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ORIGINAL ARTICLE

Comparison of rapid preparation methods for Pb isotope analysis of high-Pb ceramic glazes: A case study of late medieval Besztercebánya/Banská Bystrica-type stove tiles

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Abstract

This study identified the provenance of Pb flux used in the production of the glaze of unique, high-quality late medieval stove tiles from the northern part of the Carpathian Basin, and elaborated and evaluated a fast preparation process to measure Pb isotope ratios in high-Pb glazes. We compared three different methods of preparation. Method 1 consisted of the dissolution of bulk chips of glaze, dilution of the solution and mass spectrometric analysis without Pb purification. Method 2 collected the Pb from the surface of the glaze with acid-impregnated swabs, subsequent dilution and direct analysis of the sample solution. Method 3 used solutions from method 1, extraction of Pb by ion-exchange chromatography and analysis of the purified Pb. Each preparation method produced a similar Pb isotope ratio. The majority of the Pb isotope ratios fall into one group and indicate that lead imported from the Krakow–Silesia mining region was mainly used for production of the glazes of the stove tiles made by different workshops.

KEYWORDS

Banská Bystrica, fast preparation method, high-Pb glaze, Krakow–Silesia mining region, late medieval, Pb isotope ratio, MC-ICP-MS, provenance, stove tile

INTRODUCTION

In archaeological science, one of the key questions is to decipher from where the raw materials of artefacts originate. Glazes covering archaeological and historical ceramics are studied to reconstruct technological practices and traditions, as well as to determine the nature and origin of the raw materials used. Pb-bearing glazes, that is, glazes made of Pb compounds (predominantly in the form of Pb oxide) as a flux and occasionally mixed with silica, have been used since the first century BCE (Walton & Tite, 2010). These glazes provide the opportunity to determine the potential provenance of Pb compounds via Pb isotope analysis (e.g., Collerson et al., 2002; Cui et al., 2010; Habicht-Mauche et al., 2000, 2002; Huntley et al., 2007; Klesner et al., 2021; Marzo et al., 2009; Medeghini et al., 2020; Métreau et al., 2021; Santarelli et al., 2019; Shen et al., 2019; Walton & Tite, 2010; Wolf et al., 2003). Pb has four stable isotopes (^{204}Pb, ^{206}Pb, ^{207}Pb, ^{208}Pb). Radiogenic isotopes ^{206}Pb, ^{207}Pb and ^{208}Pb are produced in the decay chains of the primordial isotopes ^{238}U, ^{235}U and ^{232}Th, whereas the isotope ^{204}Pb is only of primordial origin. Different lead ore deposits have different U and Th concentrations, as well as different formation ages; therefore, the Pb isotope ratios of ore deposits can vary significantly and potentially allow for the determination of the provenance of archaeological artefacts (Gale & Stos-Gale, 2000; Stos-Gale & Gale, 2009), including Pb-bearing glazes.

Previous studies reporting Pb isotope measurements in archaeological Ag and Cu metals and Pb-glazed pottery have used bulk solution analyses without separation of the pure Pb fraction using column chemistry (Baker et al., 2006; Carroll et al., 2021; Cui et al., 2010; Walton & Tite, 2010). However, this approach dirties the cones, torch and other components of multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) instrumentation much faster and generally introduces a higher chance of error. Other studies highlighted the preservation of the artefacts using soft sampling methods (swabs), so as not to destroy the objects (Klesner et al., 2021; Santarelli, 2015; Santarelli et al., 2019; Thibodeau et al., 2012). In these studies, the authors did not need to use column chemistry because the Pb concentration in the sampled solution was so high that they had to dilute samples. No matrix interferences were confirmed due to the low concentration of matrix elements in the solution compared with Pb.

In the present study, our primary goal was to determine the simplest and fastest method to obtain Pb isotope ratios from high-Pb ceramic glazes. Thus, we compared three preparation methods. First, a piece of sample was chipped off from the surface of the glaze, digested and diluted to 50 ppb of Pb in a 3% HNO_3 solution (method 1). Second, swabs were used to sample the surface and to avoid destroying the ceramics (method 2). In method 3, the Pb was extracted by extraction chromatography from the diluted solutions obtained in method 1. Subsequently, the Pb isotope results obtained were evaluated to constrain the provenance of the Pb flux used to prepare the glazes of high-quality late medieval stove tiles.

ARCHAEOLOGICAL BACKGROUND

The Besztercebánya/Banská Bystrica-type stove tiles form a unique late medieval (15th–16th centuries CE) collection that comprises over 200 glazed and unglazed items. Fragments connected to this special collection were excavated from several sites throughout the northern part of the Carpathian Basin and its surroundings, in present-day Hungary, Slovakia and the Czech Republic. In the last few decades, several archaeological and art historical studies have investigated the connections between these tiles, characterized by similar circumstantial motifs and illustrated topics, along with the number and location of the possible production workshops (Anderko, 2023; Bodnár, 1988; Cserey, 1974; Gruia, 2007; Hoššo, 2005; Jančiová, 2020; Kvietok & Mácelová, 2013; László, 2012; Mácelová, 2005, 2006, 2009; Mezei, 2013, 2016; Mordovin, 2015; Parádi, 1984; Rakonczay, 2018, 2020). These studies were recently complemented by systematic archaeometric research to determine the raw materials and production technology of the ceramic body, as well as of the glaze of the stove tiles found at various archaeological sites, using a multi-analytical methodology (Györkös, 2022; Györkös et al., 2018, 2019, 2020). Based on the similarities and differences in the applied materials and production technology, the investigated tiles from seven sites were classified into three groups: (1) tiles from Besztercebánya/Banská Bystrica (Slovakia); (2) tiles from Eger, Salgó, Szécsény (northern Hungary) and Fülek/Fiľakovo (Slovakia); and (3) tiles from the castle of Csábrág/Čabraď and the monastery of Ipolyság/Šahy (Slovakia). Thus, the stove tiles were produced in at least three different workshops in the region, from where they were distributed to customers (Györkös, 2022, Györkös et al., 2018, 2019, 2020). (Note that names of the localities are shown in Hungarian and Slovakian, and in some cases in German in this article, as these three languages were the prevailing languages in the region for centuries.)

Most of the glazes applied are single layered, transparent, high-Pb (> 40 wt% PbO) and very high-Pb (> 60 wt% PbO) glazes of various tones of green and, less frequently, yellow colours. The polychrome tiles from Csábrág/Čabraď and Ipolyság/Šahy and three tiles from northern Hungary were covered by Sn-opacified high- and very high-Pb glazes of various colours (white, blue, green, yellow and brown). The only technological difference between the green glazes is the presence of angular-rhombohedral Pb antimonate particles in the green glaze of most of the Besztercebánya/Banská Bystrica tiles (Györkös et al., 2020). The maker(s) of the Besztercebánya/Banská Bystrica tiles used Pb antimonate intentionally as a colourant, generating a yellowish tone, or, alternatively, they may have had access to a different raw material that contained antimony. Pb isotope analyses of the glazes are expected to help reveal whether the Pb flux derived from the same or different ore source, which may confirm the existence of several production workshops in the region. Our additional goal was to determine the provenance of Pb, that is, if the craftsmen used lead ores from the region, such as lead from nearby Selmecbánya/Banská Štiavnica(/Schemnitz) in the Slovak Ore Mountains, or if lead was imported from farther away.

MATERIALS AND METHODS

A total of 24 tiles were selected that represent all the previously investigated archaeological sites: Besztercebánya/Banská Bystrica, Csábrág/Čabraď, Ipolyság/Šahy and Fülek/Fiľakovo from Slovakia and Salgó, Eger and Szécsény from Hungary. The ceramic body and glazes of the tiles were formerly characterized in detail by Györkös et al. (2018, 2019, 2020) and Györkös (2022). The analysed samples belong to the Museum of Applied Arts (Budapest, Hungary), the Hungarian National Museum (Budapest, Hungary), the István Dobó Castle Museum (Eger, Hungary), the Ferenc Kubinyi Castle Museum (Szécsény, Hungary), the Slovak National Museum (Bratislava, Slovakia), the Institute of Archaeology of the Slovak Academy of Sciences (Nitra, Slovakia), and the Honty Museum and Gallery of Ľudovít Simonyi (Šahy, Slovakia). All colours of the polychrome tiles were investigated so that altogether 32 glaze samples were analysed. Due to the scarce availability of the materials, the tiles from Besztercebánya/Banská Bystrica, one tile from Salgó (S_2012.1.83.13_green), three tiles from Csábrág/Čabraď (CS_2016.163.12_green, CS_2016.204.1_yellow and CS_3_green) and the white and green glazes of one polychrome tile from Ipolyság/Šahy (I_70_white and I_70_green) were investigated only with method 1 (see Table S1 in the additional supporting information). A total of 15 stove tiles (22 glaze samples) were investigated with all three preparation methods (see Tables S4–S6 in the additional supporting information). The Pb oxide content of the glazes of the investigated tiles varied between 45 and 71 wt% based on scanning electron microscopy with energy-dispersive X-ray spectrometry (SEM-EDX) measurements (Györkös, 2022; Györkös et al., 2020) (see Table S1 in the additional supporting information).

Sample preparation, except the chipping off of a tiny fragment, was conducted in a Class 1000 cleanroom. Ultrapure water (UPW) (Merck, 18 MΩ·cm) and doubly distilled 14 mol L^{-1} nitric acid were used to digest and clean the samples. We used three different protocols to prepare the glaze samples for Pb isotope analysis. As glazes contain at least 45 wt% Pb oxide, a few mg of sample were enough for the dissolution. In method 1, the chipped off glazes were digested in a mixture of nitric acid (3%) and hydrofluoric acid (20%), and then diluted to 50 ppb of Pb solution in 3% nitric acid. In method 2, Pb was leached directly from the glaze surface with a polyester-tipped swab (Clean Tips Polyester Alpha Mini Swab) to gently swabbing the surface by a few gentle hand motions. Our preparation method 2 is a bit different than the procedure established by Thibodeau et al. (2012) and applied by Santarelli et al. (2019) and Klesner et al. (2021). These papers used a 2% HNO_3 solution for their surface cleaning, swabbing and swab soaking steps, while in our procedure 8 M HNO_3 was used for swabbing the glaze surface. Pb sample solutions were prepared by soaking the swabs in 3% double distilled nitric acid for 5 min and were then diluted to the appropriate concentration. Measurements were performed without any ion-exchange chromatography. The total process blank was determined with three blank swabs soaked in 3% double distilled nitric acid for 5 min (Pb concentration of 3–5 ppt). To demonstrate that Pb separation is not necessary, the pure Pb fraction from method 1 was extracted using the extraction chromatography in method 3 (Smet et al., 2010; see also the Supporting information). The procedural blanks of method 3 were 0.12–1.16 ng of Pb. The standard reproducibility of the measurements is shown in the Table S3 in the additional supporting information.

Pb sample solutions for isotope ratios were measured by a Neptune Plus multiple-collector inductively coupled plasma mass spectrometry (MC-ICP-MS (Thermo Scientific) equipped with an Aridus-3 (CETAC)) desolvating nebulizer system (dry plasma) at (ICER) in Debrecen, Hungary (Cavazzuti et al., 2021; Haas et al., 2022; Újváry et al., 2021). The raw measurement data were normalized to a standard solution of 35 ppb prepared from the NIST SRM 981 international Pb standard (National Institute of Standards and Technology). All standards were doped with Tl of known isotope ratio to a $^{208}Pb/^{205}Tl$ ratio of about 2. All samples were doped with Tl of known isotope ratio to a $^{208}Pb/^{205}Tl$ ratio of about 2, 5–10 and around 20 (see Tables S7–S9 in the additional supporting information). The Supporting information has some examples that show that under- or overspiking the sample solutions with Tl did not significantly change the isotopic ratio (see Table S10 in the additional supporting information). The measured Pb isotope ratios were corrected for the instrument mass discrimination using the measured and nominal values of the $^{203}Tl/^{205}Tl$ ratio (Baker et al., 2004; Nagaishi et al., 2021). The optimized data acquisition parameters selected for Pb isotope ratio measurements are summarized in Table 1. Data collection was made using one block with 150 measurements, with an integration time of 2.097 s and a mass bias correction of $^{203}Tl/^{205}Tl$: 0.41891. After every five samples, the NIST SRM 981 standard solution was measured. The measurements were performed in low resolution mode. Amplification with 10^{11} Ohm resistors was primarily used, and only the Faraday cup at mass 202 was amplified with 10^{13} Ohm resistor to monitor ^{202}Hg to correct for potential ^{204}Hg interference on ^{204}Pb (see Table S2 in the additional supporting information).

RESULTS AND DISCUSSION

Methodological developments

In method 1, small fragments of glaze were chipped off, totally dissolved and, after proper dilution, measured directly with the MC-ICP-MS. In method 2, a conservative approach that did not require destruction of the glaze was applied. Here the Pb was leached directly from the glaze using swabs impregnated with acid.

TABLE 1 Measurement parameters for Neptune Plus multiple-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) in dry plasma mode.

Instrument settings (ICP ion source settings)	
Cool gas flow rate (L min^{-1})	15
Auxiliary gas flow rate (L min^{-1})	0.7
Sample gas flow rate (L min^{-1})	0.885
Cones	Nickel X sample cone, nickel jet skimmer cone
RF power	1200
Sample introduction Aridus-3 settings	
Spray chamber temperature (°C)	110
Desolvator temperature (°C)	140
Ar sweep gas flow (L min^{-1})	5.95
N_2 gas (mL min^{-1})	3
Sample uptake rate (μL min^{-1})	110

For comparative purposes, in method 3, a classic extraction chromatography (Smet et al., 2010) was applied to the solutions prepared with method 1. Comparing methods 3 and 2 with method 1 (see Tables S4–S6 in the additional supporting information), all samples gave similar results with only slight differences (Fig. 1). Note that the uncertainty usually just slightly larger than the symbols. The differences arose because the swab technique only analysed Pb from the surface of the glaze (method 2), whereas method 1 (chipped off) analysed bulk Pb in the glaze. The bulk sampling technique is isotopically more homogeneous than the swabbing technique. In group 1, a minor difference in $^{208}Pb/^{204}Pb$-$^{206}Pb/^{204}Pb$ relation may be caused by inhomogeneity of the glaze surface that results in contamination of the samples from the ceramic body. We are aware that in group 2, the Pb isotope ratios are slightly different when comparing method 1 and method 2, but we did not observe any instrumental reasons for that. No significant difference in Pb isotope ratios was observed between the three preparation methods (methods 1–3). The same three groups of glazes can be distinguished clearly in all the preparation methods. Based on these results, we can confirm that method 2 is the most appropriate preparation method for high-Pb glaze samples, as it does not destroy the cultural value and integrity of the stove tiles, and, additionally, it is fast and requires less laboratory work. The comparison of the three methods also shows that chromatographic separation is not necessary, and therefore the samples analysed only with method 1 provide reliable Pb isotope data. However, the column chemistry helps to keep the MC-ICP-MS clean and running effectively and efficiently. Without the column chemistry, usually the cones, torch and spray chamber require cleaning.

For provenance analysis, we used Pb isotope data obtained via method 1, because only this method was used for all the glaze samples (see the results in Table S11 in the additional supporting information).

Provenance of the Pb used for the glazes

Based on the geology of the region, the Slovak Ore Mountains may potentially supply the raw materials necessary for preparation of the coloured Pb glazes. Copper, used to colour green glazes, was intensively mined around Besztercebánya/Banská Bystrica/Neusohl in the medieval period (Batizi, 2018). A new technological innovation, the liquation process (*Saigerhüttenprozess* or *Saigerprozess*), was introduced to separate silver from the

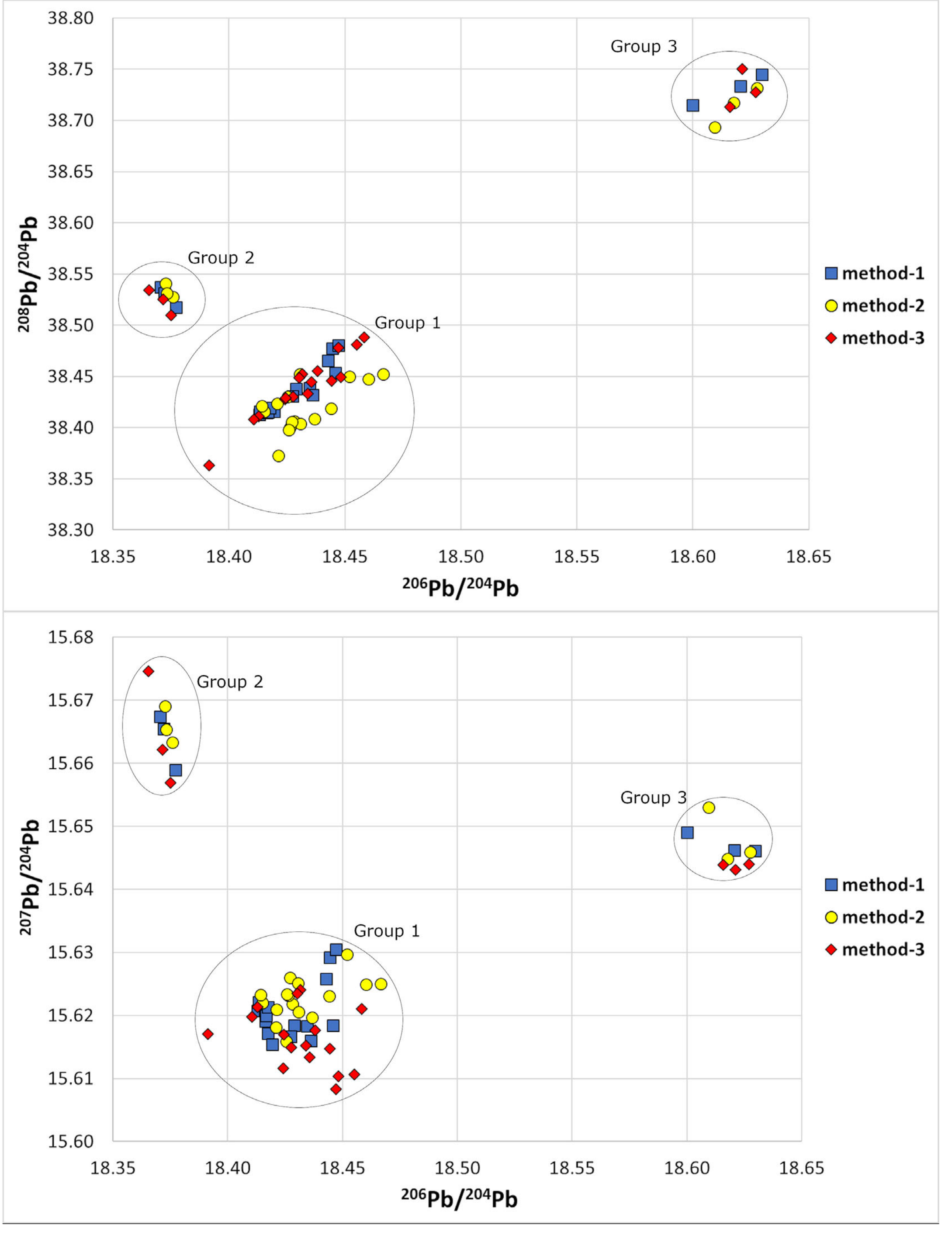

FIGURE 1 Comparison of three preparation methods (method 1: bulk; method 2: swab; and method 3: bulk + column chemistry).

Ag-containing copper ore in the territory of the Slovak Ore Mountains at the end of the 15th and the 16th centuries CE, with the first liquation plant established near Besztercebánya/Banská Bystrica/Neusohl (Hauptmann et al., 2016, *passim*). To extract silver from the copper ore, Pb or Pb oxide was added to Cu. The Besztercebánya/Banská Bystrica/Neusohl copper mines, owned by the Thurzó-Fugger company, produced several 10,160,469 kg of copper and more than 100,000 kg of silver in the first half of the 16th century CE (Hauptmann et al., 2016). Therefore, liquation required the use of huge amounts of Pb. Lead mining occurred at Selmecbánya/Banská Štiavnica/Schemnitz in the territory of the Slovak Ore Mountains (Batizi, 2018); however, the production probably did not cover the actual required amount. Written sources document that Pb was imported for the liquation process from a distance of circa 200 km, from the Krakow–Silesia mining region in Poland (Bánki & Molnár, 1997; Składany, 1997; Westermann & Denzel, 2011). Furthermore, Pb isotope ratios of copper ingots made of Besztercebánya/Banská Bystrica/Neusohl copper, found in the wreck of the *Bom Jesus* merchant ship that sank off the coast of southern Namibia on its way from Portugal to India in 1533, also verified the use of Polish lead, specifically, lead of the Krakow–Silesian ore deposits (Hauptmann et al., 2016). In addition to the lead ores from Poland, lead ores from Austria (Bleiberg) and England were also possibly used for the liquation process (Składany, 1997, Westermann & Denzel, 2011).

Based on these considerations, we compare Pb isotope ratios of the tile glazes to the Pb isotope ratios of the ores mined in the region and imported from Poland and Austria, respectively.

The Pb isotope ratios of the tile glazes vary in the range of 2.079 and 2.098 for $^{208}Pb/^{206}Pb$, 38.310 and 38.762 for $^{208}Pb/^{204}Pb$, 0.839 and 0.853 for $^{207}Pb/^{206}Pb$, and 18.370 and 18.645 for $^{206}Pb/^{204}Pb$, respectively. However, the glazes can be classified into three distinct groups based on their Pb isotope ratios (Fig. 2a). Regardless of the archaeological site, most of the glazes form one group (group 1 with 0.847–0.850 for $^{207}Pb/^{206}Pb$ and 2.083–2.089 for $^{208}Pb/^{206}Pb$). Three glazes from Eger (green and yellow glazes of tile E_1 and green glaze of tile E_10), are classified as group 2 (with 0.852–0.853 for $^{207}Pb/^{206}Pb$ and 2.096–2.098 for $^{208}Pb/^{206}Pb$) and exhibit higher Pb isotope ratios, whereas five green glazes from Csábrág/Čabraď and Ipolyság/Šahy (polychrome tiles CS_2016_117_3, CS_2016.163.12, I_70; monochrome tiles I_68 and I_69) are classified as group 3 (with 0.840–0.841 for $^{207}Pb/^{206}Pb$ and 2.080–2.081 for $^{208}Pb/^{206}Pb$) and exhibit lower Pb isotope ratios compared with the group 1 (Fig. 2a).

Although the Pb isotope ratio of the glazes of groups 1 and 2 are close to the Pb isotope ratio of the Besztercebánya/Banská Bystrica/Neusohl copper ores (Schreiner, 2007) (Fig. 2), no further indication regarding the source of Pb can be inferred, as the Pb isotope ratio of the glazes is predominantly determined by the dominant Pb flux, not by the Cu colourant. Additionally, there is not an exact match between the Pb isotope ratio of groups 1 and 2 and the Pb isotope ratio of the Selmecbánya/Banská Štiavnica/Schemnitz ore measured on galena, chalcopyrite and sphalerite minerals by Schreiner (2007) (see Table S12 in the additional supporting information) (Fig. 2a). Consequently, Selmecbánya/Banská Štiavnica/Schemnitz can be excluded as a potential Pb source for the glazes of groups 1 and 2. However, except for two glazes (one from Csábrág/Čabraď: white glaze of CS_2016.117.3 tile and another one from Besztercebánya/Banská Bystrica: green glaze of BB_314 tile), a strong overlap exists between the Pb isotope ratio of the glazes of group 1 and the Pb isotope ratio of the Pb-Zn deposits of the Krakow–Silesia mining region (Church & Vaughn, 1992; De Vleeschouwer et al., 2009; Miazga et al., 2022; Stos-Gale et al., 2012; Zartman et al., 1979) (see Table S12 in the additional supporting information) (Figs 2b and 3). Additionally, a strong overlap exists between the Pb isotope ratio of the glazes of group 1 and the Pb isotope ratio of copper ingots from the *Bom Jesus* shipwreck that were made of Besztercebánya/Banská Bystrica/Neusohl copper treated with lead from Poland in the liquation process (2.0846 and 2.0864 for $^{208}Pb/^{206}Pb$, 0.8478 and 0.8481 for $^{207}Pb/^{206}Pb$, and 18.416–18.423 for $^{206}Pb/^{204}Pb$, respectively; Hauptmann et al., 2016). A strong overlap is also present between the Pb isotope ratio of the glazes of group

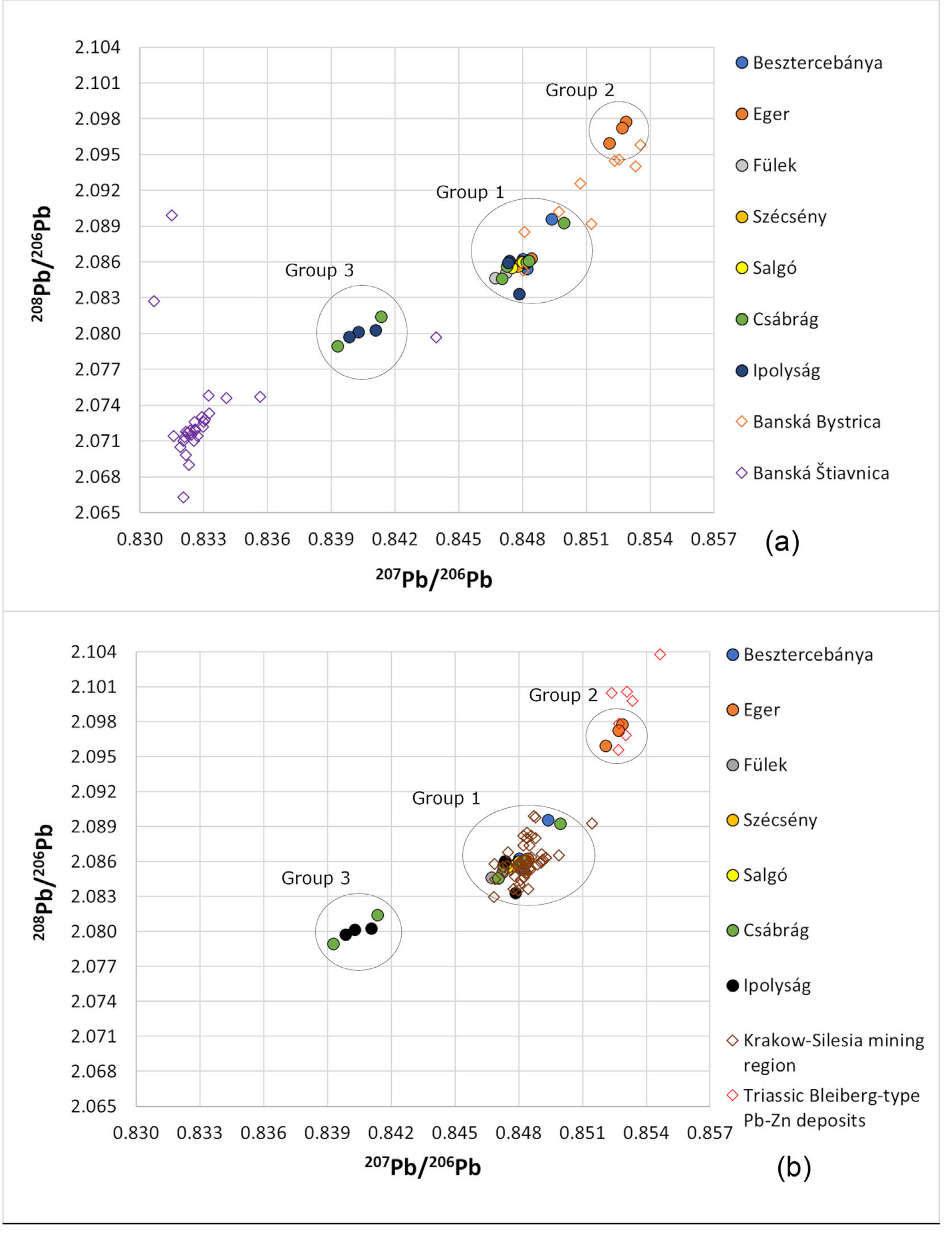

FIGURE 2 $^{207}Pb/^{206}Pb$ versus $^{208}Pb/^{206}Pb$ isotope ratios of the tile glazes compared with (a) the copper ore mined at Besztercebánya/Banská Bystrica/Neusohl and the lead ore mined at Selmecbánya/Banská Štiavnica/Schemnitz (isotope data of ores are from Schreiner, 2007; see also Table S12 in the additional supporting information; note that ^{204}Pb was measured only in one third of the ores analysed from both localities, therefore, we use only $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ ratios for comparison with Slovakian ores); (b) the lead ore mined at the Krakow–Silesia mining region (Poland) and the lead ore that originated from Triassic, Bleiberg-type Pb-Zn deposits (Austria) (isotope data of ores are from Church & Vaughn, 1992; De Vleeschouwer et al., 2009; Köppel & Schroll, 1985; Miazga et al., 2022; Schroll et al., 2006; Stos-Gale et al., 2012; Zartman et al., 1979; and see Table S12 in the additional supporting information).

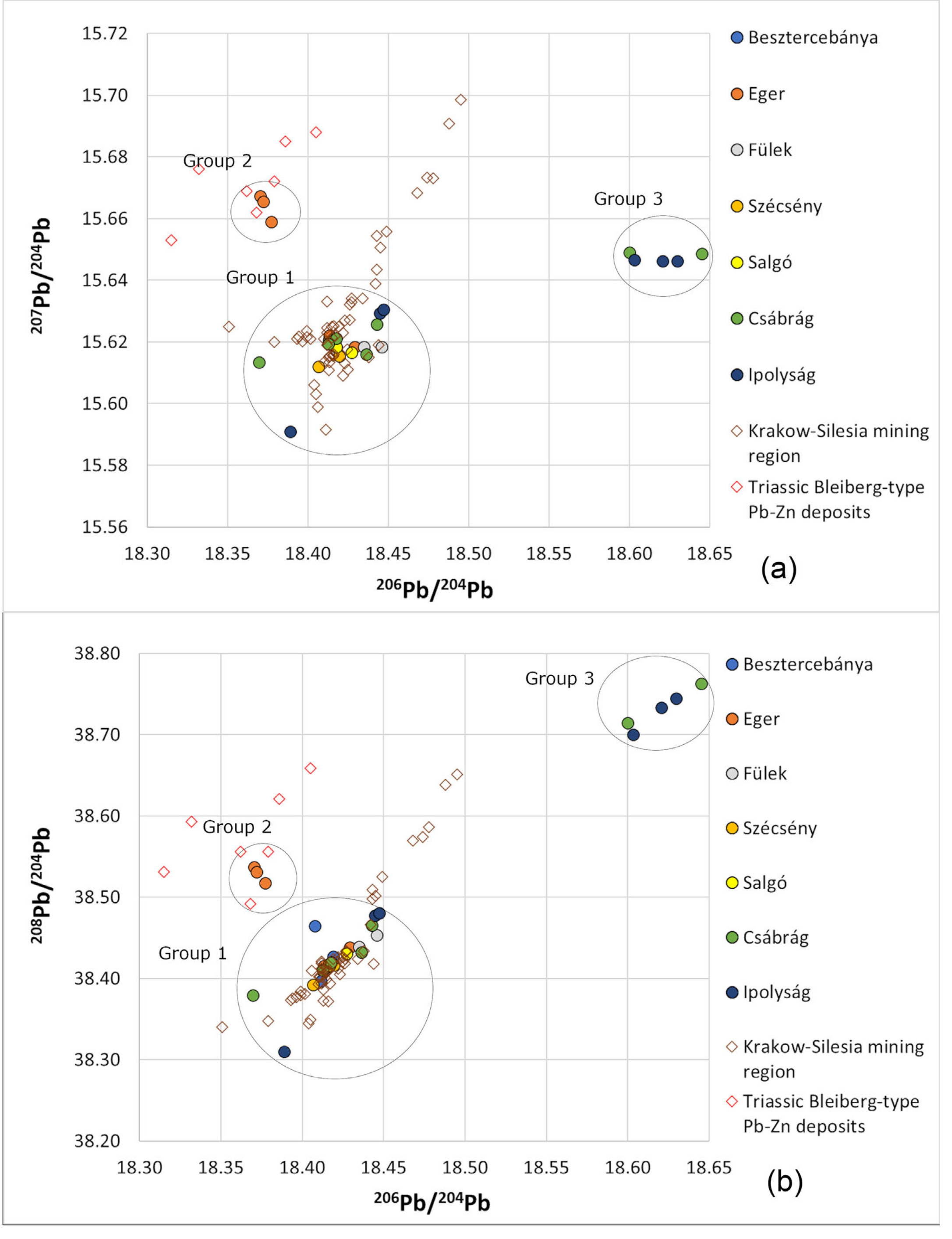

FIGURE 3 (a) $^{206}Pb/^{204}Pb$ versus $^{207}Pb/^{204}Pb$ and (b) $^{206}Pb/^{204}Pb$ versus $^{208}Pb/^{204}Pb$ and Pb isotope ratios of the tile glazes compared with the lead ore mined at the Krakow–Silesia mining region (Poland) and the lead ore that originated from Triassic, Bleiberg-type Pb-Zn deposits (Austria) (isotope data of ores are from Church & Vaughn, 1992; De Vleeschouwer et al., 2009; Köppel & Schroll, 1985; Miazga et al., 2022; Schroll et al., 2006; Stos-Gale et al., 2012; Zartman et al., 1979; and see Table S12 in the additional supporting information).

1 and the Pb isotope ratios of two medieval Pb ingots found in Wrocław and Krakow, the latter of which had a seal of Olkusz and both of which originated in the Krakow–Silesia mining region (Wrocław ingot: 2.08576 ± 0.00026 (2SD) for $^{208}Pb/^{206}Pb$, 0.84807 ± 0.00012 (2SD) for $^{207}Pb/^{206}Pb$, and 18.4200 ± 0.0025 (2SD) for $^{206}Pb/^{204}Pb$, Krakowngot: 2.08544 for $^{208}Pb/^{206}Pb$, 0.84838 for $^{207}Pb/^{206}Pb$, 18.4177 for $^{206}Pb/^{204}Pb$, Miazga et al., 2022; Stos-Gale et al., 2012). Therefore, we assume that imported Pb was used not only in the liquation process in the territory of the Slovak Ore Mountains, but Polish Pb was involved in the preparation process of the glazes of most of the stove tiles analysed, as well. Thus, tile production workshops in the region used a Pb flux mainly derived from the same ore source. Krakow and Silesia Upland area produced lead and silver since the early Middle Ages, probably from the 11th–12th centuries until early modern period, and the Pb was intensively traded in Central and Eastern Europe (Boroń & Rozmus, 2014; Miazga et al., 2022).

The Pb isotope data of the two tiles from Eger (group 2: green and yellow glaze of E_1, green glaze of E_10 tile) are similar to the Pb isotope data of the Triassic Bleiberg-type Pb-Zn ore deposits in the Eastern Alps (Köppel & Schroll, 1985; Schroll et al., 2006) (Figs 2b and 3) (see also Table S12 in the additional supporting information), potentially indicating Pb import from Austria and the use of Austrian Pb for production of some of the tile glazes. The different origins of the Pb used for the group 2 glazes are in accordance with their technological differences that were demonstrated by Györkös et al. (2020). Although the designs of these two tiles from Eger are similar to those of other Hungarian and Fülek/Fiľakovo tiles, their glazes differ in the use of colourants (Pb antimonate in the yellow glaze of E_1 tile instead of iron and Pb-Sn antimonate in the green glaze of E_10 tile, in addition to the copper colourant; Györkös et al., 2020). The two tiles from Eger may have been produced by different masters in the same workshop that produced the other Hungarian and Fülek/Fiľakovo tiles, or, alternatively, they were manufactured in a different workshop.

The green glazes from Csábrág/Čabraď and Ipolyság/Šahy (group 3) are isotopically between the group 1 glazes made of lead imported from the Krakow–Silesia mining region and the Selmecbánya/Banská Štiavnica/Schemnitz lead ores (Figs 2 and 3). For these green glazes, the mixing of Pb derived from Poland with the locally mined Pb may have been used as a flux. Interestingly, based on the Pb isotope ratios, green glazes of polychrome tiles from Csábrág/Čabraď and Ipolyság/Šahy (CS_2016_117_3, CS_2016.163.12 and I_70) belong to group 3, whereas other coloured glazes (white, yellow, blue) of the same tiles belong to group 1. It is unknown why different Pb fluxes were used in the glazes of the same tiles produced in the same workshop. However, mixing Pb of different sources may be related to, for example, a (temporary) shortage of lead imported from Poland or financial reasons.

In addition to these considerations, we must emphasize that the use of scrap Pb metal for the production of tile glazes cannot be totally excluded, although the use of Pb abundantly available from primary ore sources at the time of production is more plausible.

CONCLUSIONS

Three different sample preparation methods (methods 1–3) were used to identify the provenance of Pb flux used in the production of the high-Pb glaze of unique, high-quality late medieval Besztercebánya/Banská Bystrica-type stove tiles from the northern part of the Carpathian Basin. A total of 24 stove tiles from seven archaeological sites in present-day Hungary and Slovakia were analysed. Results demonstrate that the Pb isotope ratios are independent of the preparation methods used. Therefore, we recommend using the simplest method of surface sampling with swabs (method 2). It is a quick procedure that requires less effort in the laboratory with the benefit of preserving the sample. Regardless of the archaeological site, most of the tile glazes form one group based on their Pb isotope ratios. Comparing Pb isotope ratios of the tile glazes with the Pb isotope ratios of the ores shows a strong overlap with the lead ore deposits of the Krakow–Silesia mining region. Thus, imported Pb was used not only in the liquation process to separate Ag from the copper ore mined in the territory of the Slovak Ore Mountains but also in the preparation process of the glazes of most of the stove tiles analysed that were produced in the region. The lead ore locally mined in the Slovakian Ore Mountains may have been used, possibly mixed with Pb derived from Poland, only for the green glazes of some Csábrág/Čabraď and Ipolyság/Šahy tiles. The Pb isotope ratio of some of the tiles excavated in Eger is similar to the Pb isotope data of the Triassic Bleiberg-type Pb-Zn ore deposits, indicating a potential use of lead imported from Austria.

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DATA AVAILABILITY STATEMENT

The authors confirm that the data supporting the findings of this study are available within the article [and/or] its supplementary materials.

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