Eur. Phys. J. Plus (2025) 140:659
https://doi.org/10.1140/epjp/s13360-025-06594-5

THE EUROPEAN PHYSICAL JOURNAL PLUS

Regular Article

Multi-analytical investigation of thirteenth century slip-decorated tiles: tracing the origins of Tiebas Castle's ceramics

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Received: 8 March 2025 / Accepted: 25 June 2025

Abstract Tiebas Castle, located near Pamplona (Northern Spain), was constructed in the thirteenth century under the reign of Theobald II of Navarre. Among its most distinctive decorative elements were slip-decorated *carreaux de pavement*—dichromatic paving tiles that adorned multiple rooms within the Castle. These tiles bear strong stylistic and technological similarities to those found at various archaeological sites in the former county of Champagne (Northeastern France), indicating a connection between the two regions in terms of production techniques and artistic influences. To better understand their provenance and the artistic practices involved in their manufacture, we conducted a comprehensive analysis of the three primary raw materials: the red clay used for the ceramic body, the kaolin for the slip decoration, and the lead employed in the glaze. Comparative reference samples from both Champagne and Navarre were examined using a multi-analytical approach, including X-ray fluorescence (XRF), X-ray diffraction (XRD), and high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS). Our results revealed that the ceramic bodies from both regions were composed of decalcified clay, rich in quartz and haematite but low in calcite. However, significant geochemical differences emerged: the ceramic body of the Tiebas tiles closely matched local Navarre clay, with a notably lower zirconium content compared to Champagne samples, where zirconium levels were consistently higher. This strongly suggested that, while the production took place in Navarre, it was likely carried out by artisans from Champagne. Additionally, the kaolin used for the slip did not correspond to any known local Navarre sources, indicating it was imported. Its composition closely matched kaolin deposits from Champagne, further supporting the idea of material exchange between the two regions. Finally, this study also sheds new light on the provenance of the lead used in the glazes, offering fresh insights into medieval ceramic production networks.

1 Introduction and research aims

In the mid-twelfth century, a new typology of paving tiles known as *carreaux de pavement* emerged in England and Northern France [1]. Initially monochromatic and covered with different colored glazes, these tiles evolved at the beginning of the thirteenth century with the addition of decorative elements using a thin intermediate layer of white clay between the ceramic body and the glaze. The decoration was obtained by stamping a wooden mould on the clay block, forming recess patterns that were then filled with white clay before drying and glazing. This first variant is called *carreaux estampées* or *inlaid tiles* [2]. Since the end of the thirteenth century, the slip became progressively thinner, constituting a second variant: *carreaux à décor d'engob*e or *slip-decorated tiles* [2]. These dichromatic tiles were often combined with monochromatic ones to create intricate geometric compositions adorning the floors of prominent sites such as abbeys, churches, and palaces. Artisans frequently replicated their designs across multiple locations, enabling the identification of their client networks and areas of influence, typically within a 50 km radius, though sometimes extending up to 200 km [1]. Tile production was carried out by both stationary and itinerant workshops, with craftsmen sometimes traveling to manufacture tiles on-site, with artisans travelling to produce tiles in situ [1].

This study focuses on a set of *carreaux de pavement* from Tiebas Castle in Northern Spain, the only known Spanish archaeological site where such paving tiles have been found. Their presence is linked to King Theobald II of Navarre (1253–1270), who was also Count of Champagne in Northeastern France. During his reign, a new Castle was built at Tiebas as a royal residence near Pamplona, the capital of the mediaeval Kingdom of Navarre. This fortified palace embodied the luxury of the French court, as evidenced by its elaborate pavements. The slip-decorated paving tiles analysed in this study were found scattered around the site from the mid-twentieth century onward with part of a pavement discovered in situ in 2009 in the castle's north room. It is estimated that Tiebas Castle originally had at least three distinct pavements, each composed of approximately 7000 tiles, for a total of about 19 tons. The

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Published online: 14 July 2025

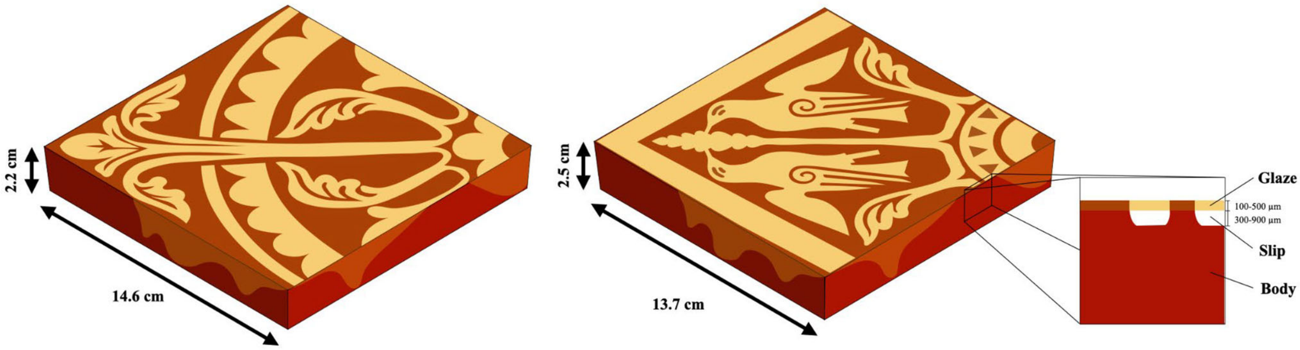

Fig. 1 Scheme of the three layers (ceramic body, glaze and slip) presented by the dichromatic *carreaux de pavement*

same artisans likely also produced the castle's glazed roof tiles, adding several more tons. A total of 33 different decorative motifs have been identified at the archaeological site. Stylistic analysis of decorative motifs on Tiebas Castle tiles revealed similarities to 13th- and 14th-century French tiles mainly within the former County of Champagne, which suggests that the Tiebas tiles were crafted by Champagnese artisans. A key question arises regarding the production of these tiles: were they manufactured in Champagne and then transported to Navarre, or were they produced locally by artisans who had travelled to the site? The first hypothesis (H1) suggests that the tiles were made in Champagne, where artisans had access to well-known sources of clay, kaolin, and lead, as well as established kilns, which would eliminate the need to build new ones. However, transporting approximately 20–30 tons of paving and roofing tiles over more than 1000 km would have represented a considerable logistical challenge. The second hypothesis (H2) proposes that the artisans travelled to Navarre and produced the tiles on-site using locally available raw materials. This would have required the construction of a new kiln and the identification of suitable clay, kaolin, and lead deposits in the region, a particularly challenging task given that these materials were not commonly extracted in Navarre.

The main objective of this study was to identify the origin of the raw materials used in the Tiebas *carreaux de pavement*, a unique case in Spanish territory, and therefore, to determine their place of manufacture. To achieve this, the composition of the three key materials was analysed: the red clay used for the ceramic body, the kaolin used for the slip decoration, and the lead used in the glaze (Fig. 1). The tiles are characterized by a reddish ceramic body, typically 2–3 cm thick, with a square base measuring approximately 10–15 cm per side. The ceramic body is primarily composed of quartz and hematite, with a low calcium carbonate content. The slip layer, ranging from 300 to 900 μm in thickness, was produced using either lime or kaolin, depending on the availability of raw materials in the region [3]. The glazes (100–500 μm) consisted of lead oxide, either pure or combined with small amounts of copper oxide. Previous research indicated that the ceramic body of the Tiebas tiles was made from decalcified clay, a material found in limestone areas where rain dissolves carbonates, leaving as residues insoluble components (mainly quartz and hematite) with a characteristic reddish colour [4–6]. Such clays are present in both Champagne and Navarre, where Eocene limestone outcrops have undergone weathering. Examples include the *Montagne de Reims* (near Hautvillers) and the *Sierra de Alaiz* (near Tiebas Castle). This geological distribution aligns with archaeological sites where slip-decorated tiles have been found, correlating with the availability of red clays (Fig. 2e). In Tiebas, decalcified clays have been identified at several locations in the *Sierra de Alaiz.* Regarding the slip, earlier studies determined that its composition was mainly based on lead feldspar ($PbAl_2Si_2O_8$), formed from the reaction between lead flux ($PbCO_3$ or PbO) and kaolinite ($Al_2Si_2O_5(OH)_4$) [4]. Champagne has significant kaolinite deposits, such as those at Poigny (near Provins) and Nesle-la-Reposte (near Chantemerle) [7, 8]. In contrast, kaolin deposits were scarce in the former Kingdom of Navarre, with only small deposits at Belate (Navarre, Spain) and Louhossoa (Basse-Navarre, France) [9, 10]. Larger deposits were located in Montguyon (Charente-Maritime, France), near the mediaeval via*turonensis* connecting Paris and Navarre [8]. Lead deposits were rare in both regions [9] and had to be imported. Lead carbonate or lead oxide, essential for glaze production, could have been sourced from processed metallic lead, which was widely available in medieval markets. By combining multiple analytical techniques, this study aims to clarify the provenance of these raw materials and to provide new insights into the technological and commercial networks that connected Champagne and Navarre in the thirteenth century.

2 Materials and methods

2.1 Materials

2.1.1 Preliminary description of the analysed tiles

The choice of 117 selected tiles (41 from Tiebas and 76 from Champagne) was made based on a stylistic analysis of decorative motifs on Tiebas Castle tiles (Supplementary Materials, Table A1). This preliminary stylistic study revealed similarities to 13th- and 14th-

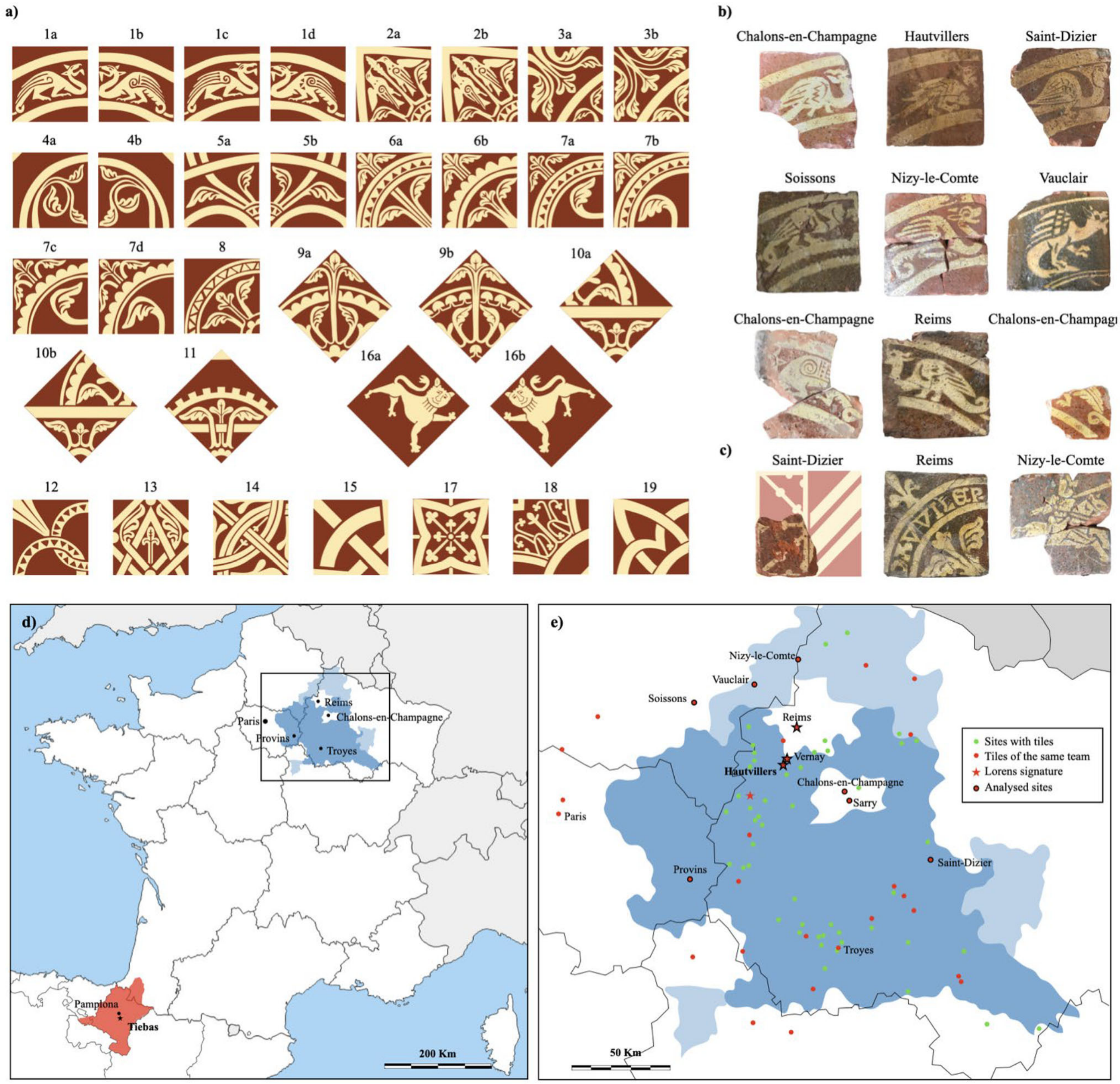

Fig. 2 Reconstruction of all the decorative motifs found in Tiebas Castle (**a**) [16–19]. Examples of decorative motifs similar to 1a and 1b from different archaeological sites in northern France (**b**). Specimens with the coat of arms of Navarre and Champagne, with the signature of the craftsman ("*d'Auvier*", trad. "from Hautvillers") and of a knight with the coat of arms of the Barony of Coucy (**c**). Location of Tiebas in the Navarre Kingdom (red, northern Spain) and the principal cities of the Champagne County (blue, north-east France) during the thirteenth century (**d**). Map of the Champagne County (blue) and its vassal counties (light blue) with the location of the archaeological sites where similar *carreaux de pavement* have been found (**e**)

century French tiles (Fig. 2a, b). With this purpose, inventories from museums in the former County of Champagne were reviewed, including those in Paris, Reims, Troyes, and Provins, among others. Similar motifs were found (Fig. 2b), with some tiles displaying highly comparable designs and others showing similar patterns. Interestingly, while tiles within the same archaeological site often had identical decorations, notable differences appeared between tiles from different locations, even nearby ones, suggesting new moulds were used for each site. Despite variations, iconography, tile size, and arrangements in sets of 16 tiles were consistent across locations [11–14]. The style analysis identified a distribution of similar motifs mainly within the former County of Champagne, particularly between Reims and Provins; and in the south, around Saint-Dizier and Troyes (Fig. 2d–e). Although historical records of the craftsmen remain unknown, an inscription on some tiles founded near Reims—"*LORENS DAVVILER MEFIT*" (Fig. 2c)—indicated that "Lorens de Hautvillers made me" [15]. This inscription also appeared at *Abbaye Saint-Pierre d'Hautvillers*, *Château de Vernay* (Saint-Imoges) and *ferme d'Heurtebize* (Orbais-l'Abbaye) sites (Fig. 2e), which featured decorative motifs resembling those at

Table 1 Major elements composition of Tiebas Castle tile ceramic bodies (red and yellow) expressed as the mean and SD

	Element	% Composition (non-portable XRF)	% Composition (portable XRF)	Difference (%)
Red body	Si	54 ± 2	57 ± 2	5
	Al	17.6 ± 0.9	15 ± 1	16
	Fe	14.5 ± 0.6	13 ± 1	12
	K	5.4 ± 0.4	9 ± 1	61
	Ca	2.6 ± 0.8	4 ± 2	54
	Mg	1.7 ± 0.1	–	–
	Ti	1.29 ± 0.08	1.7 ± 0.2	28
	Mn	0.28 ± 0.02	0.21 ± 0.07	26
	Na	0.2 ± 0.1	–	–
	Zr	0.13 ± 0.02	0.09 ± 0.02	36
Yellow body	Si	35 ± 1	33 ± 3	5
	Al	12.3 ± 0.4	10.0 ± 0.8	19
	Fe	9.9 ± 0.5	7.7 ± 0.7	22
	K	3.3 ± 0.5	5 ± 1	51
	Ca	36 ± 1	42 ± 4	19
	Mg	1.7 ± 0.3	–	–
	Ti	1.04 ± 0.05	1.1 ± 0.1	9
	Mn	0.17 ± 0.04	0.11 ± 0.04	34
	Na	0.10 ± 0.1	–	–
	Zr	0.10 ± 0.01	0.055 ± 0.009	47
	Sr	0.18 ± 0.02	0.13 ± 0.01	28

Tiebas Castle (Fig. 2a: motifs 1a, 1b, 3a, 4a, 4b, 5a, 5b, 6a and 12) [13, 14]. Hautvillers, located south of *Montagne de Reims*, was likely a production centre due to its surrounding oak and ash tree forests for kiln fuel, Eocene decalcified clay outcrops, and water sources. Its proximity to Reims and Châlons-en-Champagne and access to Paris through the Marne river made it a strategic trade hub.

2.1.2 Ceramic body

To determine the origin of the Tiebas Castle tile ceramic body, materials were selected based on two hypotheses. For H1 (production in Champagne), tile ceramic bodies from various archaeological sites in Champagne with similar decoration were used as references. These archaeological sites, identified throughout the former county of Champagne (Fig. 2d, e, Supplementary Materials, Table A1), provided insight into the clays used by local craftsmen (preventing us from taking clay samples) and indicating whether a single or multiple supply sources were used. For H2 (production in Navarre), since no other local *carreaux de pavement* existed, decalcified clays from various Navarre locations (Supplementary Materials, Table A2) and tiles from Tiebas Castle were chosen.

Tiebas castle tiles Forty-one samples from Tiebas Castle, provided by the Navarre Government's *Dirección General de Cultura—Institución Príncipe de Viana*, were analysed. The majority (34) were dichromatic, with 7 monochromatic. All featured reddish ceramic body and underwent precise, micro-destructive analysis on both surface points and powder samples. All samples were analyzed with both, portable XRF and non-portable XRF.

Clay samples from Navarre In the case of clays, those decalcified clays closest to the Tiebas Castle were selected: A1-A33 (Supplementary Materials, Table A2). Samples were analyzed in powder with the non-portable XRF.

Tiles from the Champagne region Samples from different archaeological sites and museums in Champagne were selected (Supplementary Materials, Table A1 and Fig. 2d–e): *Château de Nity-le-Comte* (NICO), *Abbaye Saint-Pierre de Hautvillers* (HAUT), *Collégiale Notre-Dame-en-Vaux* in Châlons-en-Champagne (CNDB), other tile samples from Châlons-en-Champagne (CHCH), *Palais des Comtes de Champagne* in Provins (PROV), *13 Rue du Cloître* in Reims (13RC), *Château de Saint-Dizier* (STDZ), *Château de Vernay* in Saint-Imoges (VERN), *Abbaye Saint-Jean-des-Vignes* (SOIS), *Abbaye de Vauclair* (VAUC). The analyses were authorized by the Musée de Châlons-en-Champagne, Musée de Laon, Musée de Provins et du Provinois, Musée de Saint-Dizier, Musée de Soissons and Musée Saint-Remi (Reims). These analyses were non-invasive and were conducted in situ at the respective museums, limiting the number of samples and analysis time. Analysis focused on exposed ceramic body sections from prior fractures, avoiding contamination from glaze, mortar, or soil. The number of analysed specimens varied by specimens availability and access to uncontaminated ceramic body (Supplementary Materials, Table A1). Samples were analyzed with the portable XRF.

2.1.3 Slip

The slip of dichromatic samples from Tiebas and Champagne tiles were analysed, as well as other materials such as kaolin. In the case of the slip, its non-invasive analysis without glaze was not possible because it was covered or mixed at least partially with the glaze. The composition of slip was estimated by modelling what it would be like without considering the components (mainly Pb oxide, and in some cases a small amount of Cu oxide) provided by the glaze flux.

Kaolin samples The low abundance of the raw material of slip (kaolin), compared to the decalcified clay, facilitated the selection of the most probable supply points. Kaolin samples were taken from three quarries around Provins (48.532° N, 3.274° E; 48.540° N, 3.316° E, 48.524° N, 3.220° E), which very probably supplied kaolin to all the *carreaux de pavement* craftsmen in Champagne and its surroundings. Samples were also taken from Louhossoa (43.325° N, 1.358° W) and Belate (43.051° N, 1.626° W), the only quarries in the Navarre area, although small and of low purity; and also from Montguyon (45.201° N, 0.300° W; 45.208° N, 0.285° W; 45.183° N, 0.162° W) at the Southwest of France, the large and high-purity quarries closest to Navarre. Samples were analyzed in powder with the non-portable XRF.

2.1.4 Glaze

Glaze samples were taken from a selection of tile samples from Tiebas Castle (11 samples).

Regarding the selection of samples with which to compare, the origin of the lead that makes up the glaze presents two difficulties: the scarcity of galena (PbS) and cerussite ($PbCO_3$) mining deposits and the high mobility of metallic lead through trade. For this reason, only geological reference materials from mines were considered, like the ones available in OXALID [20], IBERLID [21] databases, and others provided by the bibliography [22–27].

2.2 Methods

Two X-ray fluorescence (XRF) equipment were used on the samples: one to study in situ the tiles in the museums in Champagne and another one, not portable, to study the samples with authorization to perform micro-invasive analyses (powder and small solid fragments) and clay samples.

The non-portable system is a Bruker S2 Puma equipment (X-ray tube with a silver anode). The samples were analysed using a 4 μm polypropylene filter in a He atmosphere. The measurement conditions were triplicate scans at 20, 40, 50 kV, 50 s per scan, and a detector resolution of 10.8 eV (at 20 kV). Quantification was performed with *Spectra Results Manager* commercial software, optimised for Puma. Using this equipment, samples from Tiebas Castle were analyzed, as well as samples of red clay and kaolin.

The second, employed for non-destructive analysis, was an in-house-built XRF instrument, featuring a Pd anode end window X-ray tube (Moxtek MAGNUM) operated at 30 kV and 50 μA and a silicon drift detector (X-123FAST SDD) with an active area of 25 mm^2 collimated to 17 mm^2 and a nominal thickness of 500 μm. The X-ray tube was connected to the detector via a holder produced by 3D printing (fixing the angle between both to 45°). As a collimator primary optic, a Pd tube of 800 μm inner diameter was used, yielding a beam size of approximately 1.2 mm. The typical working distance was 2.5 cm. A laser distance measurement device (OADM20) allows for measuring the position of the primary beam on the surface of the object. The system was used with manual translation stages for single-point analysis with an acquisition time of 180 s. The X-ray tube and detector were controlled by a Raspberry 2.0 minicomputer (Raspberry Pi Foundation), which was remotely controlled via a laptop, using a LAN cable. The raw spectral data were evaluated by the software package *PyMca 5.5.1* [28]. To improve the results' accuracy, the iteration method was used. An initial matrix (55% Si, 18% Al, 14% Fe, 5.5% K, 4.0% Ca, 1.3%Ti) was defined taking as reference the mean composition of the major elements obtained using the non-portable equipment (Bruker Puma). Two iterations were enough to obtain a modelisation compatible with the spectra of the analysed samples. To make the results of both XRF techniques comparable with each other, a correction was made by applying a correction multiplying coefficient to each element. The results of the different archaeological sites were compared with those of Tiebas using the Kruskal–Wallis method to determine if there were significant differences between them. The results from the analysis using both XRF techniques were homogenized using correlation equations. The Kurstal-Wallis method allowed us to determine if there were significant differences between two samples (non-normal) with a confidence level (95%) that allowed us to accept the alternative hypothesis (samples were significantly different) if the p-value is above a certain threshold (0.05). Kruskal–Wallis method was applied by analysing the results with *Matlab* software. Using this equipment, samples from Tiebas Castle (already analysed with non-portable equipment) as well as from various French archaeological sites and museums were analysed.

The mineral composition of samples was determined by X-Ray Diffraction (XRD), with a Bruker D8 Advance diffractometer with Cu Kα radiation and an LYNXEYE XE-T detector. The experimental conditions for XRD experiments were: 2θ range from

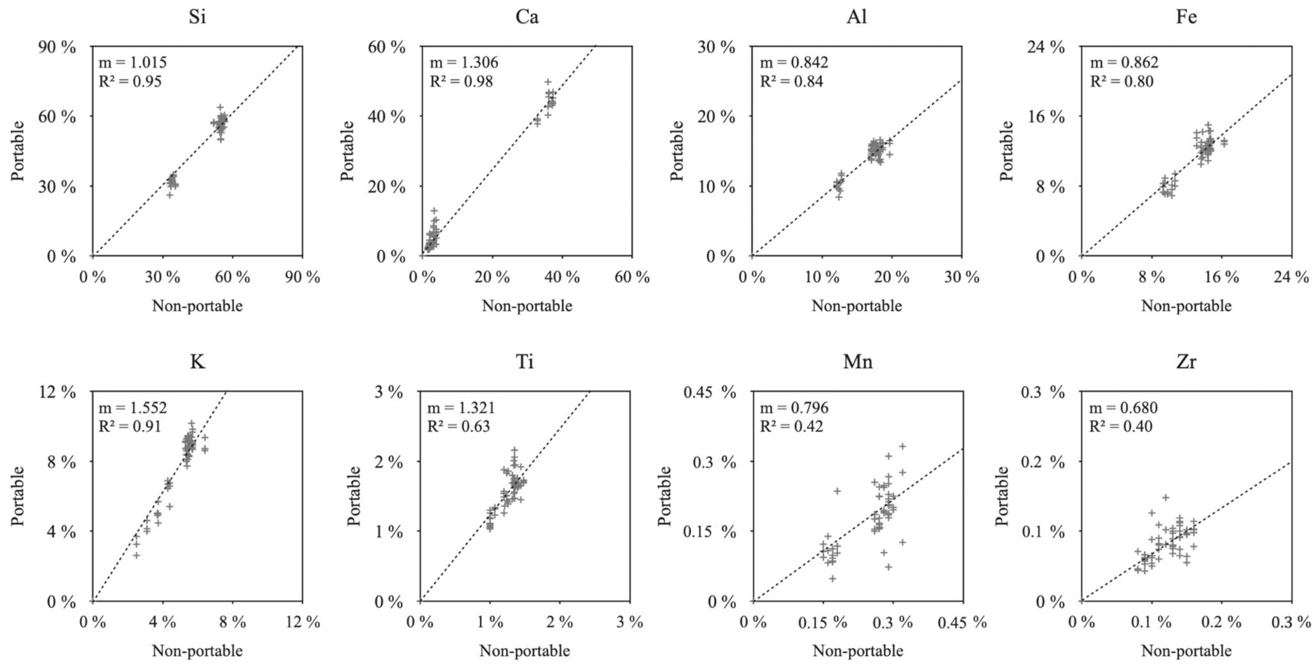

Fig. 3 Evaluation of the XRF results provided from both XRF equipment for major elements using as reference the samples from Tiebas (reddish and yellow ceramic body). The slope of the regression line (m) used as the correction coefficient, and the correlation coefficient (R2) are shown in the upper left corner of each graph

5° to 70°, 2 s per step, and step size of 0.02°. Geological samples (decalcified clays and kaolinite) and samples from Tiebas Castle were analysed. To identify some mineral phases (kaolinite, mica, illite, or chlorite) of the kaolin samples, various treatments of the samples were carried out prior to analysis: treatment with ethylene glycol, oriented aggregate and calcination. The methodology which was followed was that of Lasheras, 2002 and Lasheras, et al., 2006 [29, 30].

The lead isotopic analysis of the samples was performed in the CIEMAT laboratories (Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas, Ministerio de Ciencia, Innovación y Universidades, Madrid) using an HR-ICP-MS sector field ELEMENT 2 mass spectrometer of ThermoFisher. An optimised method to measure Pb isotopes (^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb) was used. To introduce the samples, a self aspirating nebulizer of elementary Scientific PFA with a combined spray chamber (Scott type and cyclonic) cooled by a Peltier cell system was used. To reach the optimal blanks conditions, Milli Q water and purified acids by triple distillation with a SAVILLEX DST-1000 distiller were used. Samples were filtered through 0.45 μm and acidulated with ultrapure HNO_3 to avoid clogging problems in the nebulizer system. An isotopic standard reference of lead isotopes (NIST SMR 981) was used for calibrating the obtained results with the External Standard-Sample-Standard Bracketing technique (SSB). The isobaric interference of ^{204}Hg in the ^{204}Pb was corrected, determining the abundance of ^{202}Hg and correcting with the calculated value. The results were transformed into the Lead Isotope Ratios (LIRs) ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb, and ^{208}Pb/^{204}Pb for comparison with lead ore databases.

3 Results and discussion

3.1 XRF quantification evaluation and comparison

Since two different XRF equipments and quantification procedures were used for the ceramic body analysis, quantitative analyses were first carried out on the same samples with both instruments, in order to compare the obtained results (Table 1; Fig. 3). For this objective, ceramic body samples from Tiebas Castle were used in both analyses (portable and non-portable XRF), since we were authorised to carry out invasive and non-invasive analyses. Two types of ceramic body with different compositions were used: one reddish and one yellowish. The red ceramic body was the one used in all the dichromatic tiles and in some of the monochromatic ones, while the yellow ceramic body was only used in monochromatic tiles.

The major components of the red ceramic body samples were silicon, probably coming from quartz and other silicates; aluminium, from feldspars and micas; and iron, from haematite and other iron oxides [13]. We also found potassium, probably from feldspar; and calcium, probably from calcite [13]. Other minor elements were also detected: magnesium, titanium, manganese, sodium and zirconium. The remaining elements were not detected or were below the detection limit. Sodium and magnesium could not be

Table 2 Major elements composition of each archaeological site expressed as the average composition and their standard deviation and *p*-values (95% confidence) obtained for the comparison between Tiebas tile ceramic bodies (TIEB), the ones from Champagnese archaeological sites (PROV, VERN, CNDB, CHCH, HAUT, 13RC, SOIS, STDZ, NICO, VAUC), and a Navarrese decalcified clay (A15)

	Sites	Si	Al	Fe	K	Ca	Ti	Mn	Zr
	TIEB	56 ± 2	18 ± 1	15 ± 1	5.6 ± 0.7	3 ± 2	1.3 ± 0.2	0.27 ± 0.09	0.14 ± 0.03
%	PROV	56 ± 2	15.4 ± 0.6	11 ± 1	3.7 ± 0.3	6 ± 2	1.5 ± 0.2	0.07 ± 0.02	0.23 ± 0.02
	VERN	53 ± 7	15 ± 2	11 ± 4	3.0 ± 0.8	7 ± 5	1.4 ± 0.2	0.08 ± 0.06	0.22 ± 0.04
	CNDB	53 ± 7	14 ± 2	13 ± 1	4.1 ± 0.7	10 ± 5	1.4 ± 0.1	0.10 ± 0.06	0.23 ± 0.04
	CHCH	55 ± 6	14 ± 1	13.0 ± 0.9	4.0 ± 0.5	7 ± 4	1.4 ± 0.2	0.1 ± 0.1	0.27 ± 0.04
	HAUT	57 ± 9	14 ± 2	14 ± 3	4.0 ± 0.7	4 ± 3	1.8 ± 0.3	0.2 ± 0.4	0.31 ± 0.07
	13RC	61 ± 3	16 ± 1	13 ± 2	4.2 ± 0.3	3.0 ± 0.9	1.6 ± 0.2	0.07 ± 0.02	0.25 ± 0.02
	SOIS	53 ± 9	13 ± 2	12.1 ± 0.8	2.9 ± 0.5	11 ± 7	1.3 ± 0.1	0.15 ± 0.04	0.21 ± 0.03
	STDZ	49 ± 8	17 ± 2	14 ± 2	5.3 ± 0.7	10 ± 6	1.7 ± 0.2	0.14 ± 0.07	0.18 ± 0.05
	NICO	60 ± 2	15.2 ± 0.8	12.4 ± 0.7	4.2 ± 0.3	5 ± 1	1.5 ± 0.1	0.19 ± 0.03	0.25 ± 0.03
	VAUC	61 ± 2	15 ± 2	10 ± 2	3.2 ± 0.5	6 ± 2	1.7 ± 0.3	0.12 ± 0.06	0.30 ± 0.05
	A15	55 ± 1	18.3 ± 0.6	15.6 ± 0.5	4.5 ± 0.1	2.4 ± 0.4	1.26 ± 0.06	0.4 ± 0.2	0.14 ± 0.02
p-value	PROV	1.000	0.166	**5.3e–05**	**4.4e–04**	0.142	0.151	**1.3e–05**	**0.008**
	VERN	0.959	0.066	**0.002**	**5.0e–08**	0.638	0.070	**1.0e–09**	**1.4e–04**
	CNDB	1.000	**1.0e–17**	**1.0e–08**	**8.9e–11**	**8.3e–15**	**5.4e–04**	**1.9e–17**	**2.8e–12**
	CHCH	1.000	**0**	**2.2e–10**	**2.1e–21**	**2.4e–13**	**0.001**	**1.1e–18**	**0**
	HAUT	1.000	0.079	1.000	0.580	1.000	**0.006**	0.316	**6.6e–04**
	13RC	0.193	0.799	0.422	0.053	1.000	**0.001**	**2.5e–06**	**9.0e–05**
	SOIS	1.000	**8.0e–16**	**6.0e–13**	**0**	**1.3e–10**	0.999	**5.6e–04**	**9.9e–05**
	STDZ	**0.005**	0.789	0.392	0.877	**6.0e–11**	**8.7e–18**	**6.6e–08**	**0.017**
	NICO	0.109	**0.046**	**0.002**	**0.017**	0.749	**0.004**	0.758	**3.5e–06**
	VAUC	0.213	0.208	**5.4e–04**	**6.4e–04**	0.596	0.052	0.139	**2.9e–04**
	A15	0.343	0.067	0.129	0.071	0.164	0.217	0.251	0.587

Bold values represent the significant differences (< 0.05) Na and Mg results were not included, as they could not be quantified using portable XRF. The applied method was the Kruskal–Wallis one as the results were non-normal. Values in bold represent significant differences

quantified using the portable XRF equipment, due to air absorption. The values obtained for Si, Al and Fe were similar for both XRF equipment (Table 1), while there was more variation in the quantification of Ca, Ti, Mn, Zr and especially of K (Table 1).

The yellow ceramic body showed a higher concentration of calcium and strontium and less of the rest of the elements when compared with those results obtained in the reddish ceramic body. In the yellow ceramic body, the values of Si, Al, Ca and Ti were similar in both equipment, and there was more variation in Fe, Mn, Zr, Sr, and especially of K (Table 1).

Figure 3 shows graphically the correlation between the results of both XRF equipment. A regression line can be used to describe the results which are not equivalent but rather proportional.

We consider results obtained with non-portable spectrometer as accurate. That was the reason why the portable XRF results were corrected by dividing each one by its respective slope from Fig. 3. Na and Mg results were not included, as they could not be quantified using portable XRF. Those elements not detected in the Tiebas samples (as S or Cl) could not be corrected.

3.2 Elemental composition of Navarrese and Champagnese tile ceramic bodies

Once the correction was properly performed, it was applied to all the results obtained using the non-invasive XRF apparatus. Silicon was the major component in all of them, varying between 50 and 65%. Aluminium, iron, potassium, calcium, and titanium were next in abundance, varying between 11–14%, 7.3–12%, 4.3–6.5%, 4–15%, and 1.7–2.4%, respectively. As for the minor elements (< 1%) there would be manganese and zirconium (Table 2).

If we compare the results between different archaeological sites, we can observe a great similarity in their major elements. It can be deduced that the clays used were in all cases decalcified clays, especially according to the high content of silicon and iron. This could indicate that artisans had a certain predilection for this type of clay, probably because of its characteristic red colour.

Although the general composition was similar, we must consider the low dispersion of the data within the same group, which allowed small differences between them to be identified. However, if we stick to the statistical analysis of the results (Table 2) we found several significant differences between the elemental compositions of the different French and Tiebas tiles. The *p*-values shown in Table 2 allowed us to determine with 95% confidence which samples and which elements had significantly different concentrations. To do this, all values minor than 0.05 were identified (in bold), which indicated significant differences. Iron, potassium, manganese and zirconium were the elements that showed the most differences between archaeological sites. Aluminium, calcium and titanium showed differences in only some of them. The exception was silicon, which hardly presented significant differences between archaeological sites.

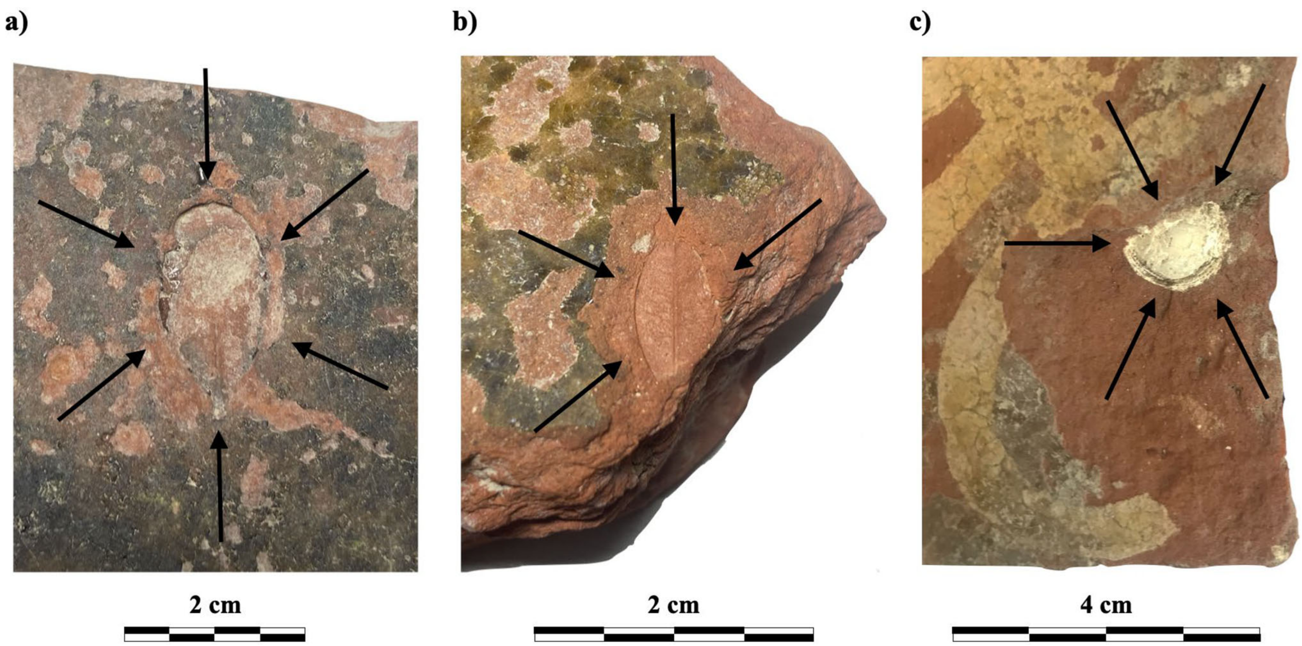

Fig. 4 Negative imprint of boxwood (*Buxus sempervirens*) leaves embedded in the ceramic body of Tiebas tiles and calcined during firing (**a**, **b**). Nummulite fossil embedded in the ceramic body of a tile from the *Abbaye Saint-Jean-des-Vignes* in Soissons (**c**)

As for the different elements, only zirconium was different in all places compared to Tiebas (except for A15 clay). Zirconium is frequently founded in granite, as quartz impurity, a mineral that stands out for its very high hardness and very low solubility, which is why it is difficult to alter. Zirconium is usually more abundant in felsic igneous rocks. All these characteristics allowed it to be considered a geochemical marker [31–33]. A possible explanation for its greater concentration in Champagne (Table 2) is the proximity of the Central Massif and the Morvan Massif in which igneous rocks are abundant. The rivers that run through Champagne (Seine, Aube and Yonne) have their source in the vicinity of the Central Massif and the Morvan Massif, and it is possible that they transported sediments, increasing the concentration of zirconium in their course [17]. On the contrary, in Navarre, the absence of nearby igneous rocks makes the zirconium content less abundant [18].

The only sample in which no significant differences were detected in any of the elements was the A15 decalcified clay. All other archaeological sites showed significant differences in at least two or three elements (HAUT in Ti and Zr, 13RC in Ti, Mn and Zr, or VAUC in Fe, K and Zr) or even more (seven elements in CNBD and CHCH). In this way, the hypothesis (H1) that Champagne artisans manufactured the tiles in Champagne and later exported their tiles could be ruled out, because important differences were found in the analysis performed in the Champagne tiles (and consequently in the French clays) in comparison with those of Tiebas. Therefore, the hypothesis (H2) that the Champagne artisans travelled to Navarre to manufacture the tiles would be the most plausible. They probably used a clay like A15 or another similar one for this.

In addition to these analytical data, the appearance of negative imprints boxwood leaves (*Buxus sempervirens*) embedded in the ceramic bodies of the Tiebas tiles was especially notable (Fig. 4a, b). This species is very abundant in the Pyrenees, Alps and Caucasus, but is not abundant in the latitude of Champagne [34], so providing a new evidence for the use of local raw materials.

It is also worth highlighting the discovery of a Nummulite fossil embedded in the ceramic bodies of one of the Saint-Jean-des-Vignes (Soissons) tiles (Fig. 4c). Nummulites are a fossil species of foraminifera that is abundant in Paleogene limestones, especially those from the Eocene [35]. It is precisely in the soils above these Eocene strata where decalcified clays are formed. *Sierra de Alaiz* (Navarra) is a limestone formation also originating during the Eocene, from where the identified declassification clay (A15) was taken.

In this way, it was confirmed that the artisans of Champagne initially used decalcified clays as raw clay and also during their work in Navarre.

3.3 Kaolin provenance

Determining the origin of the kaolin used in the Tiebas Castle slip was challenging due to the difficulty in precisely analysing the slip's composition. The thin slip layer, influenced by the underlying ceramic body and overlying glaze, complicated accurate results. Previous XRD analysis indicated lead feldspar formation from the reaction between lead in the glaze and the kaolinite from the kaolin [13]. Kaolin typically contains quartz, feldspar, or micas [17], originating from the alteration of potassium feldspar in igneous rocks, which affects kaolinite content based on the alteration degree [17].

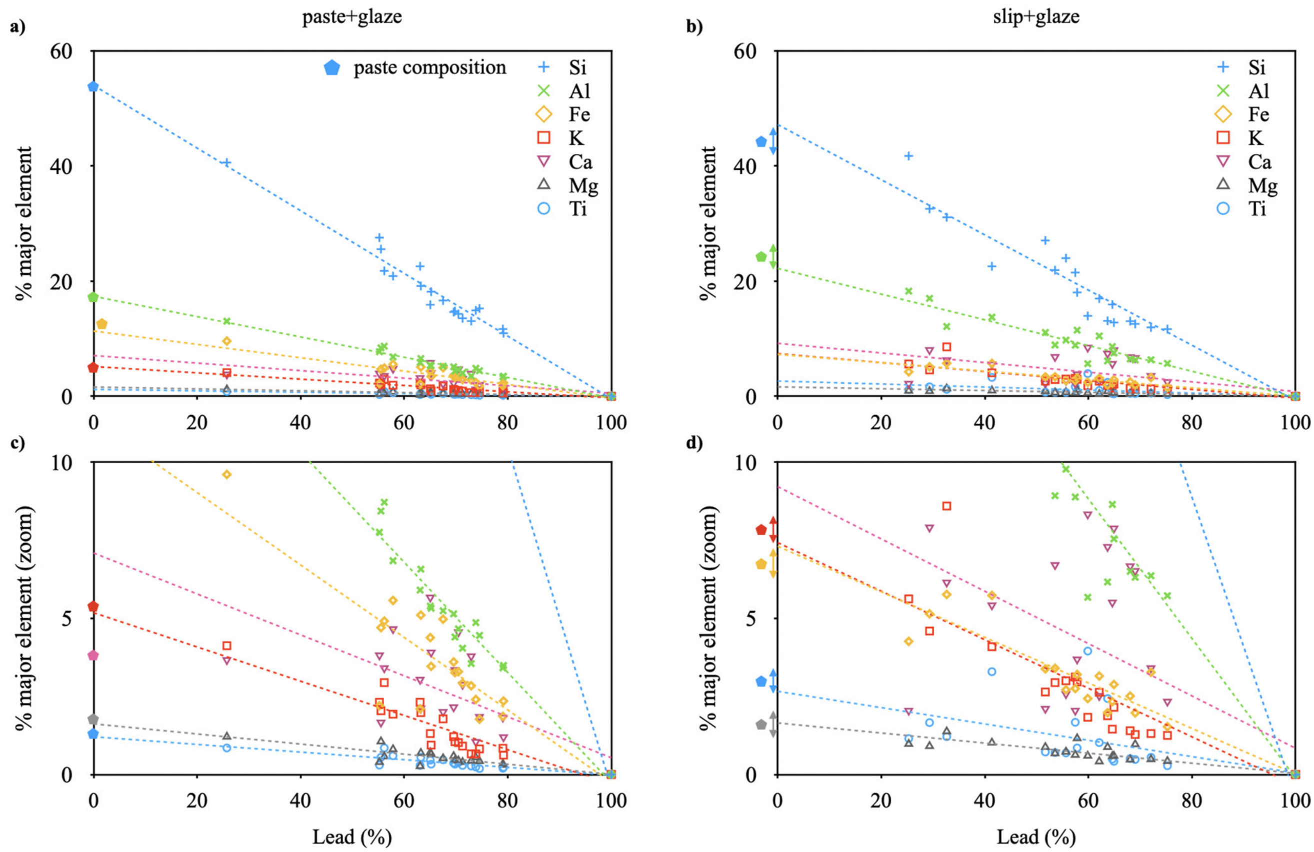

Fig. 5 Estimation of the composition of the ceramic body (**a**, **c**) and the slip (**b**, **d**) by following the variation of major components according to the lead concentration of the glaze. Figures below (**c**, **d**) are zooms of the ones above (**a**, **b**). The filled pentagonal markers indicate the actual composition of the ceramic body (at 0% Pb content) (Table 1)

Although the elemental analysis cannot provide a precise composition, it can provide an estimation of the original composition. For this, different slip + glaze fragments were analysed using non-portable XRF. The results showed lead from the glaze mixed with slip elements. Lead concentrations varied due to glaze thickness and conservation, inversely affecting slip element readings. As the proportion between the elements associated within the slip was constant, it was proposed that the isolated composition of the slip could be estimated by removing the lead concentration and normalising the results of the remaining elements. Nevertheless, the flux used for the glaze could have some components other than lead-based, like silica, so the mixture would not be as easy to discern.

The procedure was tested first on body + glaze fragments, showing that higher lead decreased other elements (Fig. 5a, c). Likewise, it could be extrapolated with some precision to an estimation of the composition of the ceramic body. The estimated values (Fig. 5a, c at 0% Pb content) were very similar to those obtained in the analysis of the ceramic body alone (Table 2). In this way it was confirmed that the flux added was only composed of lead and not a mixture of lead and silica, since any other element would have modified the estimate.

The process was replicated for slip (Fig. 5b, d). However, one additional factor had to be considered: the slip layer was very thin (300–900 μm), and so was the glaze (100–500 μm), so a certain number of X-rays could pass through them and reach the ceramic body under both, so that the quantification would be a mixture of ceramic body, slip, and glaze in a certain proportion. This interference could varied by element energy and layer thickness. For lighter elements such as sodium, magnesium, aluminium and silicon, as their Kα energy is very low (at 1.04, 1.25, 1.49, and 1.74 keV), the depth it reached would be less, so it would hardly be able to go through the slip and reach the ceramic body. The exact calculation of this interference is difficult since it depends on the thickness of the strata in each sample. That is why a certain concentration range was estimated for each element considering the presence and absence of interference from the ceramic body (see Fig. 5b, d when the Pb content was 0%).

In the last column of Table 3, the estimated values of the slip composition are shown with a < or > symbol depending on the effect that the interference of the ceramic body could have on it. Since silicon and iron were more abundant in the ceramic body than the values obtained for the slip, it is likely that they were interfering upwards in the quantification of the slip, so the original concentrations would be less than 47 and 7.3%, respectively (Table 3). On the contrary, aluminium, potassium and titanium were more abundant than the values obtained, and it is likely that they were interfering downwards in the quantification of the slip, so the original concentration would be higher than 22, 7.5 and 2.7%, respectively (Table 3).

Table 3 Element and mineral composition of the kaolin samples by non-portable XRF and XRD analysis

Element	Provins (Champagne)	Montguyon (Aquitaine)	Louhossoa (Aquitaine)	Belate (Navarre)	Tiebas slip (estimation)
Na	0.3 ± 0.3	0.7 ± 0.1	3 ± 1	0.33 ± 0.06	< 1
Mg	1.0 ± 0.1	1.25 ± 0.07	1.0 ± 0.1	13 ± 4	≈ 1.6
Al	25 ± 2	37 ± 2	30 ± 5	23.0 ± 0.1	> 22
Si	64 ± 2	51 ± 3	55 ± 4	40.5 ± 0.7	<47
P	0.01 ± 0.02	0.01 ± 0.01	0.28 ± 0.03	0.06 ± 0.08	< 1
S	0.03 ± 0.04	0.01 ± 0.02	0.02 ± 0.01	0.02 ± 0.01	< 1
Cl	0.04 ± 0.03	nd	0.07 ± 0.02	0.03 ± 0.00	< 1
K	1.1 ± 0.4	2.8 ± 0.3	9 ± 1	8 ± 3	> 7.5
Ca	0.6 ± 0.1	0.24 ± 0.02	0.6 ± 0.2	0.3 ± 0.2	–
Sc	nd	nd	nd	nd	< 1
Ti	4.1 ± 0.6	2.6 ± 0.3	0.08 ± 0.03	1.27 ± 0.03	> 2.7
V	0.08 ± 0.01	0.07 ± 0.01	0.01 ± 0.02	0.06 ± 0.01	< 1
Cr	0.09 ± 0.01	0.05 ± 0.00	nd	0.04 ± 0.00	< 1
Mn	0.03 ± 0.01	0.03 ± 0.01	0.01 ± 0.02	0.09 ± 0.05	< 1
Fe	3.2 ± 0.5	4.8 ± 0.3	1.1 ± 0.3	13.12 ± 0.05	<7.3
Co	nd	nd	nd	nd	< 1
Ni	nd	0.01 ± 0.00	nd	0.02 ± 0.01	< 1
Cu	nd	nd	nd	nd	< 1
Zn	0.02 ± 0.03	0.01 ± 0.02	nd	nd	< 1
Ga	0.02 ± 0.00	0.02 ± 0.00	0.05 ± 0.02	0.01 ± 0.00	< 1
Ge	nd	0.01 ± 0.01	nd	nd	< 1
As	nd	nd	nd	nd	< 1
Se	0.01 ± 0.01	nd	nd	nd	< 1
Br	nd	nd	nd	0.01 ± 0.01	< 1
Rb	0.02 ± 0.01	0.04 ± 0.01	0.30 ± 0.14	0.07 ± 0.01	< 1
Sr	0.09 ± 0.02	0.04 ± 0.01	0.08 ± 0.04	0.07 ± 0.07	< 1
Y	0.03 ± 0.00	0.03 ± 0.00	0.01 ± 0.01	0.03 ± 0.00	< 1
Zr	0.12 ± 0.12	0.02 ± 0.04	nd	0.07 ± 0.01	< 1
Quartz (SiO_2)	+++	+++	+++	+++	
Kaolinite ($Al_2Si_2O_5(OH)_4$)	+++	+++	+++	+++	
Mica ($KAl_2(AlSi_3O_{10})(OH)_2$)	–	+++	+++	+++	
Albite ($NaAlSi_3O_8$)	–	–	+++	–	
Orthoclase ($KAlSi_3O_8$)	–	–	+++	–	
Chlorite ($(Fe,Mg,Al)_6(Si,Al)_4O_{10}(OH)_8$)	–	–	–	+++	

Table 3 also shows the elemental concentrations of the four kaolinitic sources that were analysed as possible raw materials. Comparing their results with those obtained for the slip, the Louhossoa kaolin could be ruled out due to its high sodium content (probably due to the high albite content), high silicon and its low titanium content. Belate kaolin could be discarded due to its very high magnesium content (probably due to the high chlorite content) and high iron and low titanium content. The Provins and Montguyon kaolin samples were composed of a fairly pure mixture of kaolinite and quartz and matched with the Tiebas slip. The main difference between them was the presence of mica in the Montguyon kaolin.

From among the selected kaolin samples the most similar with Tiebas slip estimation was Provins kaolin since it only differed in the silicon/potassium or quartz/potassium feldspar ratio. In addition to its higher kaolinite and quartz content, similar to those used in the thirteenth century tiles, its proximity to the area of influence of the Champagne workshop is another important factor in its favour to consider. Champagne artisans very possibly knew the presence of these quarries around Provins which provided kaolin.

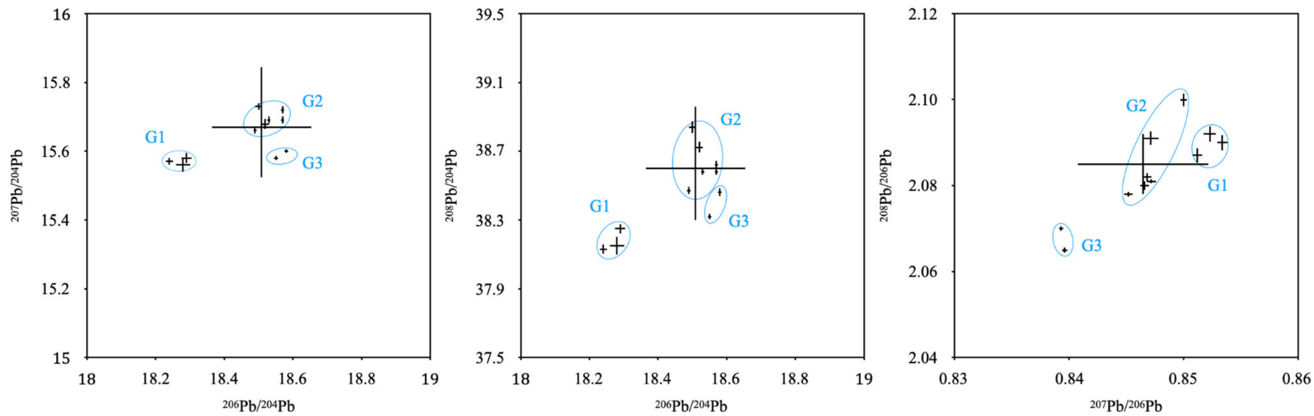

Fig. 6 Lead isotope ratios and elemental composition of glaze samples: $^{206}Pb/^{204}Pb$ vs. $^{207}Pb/^{204}Pb$ (**a**), $^{206}Pb/^{204}Pb$ vs. $^{208}Pb/^{204}Pb$ (**b**) and $^{207}Pb/^{204}Pb$ vs. $^{208}Pb/^{204}Pb$ (**c**). The length of the arms of each marker reflects its mean deviation

3.4 Lead provenance

Regarding the origin of the lead used for the glaze, it could be deduced from the isotopic analyses that there were at least three possible sources. Table A3 (Supplementary Materials) shows the different isotopic ratios and according to their distribution they could be grouped into three groups (G1, G2, and G3) (Fig. 6). The first of them (G1) was made up of three samples (M1, M6 and M10). Another six samples (M3, M18, M19, M22, M32 and M1-21) belonged to the second group (G2). And two samples (M13 and M23) to the third (G3).

The comparison of the isotopic ratios of each group with the OXALID and IBERLID databases allowed us to identify possible compatible sources. Group 2 (50% of the samples studied) would be compatible with seven samples from the Catalonian Coastal Ranges [36, 37], two from the Betic Cordillera (Southern Spain) [38] and two from the Northern Branch Iberian Massif [39]. The other two groups (G1 and G3) were not compatible with any other records in the databases.

It was also possible that lead came from some unstudied sources. It should be noted that France does not have a database, like Spain, Great Britain or Italy. Considering the proximity between Tiebas and the south of France and that the artisans also came from French territory, it is not unreasonable to think that the lead could come from France, although another provenance (Catalonian, southern, or mid-northern Spain) would be also possible.

4 Conclusions

These results shed new light on the technological and economic dynamics underlying the spread of *carreaux de pavement* in medieval Europe. The ceramic bodies of the tiles from the Castle of Tiebas and from Champagne presented a very similar elemental composition being rich in silicon (quartz) and iron (hematite), while low in calcium (calcite). These findings confirm that Champagnese artisans favored decalcified clay as the primary raw material for tile production. However, the ceramic body of the Tiebas tiles closely matched a local clay (A15) found near the castle. The key distinguishing factor was the zirconium content, which was significantly higher in all Champagne samples but notably lower in both the Tiebas tiles and the local Navarrese clay (A15). These results rule out the hypothesis (H1) that the Tiebas tiles were produced in Champagne and supports the idea that Champagnese artisans travelled to Navarre to manufacture them on-site (H2). Regarding the kaolin used in the slip, it was likely imported, as none of the nearby kaolin quarries in Navarre matched the composition found in the tile slip of Tiebas Castle. The kaolin's similarity to deposits from Champagne suggests that it was sourced from that region. Additionally, some potential sources of the lead used in the glazes were explored, providing new insights into the material procurement strategies employed in medieval tile production. The case of Tiebas Castle illustrates how artistic expertise, rather than being confined to specific geographic areas, could be transferred through the movement of skilled artisans who adapted their techniques to locally available resources. This study also highlights the complexity of medieval supply chains, where certain key materials, such as kaolin, were traded over long distances.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1140/epjp/s13360-025-06594-5.

Acknowledgements The authors thank the *Musée de Châlons-en-Champagne*, *Musée de Laon*, *Musée de Provins et du Provinois*, *Musée de Saint-Dizier*, *Musée de Soissons* and *Musée Saint-Remi* (Reims) for allowing us to analyse the tile specimens in their collections. Especially thanks to Virginia Verardi and Caroline Guerlet, Remi Bazin and Morgane Reck, Luc Duchamp, Clément Michon and Stéphane Lahierre, Christophe Brouard and Manon Jambut, and to Bénédicte Hernu and Coline Pichon. The authors also thank the CIEMAT (Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas) Hydrogeochemistry Group for their help in the analysis of lead isotopes. Especially to Lorenzo Sánchez-Moreno. The research has the support and financing of the General Directorate of Historical Heritage- Príncipe de Viana of the Government of Navarre under the following projects: "*Thibalt. Caracterización* *arqueométrica de Carreaux de Pavement procedentes del Castillo de Tiebas (Navarra)*" and "*Aplicación del arqueomagnetismo y otras técnicas fisicoquímicas para el estudio de la tecnología de fabricación de azulejos medievales navarros*", as well as of Ayuntamiento de Tiebas-Muruarte de Reta and the Fundación Sierra de Alaiz. I.R.-A. thanks to the Asociación de Amigos de la Universidad de Navarra for its doctoral scholarship.

Author contributions Iván Ruiz-Ardanaz: Conceptualization, Methodology, Writing—original draft, Data curation, Software, Funding acquisition. Laurence de Viguerie: Software, Methodology, Data curation, Writing—review & editing, Funding acquisition. Esther Lasheras: Conceptualization, Methodology, Writing—review & editing, Project administration, Funding acquisition. Adrián Durán: Conceptualization, Methodology, Writing—review & editing, Supervision, Project administration, Funding acquisition.

Funding Open Access funding provided thanks to the CRUE-CSIC agreement with Springer Nature.

Data availability The authors declare that the data supporting the findings of this study are available within the paper and its Supplementary Information files. Should any raw data files be needed in another format they are available from the corresponding author upon reasonable request.

Declarations

Conflict of 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.

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