.g. Wolf et al., 2003; Faure and Mensing, 2005). Several authors (Wolf et al., 2003; Stos-Gale and Gale, 2009; Walton and Tite, 2010; Thibodeau et al., 2012; Raepsaet et al., 2015, 2020; Carroll et al., 2021; Tomczyk et al., 2021) use this powerful technique to identify the source of lead of archeological artefacts of various ages.

Sample preparation. Lead-glazed ceramics were delicately sampled (several milligrams) using a dentist's drill. Small fragments of pure galena were carefully separated from galena-sphalerite-pyrite/marcasite ore samples using a sharp knife.

Chemical procedure. The glass fragments were crushed manually in an agate mortar and reduced to fine-grained powders. Aliquots of the powder (~40 mg) were digested in an acid mixture ($HF:HNO_3$ in proportions 4/1) on a hot plate 100–120 °C) during four days. Lead has been separated using successive acid elution on an ion-exchange column (anionic resin Bio rad AG1X8, 100–200 mesh) (for further details, see Weis et al., 2006). Galena fragments (~20 mg) were simply dissolved by nitric acid and dilutes to a desired concentration for mass spectrometric measurements.

Mass spectrometry measurements. Pb isotopic compositions were measured on a MC-ICP-MS NU Plasma I Instrument at the G-time Laboratory of the "Département Géosciences, Environnement et Société" (DGES) of the ULB. Analytical reproducibility and accuracy are regularly controlled by repeated measurements of the NIST SRM981 common lead standard. To correct for instrumental mass bias, a thallium solution of known isotopic composition is added to each sample and each standard in order to have a Tl/Pb ratio close to 6. All measurements were done with a minimum intensity of 130 mV for ^{204}Pb. The isotopic ratios were automatically corrected using the thallium fractionation law (calculated from the measured $^{205}Tl/^{203}Tl$ ratios compared to the known Tl isotopic composition. This procedure is largely described by Collerson et al. (2002) and very recently reviewed by Nagaishi et al; (2021). Mass discrimination effects were also corrected by standard bracketing (Nobre Silva et al., 2009). During the analytical session of October 2018, the average values obtained for the SRM 981 standards (n = 40) were: $^{206}Pb/^{204}Pb$: 16.9396 ± 0.0009; $^{207}Pb/^{204}Pb$: 15.4956 ± 0.0010; $^{208}Pb/^{204}Pb$: 36.7014 ± 0.0047; $^{207}Pb/^{206}Pb$: 0.9148 ± 0.0000; $^{208}Pb/^{206}Pb$: 2.1666 ± 0.0002. The Pb isotopic values were normalized using the recommended values of Galer and Abouchami (1998): $^{208}Pb/^{204}Pb$: 36.7219 ± 44; $^{207}Pb/^{204}Pb$: 15.4963 ± 16; $^{206}Pb/^{204}Pb$: 16.9405 ± 15. The global analytical errors are ± 0.001% ($^{207}Pb/^{206}Pb$), ±0.002% ($^{208}Pb/^{206}Pb$) and ± 0.04% ($^{206}Pb/^{204}Pb$).

Duplicates for 2 samples (Table 2) allow to show the excellent reproducibility of the whole procedure (chemical preparation and isotopic measurements by mass spectrometry).

Table 2

ⓘ The table layout displayed in this section is not how it will appear in the final version. The representation below is solely purposed for providing corrections to the table. To preview the actual presentation of the table, please view the Proof.

Lead isotopic compositions of lead-glazed Mosan ceramics analysed in this study.

Analytical Id.	Sample ref.	year	Place	Object type	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$
AND 03	AND13NOE.01.046.0123	2018	Andenne	Ceramic	0.85043	2.08824	18.37684	15.62823	38.37527
AND 07	AND13NOE.01.061.0001	2018	Andenne	Ceramic	0.84997	2.08706	18.38185	15.62419	38.36387
AND 09	AND15NOE.01.369.0002	2018	Andenne	Ceramic	0.84998	2.08725	18.38522	15.62743	38.37520
AND 09 bis	AND15NOE.01.369.0002	2018	Andenne	Ceramic	0.85001	2.08737	18.38681	15.62931	38.38059
Di 020	DIN03FIL.01.020	2018	Dinant	Ceramic	0.85004	2.08762	18.38157	15.62491	38.37312
Di 052	DIN03FIL.01.52	2018	Dinant	Ceramic	0.84979	2.08689	18.38702	15.62506	38.37102
Di 052 bis	DIN03FIL.01.52	2018	Dinant	Ceramic	0.84976	2.08674	18.38560	15.62329	38.36522
Di 425	DIN03FIL.01.423	2018	Dinant	Ceramic	0.84775	2.08679	18.47113	15.65880	38.54446
Di 001	DIN03FIL.01.127.0013	2018	Dinant	Ceramic	0.85106	2.08820	18.36125	15.62663	38.34213
Di 022	DIN03FIL.01.127.0022	2018	Dinant	Ceramic	0.84909	2.08711	18.41469	15.63539	38.43231
Di 010	DIN03FIL.01.130.0010	2018	Dinant	Ceramic	0.85120	2.08859	18.36098	15.62877	38.34874
Di 011	DIN03FIL.01.130.0011	2018	Dinant	Ceramic	0.85036	2.08772	18.36906	15.62034	38.34976
Di 012	DIN03FIL.01.130.0012	2018	Dinant	Ceramic	0.85089	2.08869	18.37148	15.63208	38.37244
Di 003	DIN07CHUR.01.132.0003	2018	Dinant	Ceramic	0.85819	2.09995	18.20730	15.62518	38.23324
Di 080	DIN07CHUR.01.080.0010	2018	Dinant	Ceramic	0.84966	2.08659	18.38841	15.62399	38.36914
Di 007	DIN07CHUR.01.132.0007	2018	Dinant	Ceramic	0.84994	2.08684	18.37931	15.62127	38.35416
EG-6	OHE05HAI.07.160.0001	2021	Haillot	Ceramic	0.84980	2.08630	18.3768	15.6165	38.3391
EG-7	OHE05HAI.07.205.0001	2021	Haillot	Ceramic	0.85000	2.08732	18.3855	15.6276	38.3763
EG-8	OHE05HAI.07.205.0002	2021	Haillot	Ceramic	0.85004	2.08745	18.3875	15.6299	38.3823
EG-9	HY06RU.01.608.0001	2021	Huy-Aux Ruelles	Ceramic	0.85009	2.08709	18.3734	15.6188	38.3470
EG-11	HY06RU.01.666.0001	2021	Huy-Aux Ruelles	Ceramic	0.85003	2.08739	18.3868	15.6291	38.3802
EG-12	HY05RU.01.274.374	2021	Huy-Aux Ruelles	Ceramic	0.84959	2.08645	18.3890	15.6232	38.3672
EG-13	HY05RU.01.274.378	2021	Huy-Aux Ruelles	Ceramic	0.85009	2.08722	18.3745	15.6200	38.3516
EG-14	HY05RU.01.274.379	2021	Huy-Aux Ruelles	Ceramic	0.85008	2.08714	18.3733	15.6186	38.3469
EG-16	NRGRO2.17.765.0012	2021	Namur - Grognon	Ceramic	0.85010	2.08712	18.3730	15.6189	38.3463
EG-1	Bassinia water adduction pipe	2021	Huy	Water pipe	0.85313	2.09688	18.3530	15.6574	38.4836
2s					0.00001	0.00002	0.0004	0.0004	0.0010

2.4 Reference databases

The identification of the ore deposit(s) from which the lead of the lead-glasses is derived depends crucially on the available databases for the ore deposits.

In this paper, for sourcing purposes, we use the free-access databases: 1) the Oxford Archaeological Lead Isotope database (OXALID: Stos-Gale and Gale, 2009) of ores and artefacts; 2) the database of ores Pb isotope compositions compiled by Blichert-Toft et al. (2016) and 3) the data published by Bode (2008) and Bode et al. (2009) for galenas from the Rhine mining districts as well as Augustan/Tiberian (early Roman Imperial period) archaeological lead objects. The datasets regarding Belgian ores (Pb-Zn deposits) and Roman artefacts are not yet in these databases although Pb isotope compositions were previously published by Pasteels et al. (1980), Cauet et al. (1982), Cauet and Weis, 1983 and Raepsaet et al. (2015, 2020).

2.5 Statistical treatment method

The univariate Kernel Density Estimation (KDE) plots are used to provide a visual representation of the data for the three Pb isotopic ratios. The bandwidths were estimated on the total population for each ratio using the Sheather and Jones method (Sheather and Jones, 1991). The results are overlayed on frequency histograms where the binwidth are tuned to visually support the KDE plot. For each of the KDE curves, the modes and anti-modes are identified using the R package "multimode" (Ameijeiras-Alonso et al., 2021). These features can be used to describe the distribution of each Pb isotopic ratio but should not be directly interpreted as meaningful groups since the location of the modes and anti-modes is highly dependent on the selected bandwidth. Each peak in the KDE curves is defined by a mode and limited by two anti-modes. The clustering of the data is performed on the normalised values of the three ratios through the application of the density-based ordering methods OPTICS (Ankerst et al., 1999) present in the R package "dbscan" (Hahsler et al., 2019). This method allows the detection of clusters in data of varying density and very few parameters are required to be tuned. The results of the clustering are displayed on the KDE 2D contour plot where the groups identified by the OPTICS method are enclosed in convex hulls.

3 Results and discussion

The Pb isotopic composition of lead-glazed ceramics, the fountain water pipe from Huy and galenas has been reported in Tables 2 and 3.

Table 3

The table layout displayed in this section is not how it will appear in the final version. The representation below is solely purposed for providing corrections to the table. To preview the actual presentation of the table, please view the Proof.

Pb isotopic compositions of selected galenas from the Namur-Amay area. Comparison with the data of Pasteels et al. (1980) and Cauet et al. (1982).

Sample ref.	Place (village CITY)	Context	Object type		$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$
EG-02 (2020)	Marche-les-Dames (NAMUR)	Disused mine	Pb-Zn ore	Mosan	0.84990	2.08665	18.3757	15.6174	38.3433
EG-03 (2020)	Andenelle (ANDENNE)	Disused mine	Pb-Zn ore	Mosan	0.85023	2.08728	18.3647	15.6142	38.3318
EG-04 (2020)	Seilles (ANDENNE)	Disused quarry	Pb-Zn ore	Mosan	0.84993	2.08682	18.3826	15.6239	38.3605
EG-05 (2020)	Vedrin (NAMUR)	Disused mine	Pb-Zn ore	Mosan	0.85420	2.09378	18.3007	15.6324	38.3169
				2s (mean)	0.00100	0.00200	0.0425	0.0375	0.1125
Cauet et al. (1982)	LA ROCHE-EN-ARDENNE	Disused mine	Pb-Zn ore	Ardennes	0.8526	2.0912	18.31	15.611	38.289
Cauet et al. (1982)	Longvilly (BASTOGNE)	Disused mine	Pb-Zn ore	Ardennes	0.8380	2.0747	18.286	15.623	37.938
Cauet et al. (1982)	Longvilly (BASTOGNE)	Disused mine	Pb-Zn ore	Ardennes	0.8544	2.0936	18.304	15.639	38.321
Cauet et al. (1982)	MARTELANGE	Slate quarry	Pb-Zn ore	Ardennes	0.8507	2.0824	18.321	15.585	38.152
Cauet et al. (1982)	Ave-et-Auffe (ROCHEFORT)		Pb-Zn ore	Calestian	0.8522	2.1042	18.367	15.653	38.647
Cauet et al. (1982)	BEAURAING		Pb-Zn ore	Calestian	0.8543	2.0914	18.276	15.614	38.222
Cauet et al. (1982)	BEAURAING		Pb-Zn ore	Calestian	0.8532	2.0921	18.323	15.634	38.333
Cauet et al. (1982)	Dourbes (VIROINVAL)		Pb-Zn ore	Calestian	0.8521	2.0919	18.39	15.67	38.47
Cauet et al. (1982)	DURBUY		Pb-Zn ore	Calestian	0.8487	2.0872	18.39	15.608	38.383
Cauet et al. (1982)	Mazée (VIROINVAL)		Pb-Zn ore	Calestian	0.8494	2.0874	18.425	15.651	38.461
Cauet et al. (1982)	Niverlée (DOISCHE)		Pb-Zn ore	Calestian	0.8489	2.0871	18.424	15.64	38.452
Cauet et al. (1982)	Olloy-sur-Viroin (VIROINVAL)		Pb-Zn ore	Calestian	0.8478	2.0946	18.402	15.602	38.545
Cauet et al. (1982)	Sautour 1 (PHILIPPEVILLE)		Pb-Zn ore	Calestian	0.8494	2.0843	18.417	15.643	38.386
Cauet et al.	Sautour 2 (PHILIPPEVILLE)		Pb-Zn ore	Calestian	0.8565	2.0933	18.217	15.602	38.134

(1982)									
Cauet et al. (1982)	Solre-st-Géry (BEAUMONT)		Pb-Zn ore	Calestian	0.8570	2.0976	18.209	15.605	38.195
Cauet et al. (1982)	Vierves-sur-Viroin (VIROINVAL)		Pb-Zn ore	Calestian	0.8472	2.0845	18.479	15.656	38.519
Cauet et al. (1982)	Villers-en-Fagnes (PHILIPPEVILLE)		Pb-Zn ore	Calestian	0.8481	2.0880	18.452	15.649	38.527
Cauet et al. (1982)	Heure (SOMME-LEUZE)		Pb-Zn ore	Calestian/Famenne	0.8507	2.0868	18.377	15.633	38.35
Cauet et al. (1982)	BLEIBERG/PLOMBIERES		Pb-Zn ore	East	0.8485	2.0859	18.423	15.631	38.428
Cauet et al. (1982)	BLEIBERG/PLOMBIERES		Pb-Zn ore	East	0.8540	2.0946	18.257	15.591	38.241
Cauet et al. (1982)	CHAUDFONTAINE		Pb-Zn ore	East	0.8503	2.0885	18.368	15.618	38.362
Cauet et al. (1982)	Dickenbusch (WELKENRAEDT)		Pb-Zn ore	East	0.8505	2.0847	18.397	15.647	38.353
Cauet et al. (1982)	Fossey Mine-Hergenrath (LA CALAMINE)	Disused mine	Pb-Zn ore	East	0.8501	2.0868	18.385	15.63	38.366
Cauet et al. (1982)	La Rochette (TROOZ)		Pb-Zn ore	East	0.8504	2.0931	18.361	15.614	38.431
Cauet et al. (1982)	LONTZEN	Disused mine	Pb-Zn ore	East	0.8503	2.0900	18.368	15.618	38.39
Cauet et al. (1982)	Membach (BAELEN)	Disused mine	Pb-Zn ore	East	0.8564	2.0922	18.185	15.573	38.046
Cauet et al. (1982)	Membach (BAELEN)	Disused mine	Pb-Zn ore	East	0.8565	2.0966	18.283	15.66	38.333
Cauet et al. (1982)	Rabotrath (LONTZEN)	Disused mine	Pb-Zn ore	East	0.8478	2.0840	18.406	15.605	38.359
Cauet et al. (1982)	Rocheux-Oneux (THEUX)	Disused mine	Pb-Zn ore	East	0.8510	2.0865	18.38	15.642	38.35
Cauet et al. (1982)	Rocheux-Oneux (THEUX)	Disused mine	Pb-Zn ore	East	0.8495	2.0859	18.384	15.618	38.347
Cauet et al. (1982)	Schmalgraf mine (LA CALAMINE)	Disused mine	Pb-Zn ore	East	0.8495	2.0868	18.444	15.669	38.489
Cauet et al. (1982)	Schmalgraf mine (LA CALAMINE)	Disused mine	Pb-Zn ore	East	0.8494	2.0875	18.354	15.59	38.314
Cauet et al. (1982)	ENGIS		Pb-Zn ore	Mosan	0.8502	2.0865	18.375	15.622	38.34
Cauet et al. (1982)	ENGIS		Pb-Zn ore	Mosan	0.8502	2.0875	18.368	15.617	38.344
Cauet et al. (1982)	Haie-Monnet - Seilles (ANDENNE)	Disused mine	Pb-Zn ore	Mosan	0.8480	2.0870	18.402	15.605	38.405
Cauet et al. (1982)	Haie-Monnet - Seilles (ANDENNE)	Disused mine	Pb-Zn ore	Mosan	0.8499	2.0874	18.398	15.636	38.404
Cauet et al. (1982)	Vedrin (NAMUR)	Disused mine	Pb-Zn ore	Mosan	0.8506	2.0875	18.37	15.625	38.347
Cauet et al. (1982)	Vedrin (NAMUR)	Disused mine	Pb-Zn ore	Mosan	0.8499	2.0872	18.353	15.599	38.306
Pasteels et al. (1980)	HERBEUMONT	Outcrop	Pb-Zn ore	Ardennes	0.8523	2.0907	18,319	15,613	38,299
Pasteels et al. (1980)	(BASTOGNE)	Collection	Pb-Zn ore	Ardennes	0.8544	2.0936	18,304	15,639	38,321
Pasteels et al. (1980)	B- Tamison (BEAURAING)	Borehole	Pb-Zn ore	Calestian	0.8540	2.0939	18,314	15,640	38,347
Pasteels et al. (1980)	DISON	Outcrop	Pb-Zn ore	East	0.8502	2.0896	18,379	15,625	38,404
Pasteels et al. (1980)	Le Rocheux-Oneux (THEUX)	Heaps	Pb-Zn ore	East	0.8495	2.0859	18,384	15,618	38,347
Pasteels et al. (1980)	Montzen (PLOMBIERES)	Collection	Pb-Zn ore	East	0.8540	2.0946	18,257	15,591	38,241
Pasteels et al. (1980)	Membach (BAELEN)	Heaps	Pb-Zn ore	East	0.8565	2.0966	18,283	15,660	38,333
Pasteels et al. (1980)	Neu Moresnet (SCHMALGRAF)	Collection	Pb-Zn ore	East	0.8494	2.0875	18,354	15,590	38,314

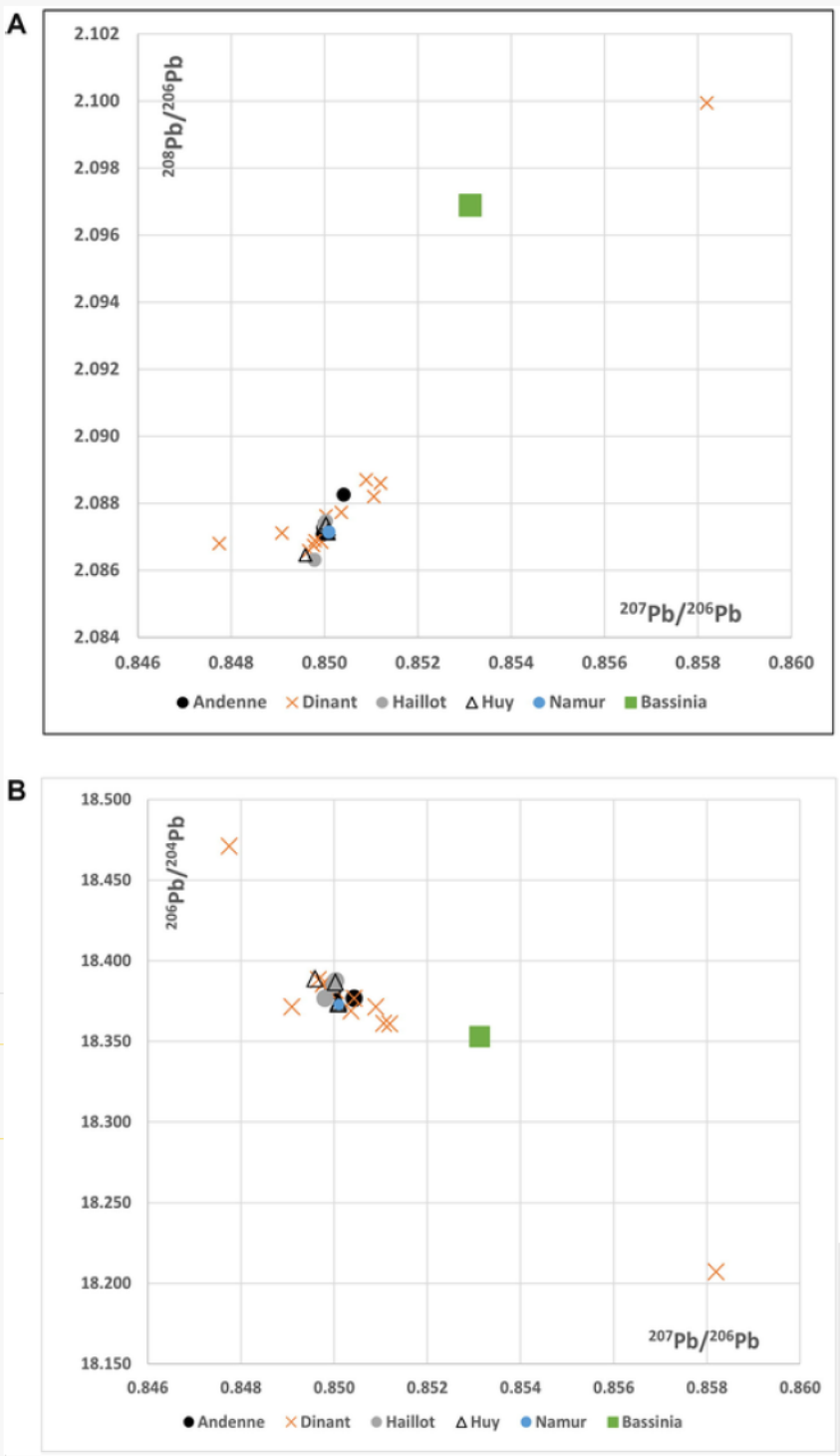
Pasteels et al. (1980)	Walhorn (RABOTHRATH)	Outcrop	Pb-Zn ore	East	0.8478	2.0840	18,406	15,605	38,359
Pasteels et al. (1980)	B-1 Tamison (BEAURAING)	Borehole	Pb-Zn ore	East	0.8532	2.0921	18,323	15,634	38,333
Pasteels et al. (1980)	Vedrin (NAMUR)	Collection	Pb-Zn ore	Mosan	0.8499	2.0872	18,353	15,599	38,306
Pasteels et al. (1980)	Haie Monet - Seilles (ANDENNE)	Heaps	Pb-Zn ore	Mosan	0.8499	2.0874	18,398	15,636	38,404
Pasteels et al. (1980)	Seilles-Tramaka (ANDENNE)	Outcrop	Pb-Zn ore	Mosan	0.8500	2.0877	18,386	15,628	38,385
Pasteels et al. (1980)	ENGIS	Collection	Pb-Zn ore	Mosan	0.8502	2.0875	18,368	15,617	38,344
Pasteels et al. (1980)	Richelle (VISE)	Outcrop	Pb-Zn ore	Mosan	0.8502	2.0815	18,363	15,613	38,222
Pasteels et al. (1980)	MAUBACH-MECHERNICH - Germany	Collection	Pb-Zn ore	(Trias)	0.8497	2.0856	18,443	15,671	38,464

3.1 Lead isotope signature of the Mosan medieval ceramic glazes

Omitting the two outliers (discussed below), the lead-glazed ceramics displays narrow ranges of isotopic compositions: $^{206}Pb/^{204}Pb$: 18.361 to 18.389; $^{207}Pb/^{204}Pb$: 15.617 to 15.635; $^{208}Pb/^{204}Pb$: 38.339 to 38.432; $^{207}Pb/^{206}Pb$: 0.8491 to 0.8512; $^{208}Pb/^{206}Pb$: 2.0865 to 2.0887 (Fig. 3). These tightly grouped values can be considered as good fingerprints for provenance studies, from the lead ore to the metal: they indicate that the provenance of the lead of the medieval glazes does not change for eight centuries (9th to 16th). One sample from the consumption site of Dinant (Di425) has a slightly different isotopic composition with lower $^{207}Pb/^{206}Pb$ (0.8477) and higher $^{206}Pb/^{204}Pb$ (18.4711) but comparable $^{208}Pb/^{206}Pb$ (2.0868). This composition is nevertheless not very far from the restricted domain of the other medieval glazed ceramics. Another sample from Dinant (Di003), with significantly higher $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ values plots clearly outside this domain. With its straight tapering lip and an oval handle with a throat, Di003 is a pitcher of very atypical typology in the Andenne-type production. Its petrographic analysis however shows that it is made with a clay similar to that used for the other potteries located in the Mosan area: this object could have been made with a different glaze recipe and presumably also with a different batch of lead. The lead filing from the Bassinia fountain is also clearly distinct isotopically: it has significantly higher $^{208}Pb/^{206}Pb$ (2.0969) and $^{207}Pb/^{206}Pb$ (0.8531) ratios.

Images are optimised for fast web viewing. Click on the image to view the original version.

Fig. 3



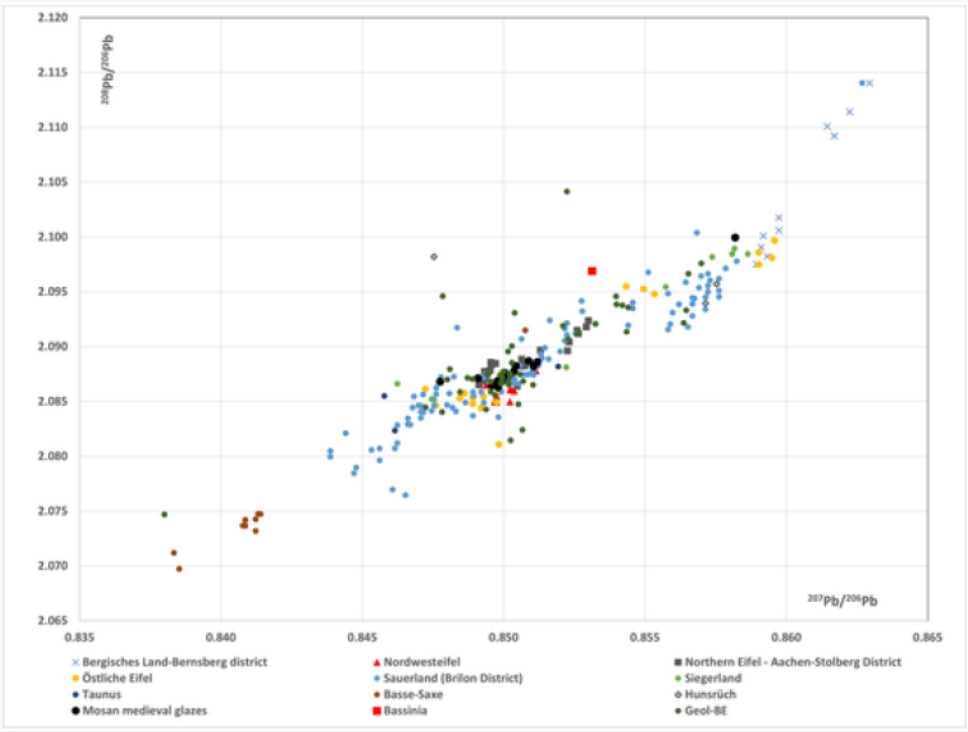
Lead isotope binary diagrams for the analysed Mosan medieval lead glazes and the Bassinia pipe (green square). The glaze data are plotted according to their location [ceramic workshops of Haillot (full grey circle), Andenne (full black circle) and Huy (empty black triangle); Dinant (red cross) and Namur (full blue circle) are consumption sites; the bassinia pipe is symbolised by a full green square].

3.2 Sourcing of the medieval Mosan glazes

The studied medieval lead glazes have been subdivided in two subgroups, those collected in the workshops and those sampled on consumption sites. Their isotopic compositions are compared to those of Belgian galenas (Table 3, European databases for galenas and galenas from German ore deposits. At the regional scale of Belgium and Western Germany, several subgroups of Pb deposits can be distinguished on the basis of their Pb isotopic compositions: for Belgium, the Belgian Ardennes and the majority of the Calestian places; for Germany, the Basse-Saxe, Siegerland, Hunsrück, Taunus and Bergisches Land-Bernsberg districts. The Pb isotopic data of the German galenas largely extends the domain of Belgian galenas towards both higher and lower isotopic ratios (Figs. 4 and 5). It is quite clear that the lead of the medieval pottery workshops, the lead from the consumption site of Namur and the majority of material from Dinant are very close, isotopically, to the geological Mosan sites (especially between Namur and Engis) as well as to several sites of Eastern Belgium (especially Theux and La Calamine) and of Western Germany (Northern Aachen-Stolberg District, the Northwest Eifel). Deposits from Ö stliche Eifel and the majority of galenas from the Brilon district (Sauerland) cannot definitively be ruled out as possible Pb sources.

Images are optimised for fast web viewing. Click on the image to view the original version.

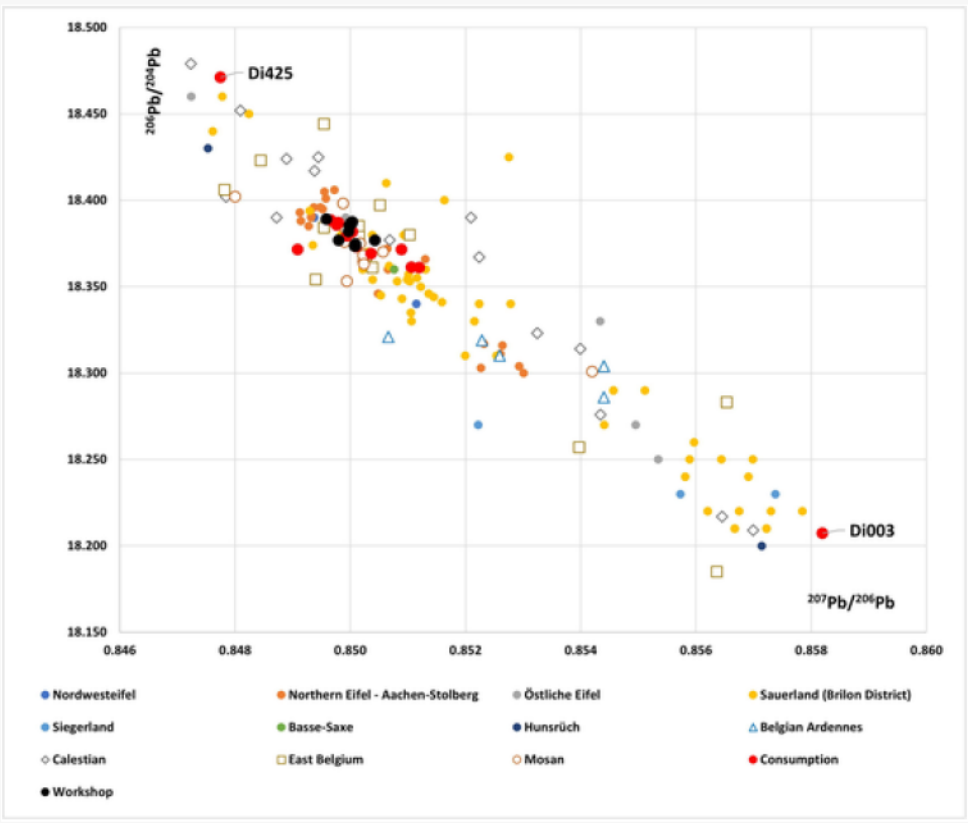
Fig. 4



Lead isotope ratios for Mosan medieval lead glazes (black dots). Comparison with undifferentiated lead ores from Belgium (Geol-BE) and many German districts.

Images are optimised for fast web viewing. Click on the image to view the original version.

Fig. 5



Lead isotope ratios for Mosan medieval lead glazes (black dots) and (selected) lead ores from Belgium and Germany. Data within the following ranges are shown: $^{207}Pb/^{206}Pb$ 0.847–0.859, $^{206}Pb/^{204}Pb$ 18.200–18.480.

The ores stem from local Pb-Zn ore deposits of the Namur Parautochthon (underground mines opened on the two Meuse valley sides, associated to the Pb-Zn-Fe veins crosscutting the Dinantian limestones) in Belgium and/or lead ore deposits in the Dinantian limestones of the Verviers Syncline (part of the Ardennes Allochthon, around 80 km eastward from Andenne) and in their extension zone to the west until the Rhine in Germany. There are no significant geochemical differences between these mining

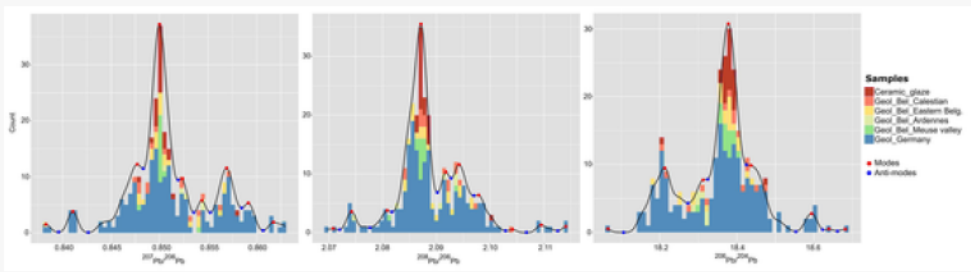
districts because they share the same mineralization process, the same age and the same host rocks: there is a geological continuum between Namur and Bleiberg. By narrowing down the data further, the mining sites that best match the lead used by the Mosan ceramic workshops are the mines of Marche-les-Dames and Seilles, but several other Mosan sites (Andenelle, Engis, Vedrin) cannot be excluded. Di425 and Di003 glazed ceramics find a good match with the lead extracted from the Brilon district (Sauerland) and to a lesser extent with the Calestian Band (Viroinval, Philippeville). It thus appears that local and regional proximity sources fit with all the studied medieval glazes.

3.3 KDE diagrams

The univariate KDE plots and the frequency histograms of the three isotopic ratios $^{207}Pb/^{206}Pb$, $^{208}Pb/^{206}Pb$, and $^{206}Pb/^{204}Pb$ are displayed in the Fig. 6. The identification of several modes in each of the KDE plot assesses the multimodality of the distributions. The comparison between the KDE plots and the populations in the histograms provides a first screening of the data.

Images are optimised for fast web viewing. Click on the image to view the original version.

Fig. 6



KDE plots and frequency histograms for $^{207}Pb/^{206}Pb$, $^{208}Pb/^{206}Pb$, and $^{206}Pb/^{204}Pb$. Glazes and geological samples from Belgium and Germany.

The $^{207}Pb/^{206}Pb$ plot shows 9 modes with a calculated bandwidth set at 0.00044. Below the second anti-mode located at 0.8426, the population only comprises geological samples from Lower Saxony in Germany and one geological sample from the Ardennes region in Belgium. The population fitting with the limits of the peak with a mode at 0.8477 is mainly comprised of geological samples from the Sauerland area in Germany, few geological samples from Belgium and one archaeological sample discovered in Dinant (Di 425). The limits of the 4th peaks with the higher probability density comprised 132 samples including almost all the archaeological samples, 75 German geological from the Sauerland area, the High Eifel, the northern Eifel, and the north-western Eifel, and 33 Belgian galenas from the Meuse Valley, the Calestian band, and the Eastern Belgium. Most of the remaining Belgian geological samples from the Calestian band and the Eastern Belgium are comprised between the 4th and the 7th anti-modes. The archaeological sample Di 003 from Dinant is also included in this range. After the 7th anti-mode at 0.8584 the population is comprised of German geological samples mainly from the Bergisches Land.

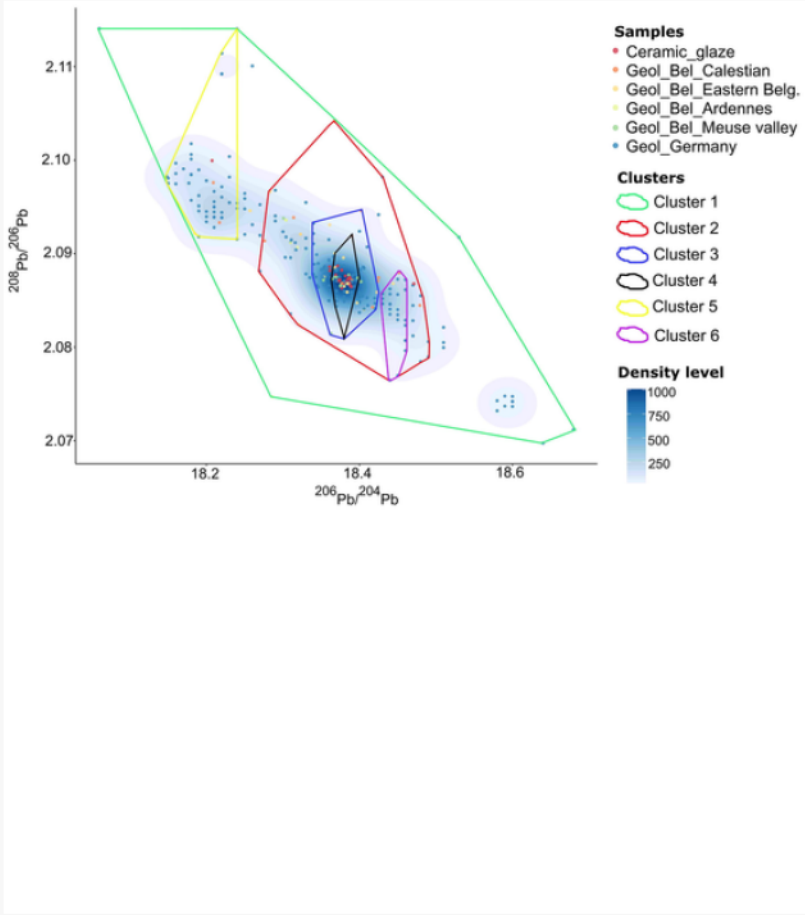
The $^{208}Pb/^{206}Pb$ plot is very similar to the $^{207}Pb/^{206}Pb$ plot: 10 modes are identified in the KDE curve with a calculated bandwidth set at 0.0073. The distribution of the samples is also quite similar to the previous one with a main mode at 2.0871 that comprises 165 samples. The main difference is the presence of more samples from the Eifel region in this peak compared to the main peak in the $^{207}Pb/^{206}Pb$ plot. The archaeological sample Di 003 from Dinant is also located outside of the main mode in this plot, with a higher $^{208}Pb/^{206}Pb$ ratio.

The plot for the $^{206}Pb/^{204}Pb$ ratio exhibits 8 modes with a calculated bandwidth at 0.0117. The second peak with a mode located at 18.2127 includes mainly geological samples from Germany with a vast majority of samples from the Sauerland area and the Bergisches Land. Only three galenas from Belgium and the archaeological sample Di 003 from Dinant have values in this interval. The population between the intervals of the 3rd peak is comprised of 12 German galenas from the Sauerland area and the Northern Eifel, and 13 galenas from Belgium, where the samples from the Ardennes area are concentrated. The 4th peak with a mode at 18.3782 has the highest probability density with 143 samples between the anti-modes. It comprised 24 archaeological samples and 129 geological samples: among them, 85 are coming from Germany, mainly from the Sauerland area and the Eifel areas in Germany; 14 are geological samples from the Meuse valley in Belgium, 14 are from the Eastern Belgium and 6 from the Belgian Calestian band. After the 4th anti-modes, the population mainly comprises German galenas with four samples from the Calestian band, one from Eastern Belgium and the archaeological sample Di 425 from Dinant.

The KDE analysis shows that most of Pb isotopic data from the medieval ceramic glazes fall in the main interval gathering a large number of galenas from Germany and from Belgium. Tracing the geological origin of the lead used for the ceramic glazes seems difficult even if some areas like the Lower Saxony, the Bergisches Land and the Ardennes area can probably be excluded as candidates. The use of density-based clustering method (OPTICS) on the three isotopic ratios can improve the resolution of the grouping. Fig. 7 shows the results of the OPTICS clustering on a KDE 2D contour plot based on the density of $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{206}Pb$.

Images are optimised for fast web viewing. Click on the image to view the original version.

Fig. 7



KDE 2D contour plot based on the total density of the $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{206}Pb$ ratios for glazes and galenas from Belgium and Germany, with a bandwidth set at 0.015. The results of the OPTICS clustering are displayed by the convex hulls.

The contour plot shows the presence of five distinct density areas which roughly correspond to the main peaks and valleys observed on the $^{206}Pb/^{204}Pb$ KDE plot. Most the ceramic glazed samples are located at the centre of the plot in the high probability density area. The partitions from the OPTICS clustering show that the central area of the plot comprises four nested hierarchical clusters with cluster 4 being the narrowest one, mostly focused on the very dense central zone of the plot. This cluster includes 23 of the 26 ceramic glazes, 35 German galenas (8 the north-western Eifel, 9 from the northern Eifel, 6 from the High Eifel, 11 from the Sauerland area and 1 from Taunus) and 19 galenas from Belgium (3 from the Calestian band, 7 from the Eastern Belgium and 9 from the Meuse Valley area). This cluster roughly corresponds to the population of the principal peak identified in the three univariate KDE plots, but its reduced size excludes several galenas from Germany and few galenas from the Calestian band and Eastern Belgium. Two other unsubdivided clusters reflect the tendency observed on the univariate KDE plots. Cluster 5 (left side of the plot) is largely made of geological samples from the Sauerland area with three galenas from Belgium and the ceramic glaze Di 003 from Dinant. Cluster 6 includes a vast majority of German galenas from the Bergisches Land, the Sauerland area and the Siegerland, as well as 3 Belgian galenas. On the lower right side of the plot, the grouping of 7 samples from Lower Saxony is not identified by the OPTICS clustering method because the minimum cluster size is set at 20 individuals. The cluster 4 from the OPTICS algorithm shows that most archaeological glazed samples are close to most of the galenas from Eastern Belgium and Meuse Valley. If the source of the lead of the archaeological ceramics cannot be determined more precisely, it appears however that many galenas from Germany cover a wide range of isotopic values that overlap the Belgian galenas in the group 4. The most parsimonious interpretation of all data favoured conclusion that the galenas come from the (local sites of) Eastern Belgium and the Meuse Valley. Obviously, it could come from further afield because there is overlap between different ores, but the fact that the local sources is a match makes this the more likely scenario.

3.4 Tracking the lead source for the lead pipe of the “Bassinia »

The Pb used for the 15th/16th century water pipe is distinct from that of the 9th-16thcentury lead-glazed ceramics. This peculiar Pb does obviously not derive from the local variscan Pb-Zn ores. To assess the source of this lead, we have used the datasets of lead from different European countries with the following search criteria: $^{207}Pb/^{206}Pb$ 0.8530–0.8532, $^{206}Pb/^{204}Pb$ 18.354–18.652 and $^{208}Pb/^{206}Pb$ 2.0965–2.0970. Three possible matches have been found in the galena data compilation of Blichert-Toft et al. (2016): two mining sites in the French Cévennes (Saint-Laurent-le-Minier and Vialas, Gard Department) and one in the Austrian Tyrol. Note that the Saint-Laurent-le-Minier area has been mined since the Bronze Age and continued until the beginning of the 20th century. Additional historical research must be conducted to verify this tentative source identification.

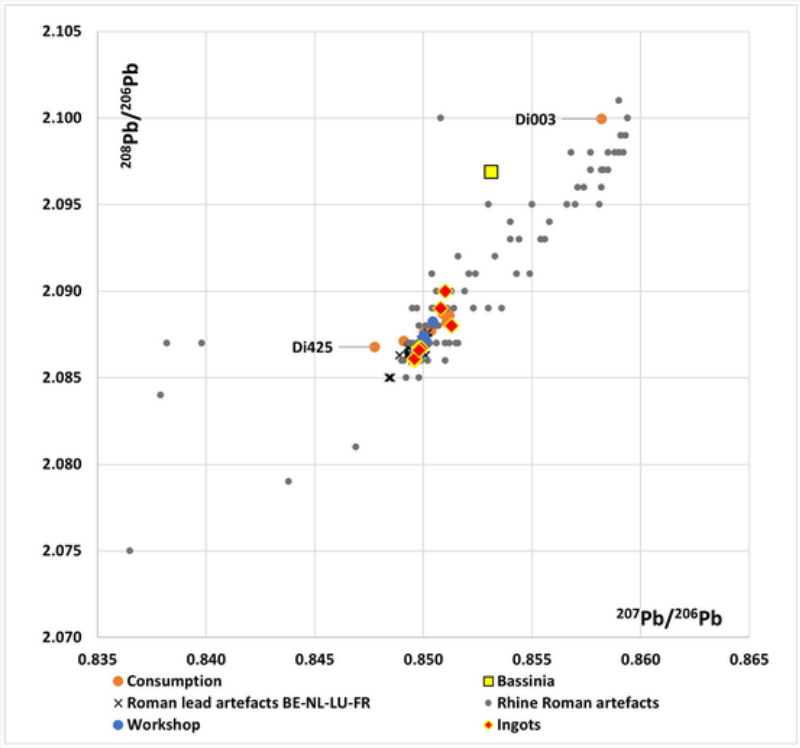
3.5 Continuity of lead mining since the Early Antiquity in the Northwest Gaul

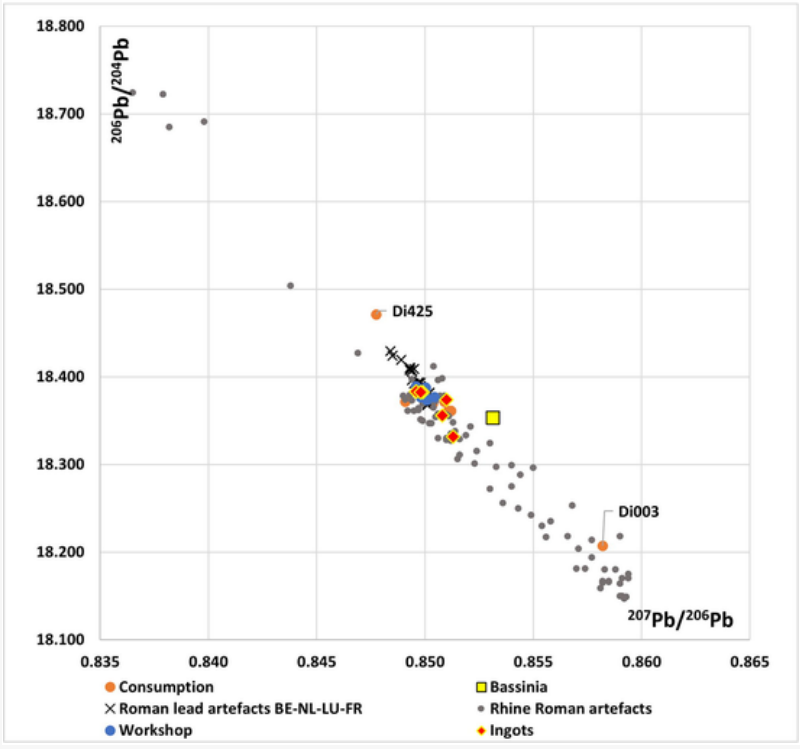
A comparison of the Pb isotopic compositions of lead-glazed medieval ceramics was attempted with three groups of archeological items: 1) a group of five Roman lead ingots, one from the famous Roman Tongres city (*civitas Tungrorum)* and four from shipwrecks in the Mediterranean) whose inscriptions point to a production in Germania (Bode et al., 2009; Raepsaet et al., 2015, 2020); 2) a group of 29 Roman artefacts from Belgium, Luxemburg, Northern France and The Netherlands (Raepsaet et al., 2015, 2020) and 3) a large group (n = 90) of Augustan/Tiberian Germania lead artefacts from Roman military fortresses and camps located to the east of the river Rhine in Germany (Bode, 2008; Bode et al., 2009).

Binary Pb isotopic diagrams (Fig. 8) clearly show that the Roman lead ingots from Germania (group 1) have the same isotopic compositions as the Mosan medieval glazes. The cluster of Roman artefacts (group 2: Roman lead artefacts BE-NL-LU-FR) largely overlaps with the ingots and the medieval glazes. The lead from Roman ingots and artefacts from the Northern Gaul as well as the lead from the medieval Belgian glazes probably derive from the same regional metal sources which would imply a continuity in the Pb source since the Antiquity to the medieval age. This is a strong argument in favor of continuous operations in local and regional mining districts. By contrast, the lead objects of the Augustan/Tiberian period (group 3: Rhine Roman artefacts) overlap with the medieval glazes but display a wider distribution. The comparison of the Pb isotopic compositions of 240 Roman lead objects from several archaeological sites in Germany (group 3) with those from German ore deposits (Durali-Mueller et al., 2007) indicates a wider range of deposit types mined during the Early Roman period on both sides of the Rhine river, including the same deposits as those used for the medieval glazes and the Roman artefacts discovered in Northern Gaul. The Pb of the large majority (>85%) of the objects from the group 3 is derived from the Eifel ore deposits. This range appears more limited for the Late Antiquity than for the Augustan/Tiberian period, probably because the deposits east of the Rhine were no longer accessible.

Images are optimised for fast web viewing. Click on the image to view the original version.

Fig. 8





Lead isotope ratios for Mosan medieval lead glazed pottery (workshops and consumption sites, this study) compared to Roman artefacts from Belgium (Raepsaet et al., 2015, 2020) and Germany (Bode, 2008; Bode et al., 2009). The two groups of glazed ceramics (ceramic workshops and consumption sites) are distinguished.

Sourcing the lead used in the archaeological ceramic glazes analysed in this study would require crossing the Pb isotopic ratios with other geochemical data such as trace elements. But geochemical studies will face other problems that are difficult to solve as the addition of colouring agents (Cu, Fe, Mn) or frits by the potter, the migration of chemical elements from the paste to the glaze, the lack of detailed analyses from the ores.

4 Conclusions

The Pb isotopic compositions of lead-glazed medieval ceramics from the 9th to the 16th centuries AD, sampled along the Meuse Valley in Belgium, were measured in an attempt to identify the geographical/geological origin of the metal and to check whether the Pb source changes over an eight century time span. It is known that some mining regions were gaining and/or losing their importance according to the social, political and economic factors in the area. The tightly grouped Pb isotopic compositions of the 25 analyzed archeological samples imply that the metal source(s) remain unchanged, without any mixing. The main glazed ceramics found in Mosan medieval consumption sites have been produced regionally with raw material (clays and lead) similar of those found in the three studied workshops.

The best match for the metal is probably the local Pb-Zn mines from Andenne and surrounding area, but it is important to note that there are no isotopic differences between several mining districts all along the 120 km-long Variscan belt that extends from Central Belgium (Namur area) to Western Germany (Bleiberg district).

Rare ceramics found in the consumption site of Dinant are glazed with lead from other regional mining districts. Due to the scarcity of written sources, historical data regarding the beginning of mining activity are widely lacking for the mines opened in the Meuse valley. On the oldest (18th century) Pb-Zn-Fe mine maps, it is only mentioned “old workings”.

The Pb-glazed medieval ceramics display isotopic compositions quite similar to those of Roman objects (Pb ingots labelled “Germania” and artefacts found in NW Europe in the Early Roman period) It thus appears that the same regional/local ore deposits were mined from the Roman period to the Middle Age. The lead of the 15th/16th (?) century Bassinia pipe from Huy has an unexpected clearly distinct isotopic composition which requires an exogenous source.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors want to thank Wendy Debouge (ULB) for the careful chemical preparation of the samples, Jeroen Dejong (ULB) for the maintenance of the MC-ICP-MS instrument and Thierry Leduc for the access to the mineralogical collection of the RBINS. AWaP and GSB are thanks for funding. The authors thank the two anonymous reviewers for their comments and discussion.

References

The corrections made in this section will be reviewed and approved by a journal production editor. The newly added/removed references and its citations will be reordered and rearranged by the production team.

Ameijeiras-Alonso, J., Crujeiras, R.M., Rodriguez-Casal, A., 2021. Multimode: an R package for mode assessment. J. Statistical Software 97 (9). doi:10.18637/jss.v097.i09.

Ankerst, M., Breunig, M.M., Kriegel, H.P., Sander, J., 1999. OPTICS: ordering points to identify the clustering structure. ACM Sigmod Rec. 28 (2), 49–60. doi:10.1145/304182.304187.

Blichert-Toft, J., Delile, H., Lee, C.-T., Stos-Gale, Z., Billström, K., Andersen, T., Hannu, H., Albarède, F., 2016. Large-scale tectonic cycles in Europe revealed by distinct Pb isotope provinces. G-cubed 17 (10), 3854–3864. doi:10.1002/ggge.v17.1010.1002/2016GC006524.

Bode, M., Hauptmann, A., Mezger, K., 2009. Tracing Roman lead sources using lead isotope analyses in conjunction with archaeological and epigraphic evidence- a case study from Augustan/Tiberian Germania. J. Archaeol. Anthropol. Sci. 1, 177–194. doi:10.1007/s12520-009-0017-0.

Bode, M., 2008. Archäometallurgische Untersuchungen zur Blei-/Silbergewinnung im Germanien der frühen Römischen Kaiserzeit. Dissertation, University of Münster, online: http://nbn-resolving.de/urn:nbn:de:hbz:6-22579580819.

Brognet E., Léonard Y., Maes J., Moisse M ; Mordant R. & Wascotte P., 1993. Andenne. Le temps des Libertés 1875-1975. Imprim. Lallemand, 383 p.

Carroll, M., Evans, J., Pashley, V., Prowse, T., 2021. Tracking Roman lead sources using lead isotopes analysis. A case study from the imperial rural estate at Vagnari (Puglia, Italy). J. Archaeol. Sci. Rep. 36 (7), 102821. doi:10.1016/j.jasrep.2021.102821.

Cauet, S., Weis, D., 1983. Modèle génétique et incidence sur la prospection des gîtes Pb-Zn belges en milieux carbonatés. B.S.B.G. 92, 77-87.

Challe, S., de Longueville, S., 2013. La production médiévale mosane en Belgique : état de la question. In: Mouny, S. (Ed.), Des productions céramiques de l'époque gallo-romaine à la Renaissance, Actes des journées d'étude de Fosses (95) et Amiens (80) (2008-2009-2010), Revue archéologique de Picardie 1-2, 155–163.

Challe, S., de Longueville, S., Delaunois, E., Hardy, C., 2017. Fouilles préventives dans le parc et sur les abords du Château Noël à Andenelle: du chantier au laboratoire, dialogue entre la réalité de terrain et la recherche céramologique. In: Piechowski, C. (Dir.), La derle - Li dièle. L'habile argile du Condroz. Vingt siècles de céramiques en terres d'Andenne. Dossiers de l'IPW 22, 141–149.

Challe, S., de Bernardy de Sigoyer, S., Péters, C., Taildeman, F., Mélon, A., in press. Huy « Aux Ruelles », tessonnière liée à l'atelier de potier du second quart du XIVe siècle. Cahiers du G.R.A.S.B. 50.

Challe, S., 2007. Dinant/Dinant : céramiques médiévales et modernes mises au jour sur le site artisanal des anciennes filatures à Bouvignes. C.A.W. 14, 212-213.

Collerson, K.D., Kamber, B.S., Schoenberg, R., 2002. Applications of accurate, high-precision Pb isotope ratio measurement by multi-collector ICP-MS. Chem. Geol. 188, 65-83. 10.106/s0009-2541(02)00059-1. [dataset] OXALID http://oxalid.arch.ox.ac.uk/default.html.

de Longueville, S., Plumier, J., 2007. Les fours de potiers de Mozet (Gesves, prov. de Namur/Belgique). In: Heege, A. (Ed.) Töpferöfen - Pottery kilns. Die Erforschung frühmittelalterlicher bis neuzeitlicher Töpferöfen (6.-20. Jh.) in Belgien, den Niederlanden, Deutschland, Österreich und der Schweiz, Basler Hefte zur Archäologie, Basel 4, 245-262.

de Longueville, S., Vanmechelen, R., 2017. Haillot et les ateliers de potiers ruraux du Premier Moyen Âge: une économie organisée au départ des campagnes. In: Piechowski C. (dir) La derle - Li dièle. L'habile argile du Condroz. Vingt siècles de céramiques en terres d'Andenne. Les Dossiers de l'IPW, Namur 22, 113-121.

de Longueville, S., 2006. Le Grognon (Namur, Belgique): un site de consommation au secours de la recherche céramologique du VIII^{e} au XI^{e} siècle. In: Hincker ,V. et Husi, Ph. (Dir.), La céramique du Haut Moyen Âge dans le nord-ouest de l'Europe (V^{e}-X^{e} siècles). Actes du colloque de Caen, 18-20 mars 2004, Caen, 107-129.

de Longueville, S., 2015. Les sites de production de céramiques aux X^{e} et XI^{e} siècles dans la vallée de la Meuse moyenne (Belgique). In: Thuillier, F., Louis, E. (Eds.), Tourner autour du pot… Les ateliers de potiers médiévaux du V^{e} au XII^{e} siècle dans l'espace européen. Publications de CRAHM, Centre Michel de Boüard, Caen, pp. 351-360.

Cauet, S., Weis, D., Herbosch, A., 1982. Genetic study of Belgian lead zinc mineralizations in carbonate environments through lead isotopic geochemistry. Bull. B.R.G.M. 2 (section II, n°4), 329–341. In this issue.

Dejonghe, L., 1998. Zinc-lead deposits in Belgium. Ore Geology Reviews 12, 329–354.

Dejonghe, L., Boni, M., 2004. The "Calamine-type zinc-lead deposits in Belgium, and West Germany: a product of Mesozoic palaeoweathering processes. Geol. Belgica 8 (3), 3–14.

Dejonghe, L., Ladeuze, F., Jans D., 1993. Atlas des gisements plombo-zincifères du synclinorium de Verviers (Est de la Belgique). Mémoires explicatifs Cartes géologiques et minières de Belgique, 33, Bruxelles.

Dejonghe L., 2010. Les gisements plombo-zincifères de la région d'Andenne. In Eric Goemaere, Terres, Pierres et Feu en vallée mosane. L'exploitation des ressources naturelles minérales de la commune d'Andenne : géologue, industries, cadre historique et patrimoine culturel et biologique. Collection Géosciences 3, SGB-IRSNB, 544p., 285-310.

Durali-Mueller, S., Brey, G.P., Wigg-Wolf, D., Lahaye, Y., 2007. Roman Lead Mining in Germany: its origin and development through time deduced from lead isotope provenance studies. J. Archaeol. Sci. 34 (10), 1555–1567. doi:10.1016/j.jas.2006.11.009.

Faure, G., Mensing, T.M., 2005. Isotopes. Principles and Applications, Third Edition, J. Wiley.

Galer, S.J.G., Abouchami, W., 1998. Practical application of lead triple spiking for correction of instrumental mass discrimination. Mineral. Mag. 62A, 491–492. doi:10.1180/minmag.1998.62A.1.260.

Génicot L., 1964. Le Namurois politique, économique et social au Bas Moyen-Age. Annales de la Société Archéologique de Namur, Namur, 52, 224 p.

Giertz, W., 1996. Middle Meuse ceramics of Huy-type: a preliminary analysis. Medieval Ceramics 20, 33–64.

Goemaere, E., Challe, S., de Longueville, S., Golitko, M., Verbeek, M., Goovaerts, T., Leduc, T., 2015. Caractérisation archéométrique des céramiques glaçurées médiévales de Dinant et Bouvignes: quelques résultats préliminaires. In: Frébutte C. (Dir.), Pré-Actes J.A.W., Rochefort. Rapports, Archéologie 1, 89-91.

Hahsler, M., Piekenbrock, M., Doran, D., 2019. Dbscan: Fast density-based clustering with R. J. Stat. Software, 91 (1). 10.18637/jss.v091.i01.

Hasquin H., 1980. Communes de Belgique – dictionnaire d'histoire et de géographie administrative, 4 tomes, Crédit Communal de Belgique.

Hurst, J.G., 1969. Red-painted and glazed pottery in Western Europe from the eight to the twelfth century. Med Archaeol. 13, 93-147. doi:10.1080/00766097.1969.11735317.

Husi, Ph., 2006. La céramique peinte et glaçurée du haut Moyen-Age dans l'ouest de la France : nouvelles données pour d'anciennes interprétations, un bilan pour le nord-ouest de l'Europe. In : Hincker, V., Husi, Ph. (coord.), La céramique du Haut Moyen Âge dans le nord-ouest de l'Europe (V^{e}-X^{e} siècles), Actes Colloque de Caen, 107–129.

Ladeuze, F., Dejonghe, L., Pauquet, F., 1991. Historique de l'exploitation des gisements plombo-zincifères de l'Est de la Belgique: le rôle de la 'Vieille Montagne'. Chronique Recherches Minières 503, 37–50.

Nagaishi, K., Nakada, R., Ishikawa, T., 2021. High-throughput isotope analysis of sub-nanogram sized lead using MC-ICP-MS with on-line thallium doping technique and desolvating nebulizer system. Geochem. J. 55 (1), 1–9. doi:10.2343/geochemj.2.0612.

Nobre Silva, I.G., Weis, D., Barling, J., Scoates, J.S., 2009. Leaching systematics and matrix elimination for the determination of high-precision Pb isotope composition of ocean island basalts. G-cubed 10. doi:10.1029/2009GC002537.

Pasteels, P., Netels, V., Dejonghe, L., Deutsch L., 1980. La composition isotopique du plomb des gisements belges. Implications sur les plans génétique et économique. B.S.B.G. 89 (3), 123-136.

Péters, C., 2018. Le *Bassinia*, ancienne fontaine du marché à Huy: études et restauration. Vestiges 15, SPW-AWaP, Namur.

Raepsaet, G., Demaiffe, D., Raepsaet-Charlier, M.T., 2015. La production, la diffusion et la consommation du plomb «germanique» en Gaule du Nord. Apports des isotopes du plomb. Vie Archéol. 74, 65–89.

Raepsaet, G., Demaiffe, D., Raepsaet-Charlier, M.T., 2020. La production du plomb en Gaule du Nord. Un nouveau secteur économique. Archeo-Situla 39, 159-168.

Sheather, S.J., Jones, M.C., 1991. A reliable data-based bandwidth selection method for kernel density estimation. J. R. Stat. Soc. Ser. B (Methodological) 53 (3), 683–690. doi:10.1111/j.2517-6161.1991.tb01857.x.

Stos-Gale, S., Gale, N.H., 2009. Metal provenancing using isotopes and the Oxford archaeological lead isotopes database. J. Archaeol. Anthropol. Sci. 1, 195–213. doi:10.1007/s12520-009-0011-6.

Thibodeau, A.M., Chesley, J.T., Ruiz, J., 2012. Lead isotope analysis as a new method for identifying material culture belonging to the Vasquez de Coronado expedition. J. Archaeol. Sci. 39 (1), 58–66. doi:10.1016/j.jas.2011.07.025.

Tite, M.S., Freestone, I., Mason, R., Molera, J., Vendrell-Saz, M., Wood, N., 1998. Lead glazes in antiquity - methods of production and reasons for use. Archaeometry 40, 241–260. doi:10.1111/j.1475-4754.1998.tb00836.x.

Tomczyk, C., Costa, K., Giosa, A., Brun, P., Petit, C., 2021. Provenance studies using lead isotopy: contribution of the consideration of geological contexts in archaeological databases, BSFG. Earth Sci. Bull. 192 (1), 20. doi:10.1051/bsgf/2021008.

Van de Roy, J.L., 1996. Andenne et Sclayn. Les mines et les recherches minières. La vallée de la Meuse, 1-96.

Van Wersch, L., de Longueville, S., Dussubieux, L., Fagel, N., Hatert, F., Degryse, P., 2020. White pottery production in the Middle Meuse valley: sustainability of clay resources during the early Middle Ages. J. Archaeol. Anthropol. Sci. 12, 150. doi:10.1007/s12520-020-01103-4.

Verbeek, M., Danese, V., 2009. Dinant/Dinant: opération préventive le long de la Meuse, dans le centre ancien de la ville, avenue Churchill. C.A.W. 16, 225-226.

Verbeek, M., Siebrand, M., 2011. Dinant/Dinant: deuxième intervention avenue Churchill. Origines de la ville, parcellaire médiéval et artisanat. C.A.W., Namur 18, 250-253.

Verhaeghe, F., 1995. Het vroeg-Middeleeuwse geglazuurde aardewerk uit Oost-Souburg. In : van Heeringen R.M., Henderikx P.A. et Mars A. (eds), Vroeg-Middeleeuwse ringwalburgen in Zeeland, Goes-Amersfoort, 155-169.

Vogel, A., Miller, H., Greiling, R., 1987 (eds). The Rhenish Massif. Structure, Evolution, Mineral deposits and present Geodynamics. Earth Evolution Sciences. Springer Fachmedien Wiesbaden GmbH, 161 p. 10.1007/978-3-663-01886-5.

Walther, H.W., 1986. Federal Republic of Germany. Mineral Deposits in Europe, vol. 3, Central Europe. The Institution of Mining and Metallurgy, Min. Soc., 175-301.

Walton, M., Tite, M.S., 2010. Production technology of Roman lead-glazed pottery and its continuance into Late Antiquity. Archaeometry 52 (5), 733–759. doi:10.1111/j.1475-4754.2009.00506.x.

Weis, D., Kieffer, B., Maerschalk, C., Barling, J., de Jong, G., Williams, G.A., Hanano, D., Pretorius, W., Mattielli, N., Scoates, J.S., Goolaerts, A., Friedman, R.M., Mahoney; J.B., 2006. High-precision isotopic characterization of USGS reference materials by TIMS and MC-ICP-MS. G-cubed, 7. 10.129/2006gc001283

Wolf, S., Stos, S., Mason, R.B., Tite, S., 2003. Lead isotopes analyses of Islamic pottery glazes from Fustat, Egypt. Archaeometry 45 (3), 405-420. doi:10.1111/1475-4754.00118.

Published by Elsevier. This is the Author Accepted Manuscript issued with: Creative Commons Attribution Non-Commercial No Derivatives License (CC:BY:NC:ND 4.0).
The final published version (version of record) is available online at DOI:10.1016/j.jasrep.2022.103366. Please refer to any applicable publisher terms of use.

https://dspace.org/

Tracking the source of lead of medieval glazed pottery of the Meuse valley (Belgium) through lead isotope analyses

Goemaere, Eric; Challe, Sophie; de Longueville, Sylvie; Delbey, Thomas; Demaiffe, Daniel

2022-04
Elsevier
https://doi.org/10.1016/j.jasrep.2022.103366
Goemaere E, Challe S, de Longueville S, et al., (2022) Tracking the source of lead of medieval glazed pottery of the Meuse valley (Belgium) through lead isotope analyses. Journal of Archaeological Science: Reports, Volume 42, April 2022, Article number 103366

Downloaded from a DSpace repository. https://dspace.org/