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Analytical studies on medieval lead ingots from Wrocław and Kraków (Poland): a step towards understanding bulk trade of lead from Kraków and Silesia Upland Pb–Zn deposits

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Abstract

Origins of medieval lead artefacts are hard to establish due to re-smelting and mixing. One can obtain conclusive evidence from ingots that served for bulk trade and originated directly from the mines. This paper aims to analyse the thirteenth century lead ingot from Wrocław (Poland). To establish its origins we analysed its structure and chemical composition. We used archaeometric methods: light and electron microscopic observations, X-ray fluorescence spectrometry, X-ray diffraction, infrared spectroscopy, inductively coupled plasma-optical emission spectrometry and Pb isotopic analysis. We compared our measurements with measurements of analogical ingot found on Kraków Market Square and a database of lead ores from Europe and the Middle East. The research indicated that both ingots originated from -Kraków and Silesia Upland Pb–Zn ore deposits (Poland), intensively mined from the twelfth century. The results complement the view of trade routes established based on written records and add valuable data for future comparative studies.

Keywords: Lead, Ingot, Trade, Archaeometry, Spectroscopy, Lead isotopes

Introduction

Lead was in the Middle Ages, apart from copper, a mass-produced and used non-ferric metal. A low melting point of lead which makes it easy to process and recycle multiple times as well its relative resistance to corrosion made lead perhaps not very prized but extremely useful material [1]. Lead was widely applied for jewellery production [2], glazing pottery [3] or production of glass [4]. Larger amounts were used in buildings (windows, roofing and joints) (e.g. [5]). Still, the most significant consumer of lead was metallurgical production: refining gold and silver from copper and lead ores (so-called cupellation) [6] and since the end of the fifteenth century in liquidation and drying of argentiferous copper ores (so-called *Seiger-process*) [7]. The demand for silver triggered an intensification of lead production. Lead was often accompanying silver in metallic ores, but not always in quantities necessary for refining silver. Only a few mining regions were able to produce pure lead on a larger scale. Among them were England, Sardinia, the Harz Mountains [8] and the area today known as the Kraków and Silesia Upland Pb–Zn deposits [9]. The lead bulk trade was well studied by historians for the early modern period [10, 11]. Our knowledge concerning the lead trade in the twelfth to fourteenth century is much ambiguous and varied according to localization [8, 12, 13] and is still quite fragmentary. Especially the role of the area of the Kraków and Silesia Upland Pb–Zn deposits is not satisfactorily recognized. This area probably produced lead and some silver since the twelfth century [14] and maintained production until the seventeenth century. General directions

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of the medieval bulk trade of the so-called "Polish" lead are known [11], but the scale and geography of this trade still need to be studied. Fortunately, the dissemination of lead isotope analyses of mediaeval artefacts found during excavations gives us a new perspective on lead trade, especially in the early Middle Ages [15] but seems to be less explored in later periods.

Since the practice of re-smelting of lead and mixing various bits together may lead to difficulties in identifying the origins of a particular item [16], therefore any find of pure lead destined for long-distance trade has special significance. The ingots were originally produced in the mining area, so they should contain only the local material from a given time. Moreover, their archaeological context may provide us with a rather narrow chronology.

The purpose of this article is the identification of the physical and chemical properties of lead ingot discovered in Wrocław (Poland) and dated to the thirteenth century, to establish its origin. Further we will compare it with an analogous ingot from Kraków Market Square as well as a database of lead ores from Europe and the Middle East. Medieval lead ingots are not common artefacts so, the research results will contribute to the analysis of the bulk trade of lead in the Middle Ages by supplementing the scare written records.

Problems in researching the origins of lead items

One of the main issues in archaeology is determining the origins of discovered items. It is assumed that by tracing the source of material it is possible to partially determine the network of contacts in the researched area, which may, in turn, reflect the trade routes, political relationships, migrations of individuals and groups, as well as transfer of knowledge and ideas. A particular spot is this research is reserved for items made of non-ferric metals. Such metals, especially the precious ones, were available only in a few places and access to them was controlled. The circulation of metals is, therefore, an important indicator of economic and political relationships. Introducing the chemical composition analysis of metals and isotope analysis on a larger scale was a real breakthrough in the research of the origins of metal items. Isotopes of lead play a crucial role, as they are stable and allow for tracing their origins even after being re-melted multiple times. Therefore, a significant amount of research on the origins of silver coins uses lead isotopes, as lead accompanies the majority of silver deposits [17]. This is particularly significant for the periods before common, detailed documentation was introduced. For instance, the analysis of lead isotopes in a series of early-medieval coins from northern Italy showed that the metal came from the deposits located in the Massif Centrale (Melle), the Harz or Schwarzwald, and not the local Italian deposits [18]. Analysis of the sources of silver may also help clarify the issue of silver exchange on a global scale, e.g. in the case of the trade of silver from Potosi (Peru) in the sixteenth century [19] or the circulation of silver in the modern-era Spain [20].

Lead (Pb), a metal less significant for the economy, seems to raise less enthusiasm among the researchers than silver (Ag). This might be caused by the fact that lead is so easy to process and recycle, and thus metals of various origins and chronology were mixed together. So far, most of the lead research has been conducted in the Mediterranean area and focused on the Roman Republic and the Roman Empire periods. The analysis of lead items found in both rural and urban areas [21] shows a great diversity of their origins. This diversity, visible in the isotope analysis, results from both multiple sources from which the material was acquired and from recycling. Similar conclusions were reached after the analysis of a small assemblage of Byzantine lead seals. In that case the lead not only came from different sources, but also was extensively recycled from older lead items, such as water pipes [22]. The practice of recycling lead was common not only in Antiquity, but also later, in the Middle Ages and the early modern era [23]. We may, therefore, assume that a direct link between a find of a lead item and its place of origin in a specific chronology can be made in case of traces of wholesale trade, such as large ingots of lead or elements of big investments (such as roofs of cathedrals). This is perfectly visible in the case of lead bars found in wreckages of Roman vessels. Isotope analysis quite clearly indicates their place of origin (often further confirmed by markings stamped on the bars themselves) [9, 24, 25]. Another example comes from a medieval wreckage near Ascalon – the ship transported a cargo of lead bars from Mont-Lozère in France [26]. The full potential of physical–chemical analysis of metal origins becomes visible only after the results have been compared with the archaeological and historical context. An interesting example here might be the wreckage of a Portuguese ship *Bom Jesus*, which sank near Namibia during its voyage from Lisbon to India. Its cargo included 1845 bars of copper, produced by the Fugger company. The isotope analysis showed that the copper was produced in the area of Banská Bystrica (Neusohl) in modern-day Slovakia. Interestingly, the copper contained trace amounts of lead. Further research showed that it arrived there for the process of extracting silver from copper and that it was mined from the deposits in Kraków and Silesia Upland [27].

Kraków and Silesia Upland deposits and lead trade

The growing demand for lead in Early Middle Ages was most probably connected with the metallurgy of silver. It resulted from the population and economic development of Europe since the tenth century. [28]. Growing towns and trade led to the commercialization of the economy and the monetization of markets [29]. Silver became a crucial resource. It occurred often in polymetallic deposits (accompanied by copper, lead and other elements). To obtain pure silver from ores smelters used the cupellation process. It required large quantities of lead that, in case of lack of local source, had to be imported from other places. Such a situation took place in significant mining centres like Freiberg and Kutná Hora [30]. Therefore metallurgy was the major basis for the development of a bulk trade of lead.

Traces of atmospheric lead pollution in lake sediments indicated that production of lead started to rise in the tenth century, increased until the thirteenth century, and then decreased slowly until the fourteenth century when it shrank [31]. In the first early phase the production was most probably connected with extraction of rich silver ores, containing lead [8]. Such ores occured in the Harz Mountains, where the extraction of silver started in the tenth century [32], in Schwarzwald (tenth century) [33], Siegerland (eleventh century) [34], the Ore Mountains (Germany) where Freiberg started to exist in the end of twelfth century [35] or Bohemian Moravian Highlands from the thirteenth century [36], not to mention the large-scale mining in Upper Hungary (Banská Štiavnica) [37]. Lead from such mining regions was used firstly on spot to extract silver and after it was de-silverised it could be sold on a local market [8]. The scale of such production is hard to establish due to the concentration of miners on silver extraction and not by-products like base metals. Nevertheless, the demand for lead in Europe grew further. In England, growing production of silver led to the emergence of completely lead-oriented mining [8]. In Central Europe lead market was dominated by products of mines in the Harz (especially Rammelsberg), where after the decrease of silver production mines started to be profitable again thanks to lead production [32]. It was exported to Upper and Lower Germany as well as the Netherlands [38]. Additionally, larger amounts of lead were produced by the centres in Bohemia like Oloví and Stříbro [39].

Our main point of interest is lead acquired in the Middle Ages and modern era from deposits in Silesia Upland and western Lesser Poland [40, 41]. The primary ore used in those areas was galena (PbS), which contained up to 70% of pure lead. The remaining part consisted of other minerals, such as argentite (silver sulfide – Ag_2S) and zinc sulfides. They can be found in in limestone and dolomite rocks, in an area of roughly 2500 km^2 (Fig. 1); [42–44].

Extraction of lead (Pb) and silver (Ag) from the deposits in Kraków and Silesia Upland began, at the latest, in the twelfth century as it is indicated by the chronology of several archaeological sites connected with lead ore smelting discovered in that area [14]. Large-scale production of lead developed in the thirteenth century and formed the basis of the economy of several towns in late Middle Ages and early modern period, like Olkusz, Chrzanów, Sławków and Tarnowskie Góry [41, 44, 45]. Written records concerning trade show that lead from the discussed area was mainly sold in Central and Eastern Europe. In the Middle Ages, "Polish" lead was mostly exported abroad, with the number of domestic bulk buyers increasing in the modern period. The main markets were located in Upper Hungary (modern day Slovakia), Bohemia and in metallurgy centres in Germany. All those places required lead for refining silver and gold ores. Apart from that, some amounts of lead were also transported to Gdańsk and from there probably shipped to Flanders [11].

Kraków merchants played a prominent role in the medieval lead trade. They were strongly involved in the organization of mining as well as lead bulk trade with Hungary. It is hard to establish when Kraków started to be a centre of lead trade, but the fact that it is only 40 km from the mining town of Olkusz as well as that the deposits were under the mining monopoly of Kraków's dukes suggests that it had started very early. In the case of Wrocław it is possible that lead was going through the town since the twelfth century and for sure in the thirteenth and fourteenth century [46].

Materials and methods

The primary material for the analysis are heavyweight ingots of lead found during excavations in southern Poland. So far we knew that such ingots, described as *prustrum, pecia, unum bancum, Stück*, were the main objects of wholesale trade [40]. Their shape is hemispherical, resembling the bowl-shaped mould in which lead solidified after being poured out of the furnace. Sometimes small wedges of lead were chipped off from the edge of the ingot to correct its weight. The recesses left after chipping were helpful in handling the ingots which weighed several hundreds of kilograms. The first discoveries of such lead ingots in Silesia Upland which are known to us come from 1786. Efraim L.G. Abt, a Prussian mining counsellor [47] described them as coming from Bytom and Gliwice and added a drawing to his report (Fig. 2). That material is no longer available for further research.

We do have, however, complete information on the piece found next to the Great Scales on the Main Market in Kraków during the archaeological works conducted in 2005–2006 (Fig. 3). The Kraków find has a diameter of 81–88.7 cm and its thickness reaches 19 cm. Its total

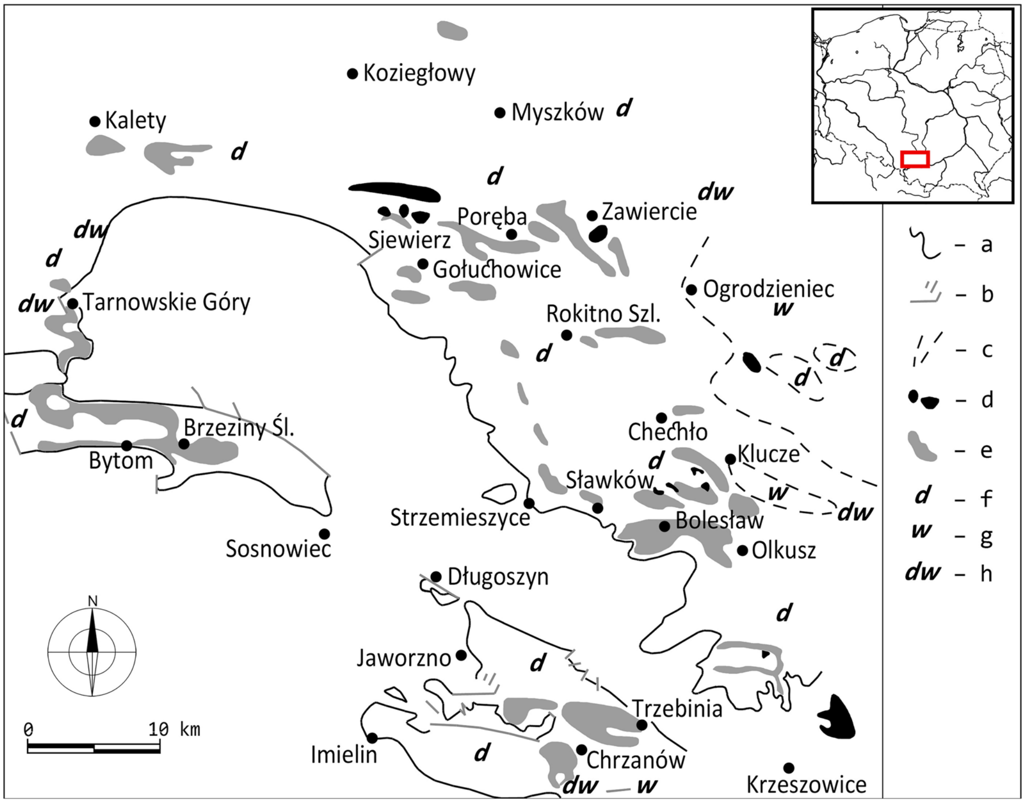

Fig. 1 Schematic map of Kraków and Silesia Upland Lead–Zinc deposits: **a** erosional edge; **b-** fault; **c-** the boundary between dolomites, calcareous dolomites and dolomitized limestones; **d-** Devonian formations; **e-** Zn-Pb-Ag mineralization; **f-** dolomites; **g-** limestones; **h-** calcareous dolomites. *Reprinted from* [44]: Fig. 7, p. 24, 2014, *with permission from Dariusz Rozmus (Copyright)*

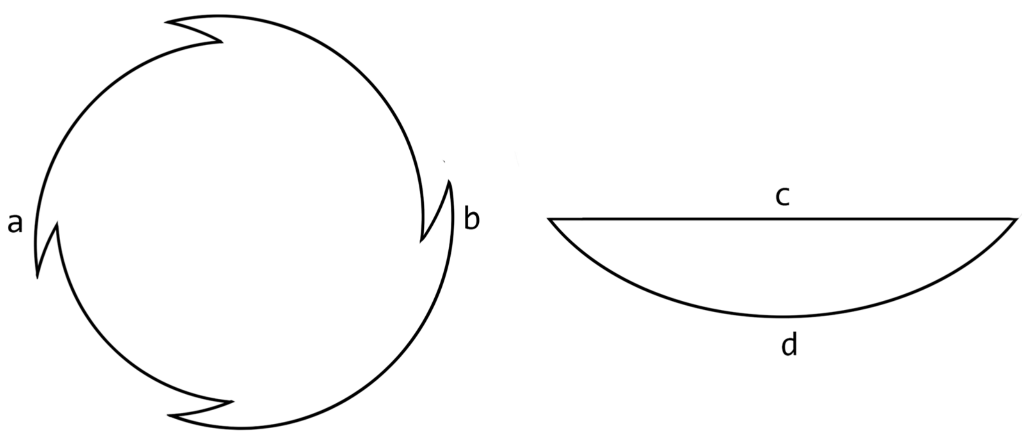

Fig. 2 Drawing of a lead ingot found in 1786. The dimension (from **a** to **b**) is 3 Rhine feet, that is 84 cm (according to Wrocław's linear measure from eighteenth century) or 93 cm (according to Prusian linear measure dated on the beginning of nineteenth century); the thickness from **c** to **d** is 8 inches that is 20 cm. *Reprinted from* 40: Fig. 1, p. 17 *with permission from Wydawnictwo Polskiej Akademii Nauk*

weight is 693 kg [48]. Markings stamped on its upper part allow us to link it with the royal mine in Olkusz and date to the reign of king Ladislaus I the Short (1320–1333). Chemical analysis of the ingot showed that it is made of almost pure lead (99.96% Pb), with small additions of iron (Fe), silver (Ag) and zinc (Zn) [48–50].

A new discovery is an ingot of lead from 4, St. Catherine Street in Wrocław, dated generally to the 1st half

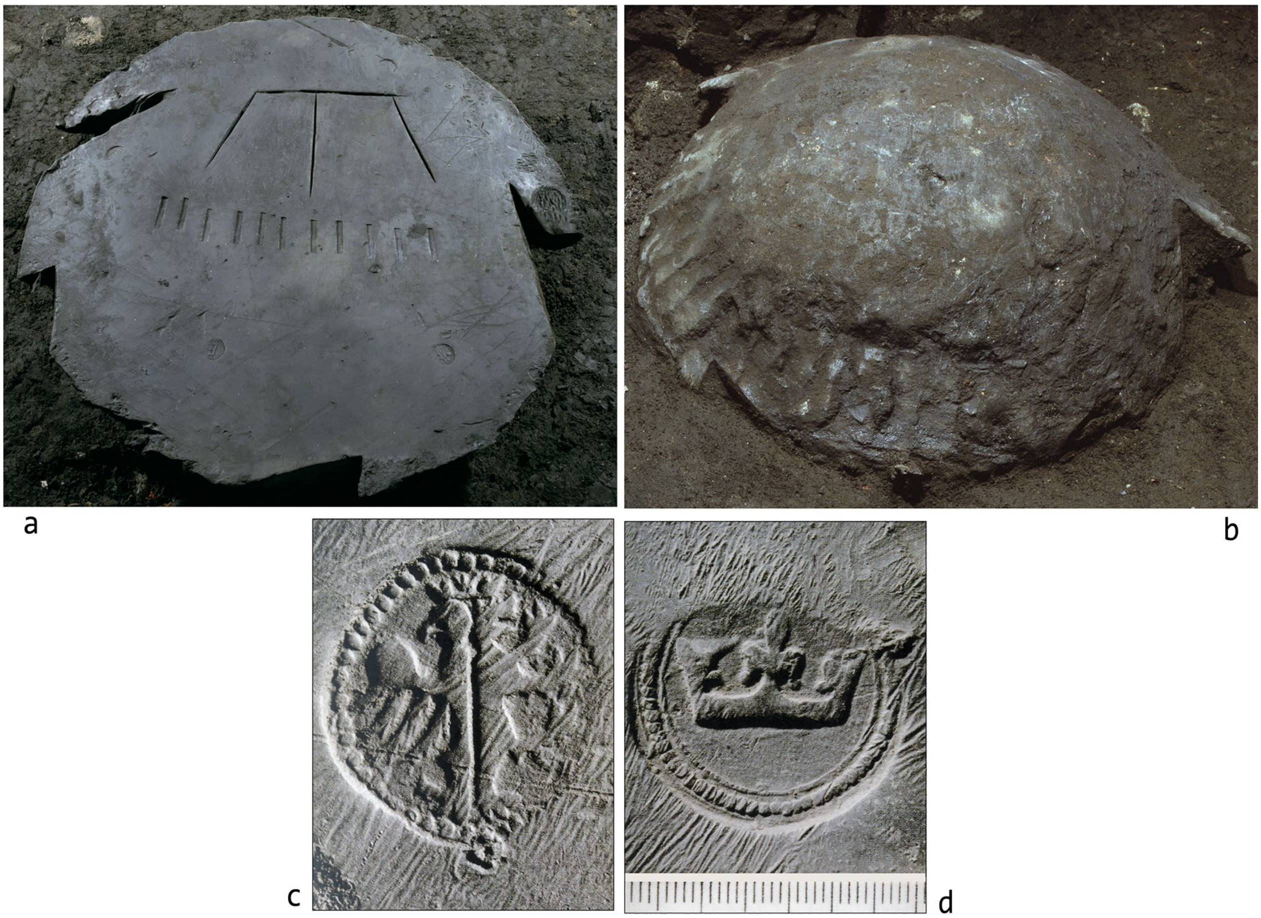

Fig. 3 Kraków, lead ingot found near the Great Scales in the Main Market Square (dimensions: 88.7 × 81 cm, thickness up to 19 cm, weight 693 kg); Pic. by T. Kalarus. *Reprinted from* [48]: Fig. 3. p. 35, *with permission from* Muzeum Historyczne Miasta Krakowa

of the thirteenth century (Fig. 4a); [51]. The ingot measuring 60 × 65 × 11.5 cm (Fig. 4b, c), was subjected to archaeometric analysis in order to precisely determine its composition. The artifact was created in the process of reduction of lead ore and is loaf-shaped—its upper part is flat whereas the lower part is curved and resembles the shape of the mould in which the reduced, liquid metal settled. The find was firstly documented, which allowed for identifying the stamped markings located on the bottom part and presented in Fig. 4d, e. The markings were repeatedly placed with at least three different tools and their true function is difficult to determine. We can, however, surely rule out the presence of any third objects in the casting basin. The markings were clearly punched, in one case at least three times with the same tool. They consist of combinations of empty circles, lines and triangles and bear no legible symbolic meaning. They were probably made with a metal (iron?) punch and might have had some coded information on the weight. Unfortunately, they have no analogies. The surface of the flat part is contaminated with bits of soil and corrosion, mainly white-coloured, with individual orange-brown deposits and traces of charcoal. The ingot was weighed with Radwag WTC/4 3000C10 technical scales and its mass is 215 kg.

A small fragment of the ingot (ca. 1 × 0.5 × 0.5 cm) was extracted with a scalpel and then prepared for microscopic observation by grinding and polishing with different materials. Firstly, 320-grit silicon carbide paper was used [52–54]. Further polishing was achieved by using MD-Largo, MD-Dac and MD-Chem shields with DiaPro Allegro, Largo and Dac diamond liquids, and finally OP-S colloid. The microscopic analysis of the sample was carried out with a Nikon metallographic microscope and a Hitachi TM 4000plus scanning electron microscope, coupled with an EDS spectrometer (SEM–EDS). The sample was observed with detectors of secondary electrons and backscattered electrons. After the initial observation, the sample was treated with a mixture of nitric acid (139 ml

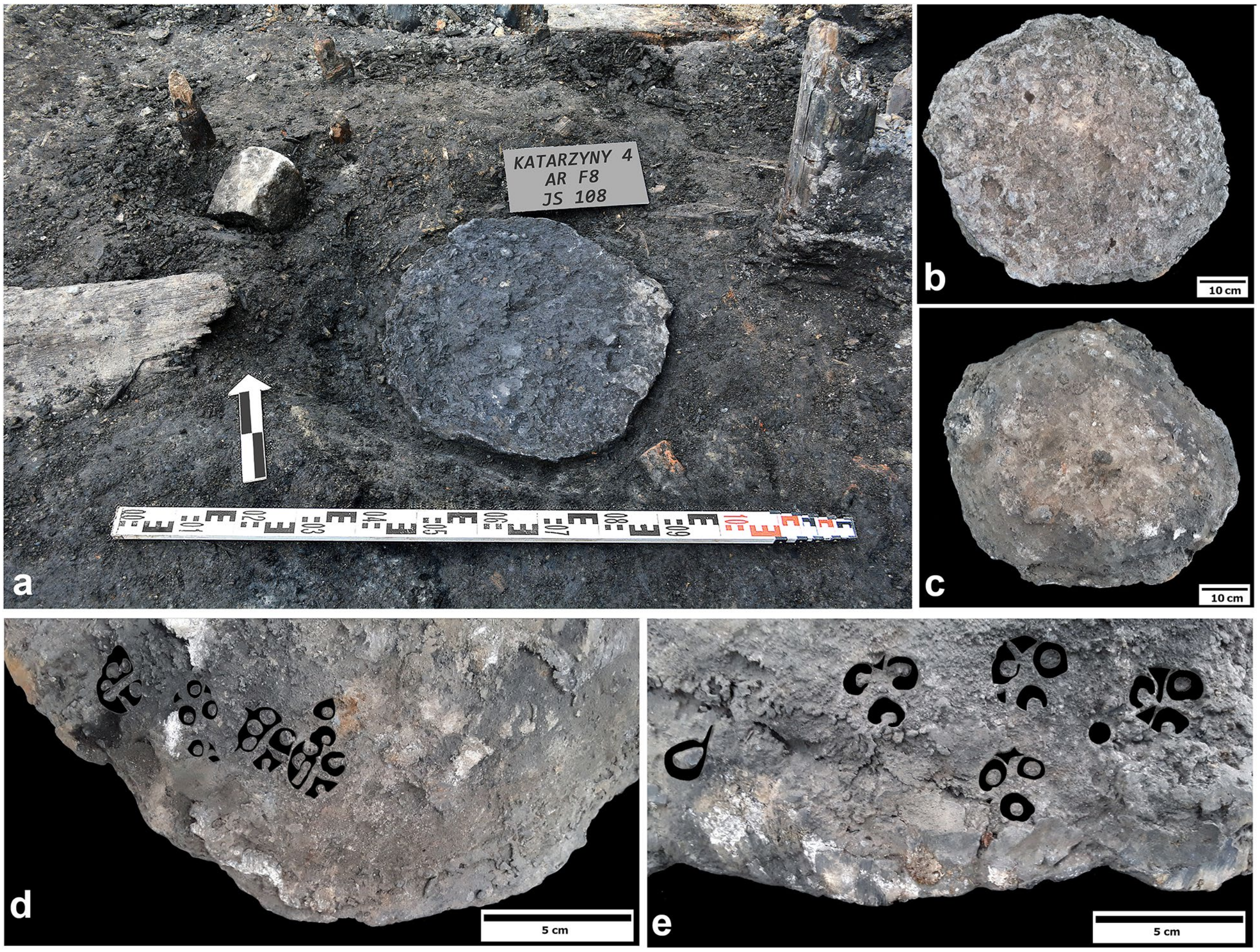

Fig. 4 Wrocław, 4 St. Catherine St.. Lead ingot in situ (**a**) and extracted from the ground (**b**- topside view, **c**- bottom view). Markings stamped on the bottom side of the ingot (**d**, **e**)

HNO_3 and 100 ml H_2O) and OP-S colloidal silica and then further analysed.

Thanks to the coupling of the SEM with an EDS spectrometer an elementary analysis of the sample was conducted parallel to the microscopic observation. Semi-quantitative analysis of the composition of the lead sample was conducted using an EDS AztecOne detector (Oxford Instruments) in the conditions of a low vacuum and 15 kV as accelerating voltage and resolution of 137 eV for K Mn_{α}. The second semi-quantitative analysis was conducted with an energy-dispersive X-ray fluorescence spectrometer (ED-XRF, Spectro Midex), constructed using an X-ray lamp with a molybdenum anode and a SDD detector, in the following measuring conditions: excitation energy 46 kV, 40 mA current, 100 eV energy resolution. Detailed elementary analysis, including the identification and indication of content of trace elements was conducted by using the method of inductively coupled plasma-optical emission spectrometry (ICP-OES), using an Agilent device, model 5110, with an option of registering the signal in the axis of the burner or side observation. The device was fitted with an Easy-fit torch one piece 5100 DV burner. As a reference material certified, multielemental patterns by Merck were used, with the initial concentration of 1000 μg/cm^3.[1] The Pb isotopic composition analyses were carried out at Geochronology and Isotope Geochemistry Laboratory, Kraków Research Centre of Institute of Geological Sciences, Polish Academy of Sciences. The analysis of the Pb ingot was conducted on a small, roughly 0.1 g sample. The fragment was cleared of surface Pb contamination with 3 N HNO_3. It was then rinsed several times in ultrapure water. The sample was then dissolved in 6 N HCl, and the lead

[1] The research was conducted by Anna Leśniewicz, PhD, from the Department of Analytical Chemistry and Chemical Metallurgy of Wrocław University of Science and Technology.

fraction was separated on ion exchange columns using Sr-spec resin (Eichrom). The purified lead was dried down and then re-dissolved in 2% HNO_3 doped with thallium. The isotope composition was measured in static mode using MC ICPMS Neptune by Thermofisher. The data quality was monitored by multiple measurements of the SRM981 standard, whose reproducibility over the course of analyses was: $^{206}Pb/^{204}Pb = 16.9418 \pm 24$, $^{207}Pb/^{204}Pb = 15.4987 \pm 31$, $^{208}Pb/^{204}Pb = 36.7220 \pm 10$ (n = 24, error is 2 standard deviations and refers to the last significant digits). The obtained ratios are accurate and in agreement with those obtained by Stos-Gale [55] whose data is used for comparison in this study. The isotope composition of the lead loaf from Wrocław was compared with the database of ores from Europe and Middle East, using the TestEuclid numerical method [55–57].

Samples of layers situated on the surface of the ingot were analysed spectroscopically in order to identify the molecular products of corrosion [58]. An infrared spectroscopic analysis (FT-IR) was conducted, using a Thermo Nicolet 380 spectrometer with a spectral range of 4000–400 cm^{-1}. 16 scans of the sample were made, using 4 cm^{-1} resolution and registering the spectral image in the absorbance mode. The results were interpreted with available spectral libraries, e.g. HR Inorganic. The final phase identification of the corrosion sample was conducted via X-ray diffraction (XRD) on a MiniFlex 600 diffractometer (Rigaku) with a CuK_α 1.5 kW X-ray lamp and a 600 W generator working under the conditions of 40 kV voltage and 15 mA of cathode current. The analysis was conducted in the diffraction angle range of 3–140° 2θ, using a detector allowing for 2D measurements. The interpretation of diffractograms was conducted using Smart Lab Studio II software and ICDD PDF-4 + 2020 database.

Results and discussion

The sample from the Wrocław ingot was subject to a two-track analysis. Apart from the spectroscopic analysis, whose purpose was to determine the chemical composition of the find, a parallel microscopic analysis was carried out to better recognise the artifact on the structural level. During the microscopic analysis high softness of lead had to be taken into consideration, as it heavily impedes the preparation of a microscope slide [52].

Determining the elemental composition of the ingot began with an analysis using X-ray fluorescence spectrometry, which is a common archaeometric practice [59, 60]. Point XRF analysis of the metal content showed that the main component was lead, constituting 99.2% Pb and the content of other metallic elements do not exceed 0.1% of the total weight respectively. The results of the ICP-OES analysis showed that apart from lead (99.98% Pb) the ingot also contains tin (0.154% Sn) and trace amounts of other metallic elements (Table 1). This chemical composition is slightly different from the one of the loaf found in Kraków [48, 49], especially in case of tin (Sn), iron (Fe), copper (Cu), zinc (Zn) and arsenic (As). Garbacz-Klempka with the team found out that apart from lead (99.96% Pb), there was also iron (0.016% Fe), silver (0.0103% Ag), antimony (0.0052% Sb), copper (0.0022% Cu), bismuth (0.002% Bi), zinc and nickel (0.0009% Zn and Ni), cadmium and tin (0.0001% Cd and Sn) and arsenic (0.0004% As). The levels of silver (Ag) and nickel (Ni) might be considered as approximate, although the resemblance is not high [48, 49]. Therefore, to decisively confirm or reject the common origin of both ingots, an isotopic analysis of lead was conducted and the results for the Wrocław find were compared with the database of ores from Europe and Middle East. The comparison showed that the results are fully compliant with the isotope characteristics of lead–zinc ores found in Olkusz deposits (Waryński mine, Matylda mine, etc.). Moreover, the ratios of isotopes in the sample are identical with the results of measurements of the lead ingot found in the Main Market Square in Kraków [50]. Table 2 presents the isotope ratios which present this complete resemblance (the lead ore ratios are exemplary, as the comparison was made for 46 ore samples from that region). Figure 5a, b present the comparison of the isotopic composition of the Wrocław find with the lead ores from Olkusz [61]. Lead ores from the Harz have similar isotope characteristics and data on them is also presented in the charts [62, 63]. However, numerical comparisons clearly indicate that the ores from Olkusz are isotopically identical with the samples taken from the lead ingots found in Wrocław and Kraków.

We assume that lead circulating in Silesia and Lesser Poland might also have originated from other parts of Central and East Central Europe. To further prove the origins of Wrocław ingot we compared the obtained results with the published data from mining districts known for lead production: Lower Silesia, the Ore Mountains, Bohemia, Moravia, Harz. Novak et al. [64] studied several Ag and Pb deposits in the Czech Republic, south eastern Germany and southern Poland. The determined Pb isotopic ratios are various, but on the based of this data we can excluded Freiberg (Germany), Kutná Hora, Horní Benešov, Jáchymov, Příbram, Ratibořské Hory, Jihlava, Rudolfov, Stříbro as a source of the lead ore used to produce the ingot found in Wrocław. Some of those sites can be excluded because mining started there after the thirteenth century: Jáchymov, Příbram and Rudolfov in the sixteenth century, Ratibořské Hory in the fourteenth century [39]. The oldest one is Stříbro which

Table 1 Concentration of elements in an ingot sample, presented as % of mass and ppm (with standard deviation, SD)

Chemical composition of ingot														
% mass, SD		ppm, SD												
Pb	**Sn**	**Ag**	**Sb**	**Al**	**Ni**	**Cd**	**Fe**	**Zn**	**Mn**	**Hg**	**Cr**	**As**	**Cu**	**Bi**
99.98	**0.15**	**84.22**	**21.10**	**8.01**	**7.71**	**3.88**	**3.26**	**2.88**	**1.29**	**0.45**	**0.15**	**0.13**	**0.01**	**< 0.003**
0.28	0.02	7.16	1.47	0.57	0.72	0.43	0.24	0.44	0.16	0.06	0.05	0.003	0.007	

Bold values are the determined value (%mass or ppm)

Table 2 Lead isotopic composition of the ingot from Wrocław and lead/zinc ore from the mine in Trzebinia and the lead ingot with the stamp of the Olkusz mine analysed by MC-ICP-MS and TIMS. For MC-ICP-MS errors are 2 SD (standard deviation) propagated for standard reproducibility and refer to the last significant digits. TIMS data were published previously [50] and have the analytical errors better than ± 0.1% for each independent ratio

MC-ICP-MS					
Lead, ingot, Wrocław	$^{208}Pb/^{206}Pb$	$^{207}Pb/^{206}Pb$	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$
	2.08576 ± 26	0.84807 ± 12	18.4200 ± 25	15.6215 ± 32	38.420 ± 21
TIMS					
T1—galenite-sphalerite from Trzebinia mine	$^{208}Pb/^{206}Pb$	$^{207}Pb/^{206}Pb$	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$
	2.08526	0.84765	18.4245	15.618	38.420
W1 Lead ingot with a seal of Olkusz	2.08544	0.84838	18.4177	15.625	38.409

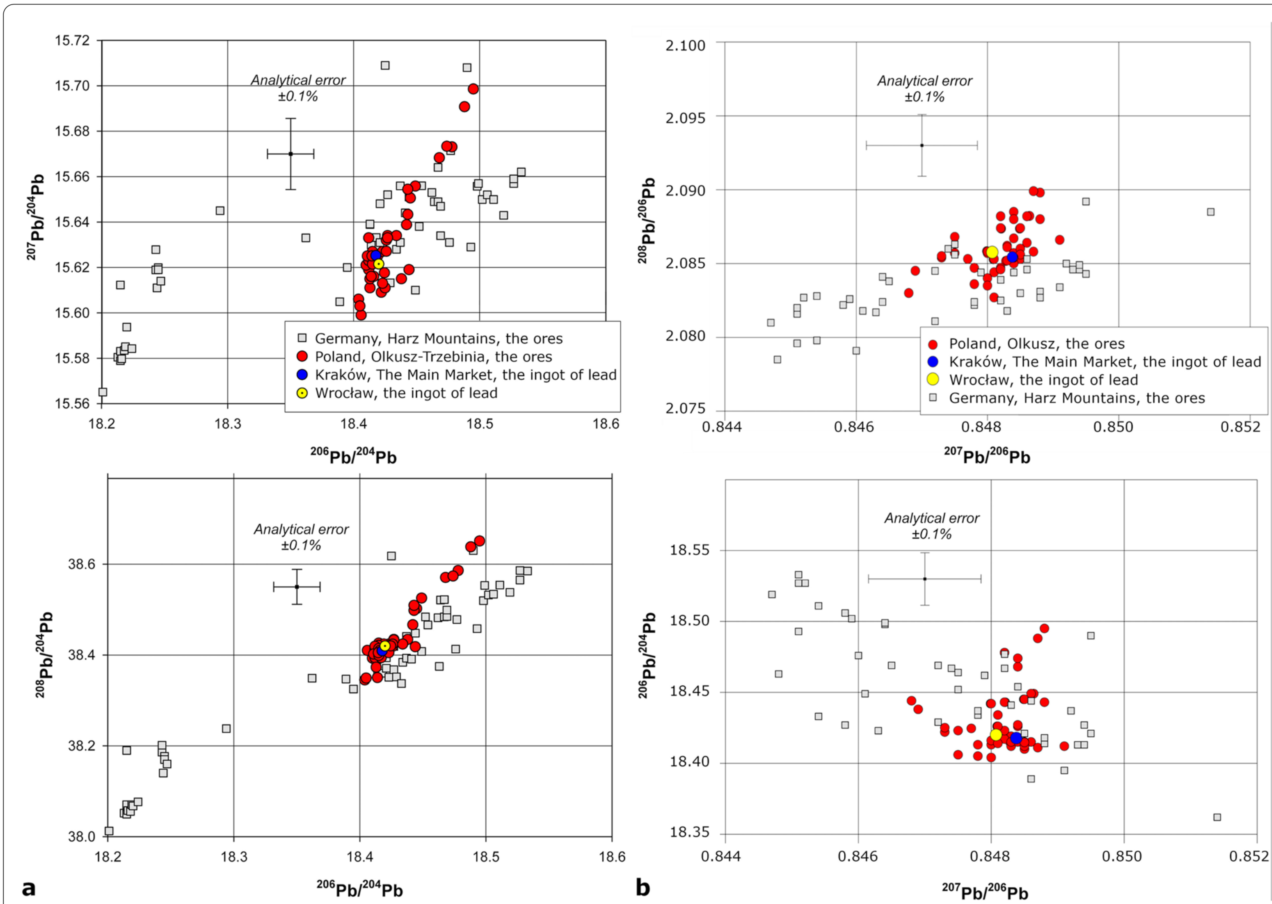

Fig. 5 Comparison of lead isotope ratios: **a-** $^{207}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$; $^{208}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ and **b-** $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$; $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{206}Pb$ for ingots from Wrocław, Kraków, ores from Olkusz mines and from the Harz. By Z. Stos-Gale

started production at the end of the twelfth century [39]. Mining of silver ores containing lead started in Freiberg also in the twelfth century [35]), nevertheless the production was not sufficient and Freiberg had to import lead [30]. Mining in Jihlava started in the thirteenth century [36], but also there lead had to be imported [13]. Kutná Hora, one of the most prominent producers of silver, started mining during the thirteenth century [65], and similarly to the already-mentioned regions needed a lot of lead for refining silver [66]. Thanks to the results of Ettler et al. studies [67] we can also compare the data from Olkusz (Poland) with those from Bohemia or Germany and also the slightly more remote regions like Austria or Slovakia. With this data it is possible to identify

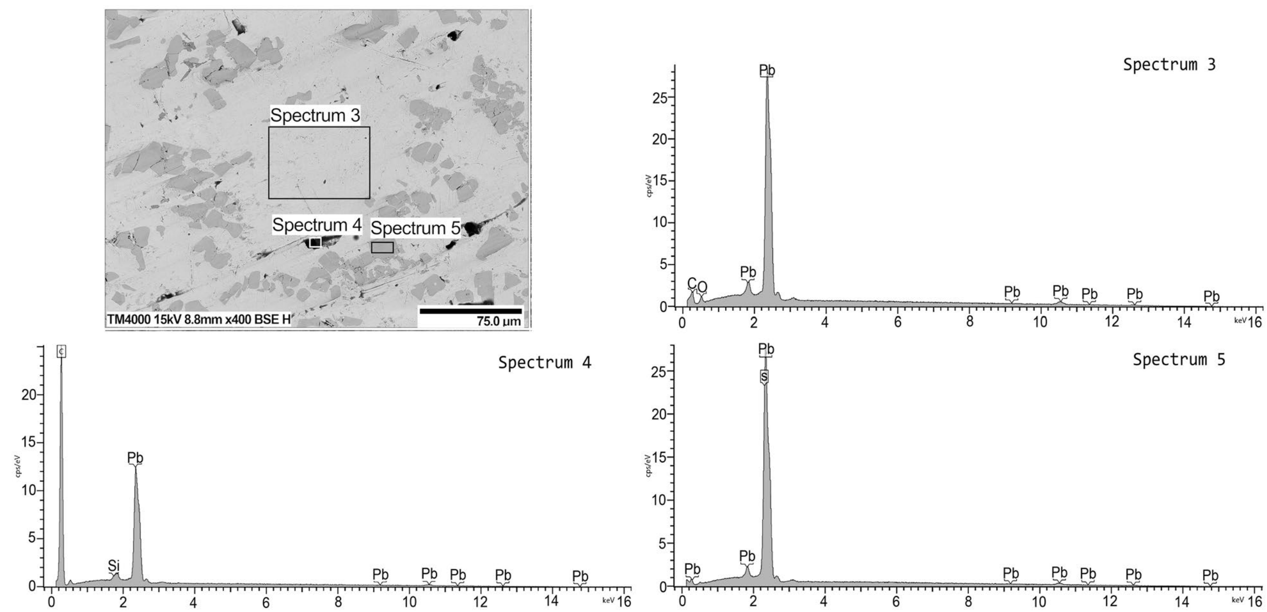

Fig. 6 SEM image and results of EDS spectral analysis of selected areas on the ingot's surface

metal provenance and confirm that the lead ingot found in Wrocław was made of Pb–Zn ores from Poland. Thus Slovakia (e.g. Gemeric unit or Slovakian neovolcanites), Germany (e.g. Oberlausitz or eastern Erzgebirge) were excluded as a potential source of raw-materials for the Wrocław find. Mining in Gemeric unit – in Middle Ages part of Hungary, started in towns like Smolnik or Gelnica in thirteenth and fourteenth century and was highly concentrated on copper [68]. Like other mining districts in Slovakia we can assume that it needed to import lead, as it happened in later periods [69]. Tyszka et al. [70], determined Pb ratio in various samples: ores, slags, fly ashes and coals. Few Cu ores were examined from Lower Silesia (two samples of bornite, one sample of chalcopyrite/marcasite) and one from Upper Silesia (galena from Trzebinia). The results show that the isotopic composition of the ores from Lower Silesia have the following $^{208}Pb/^{206}Pb$ ratios: 2.111 (sample KGHM1-bornite from Legnica), 2.081 (sample KGHM2- bornite from Legnica) and 2.083 (marcasite/chalcopyrite from Miedzianka). The authors studied also galena from Trzebinia- $^{208}Pb/^{206}Pb$ ratio is 2.089, which overlaps with our results of the ingot from Wrocław: $^{208}Pb/^{206}Pb$ is 2.08576.The authors [70] mentioned that in their studies the Pb–Zn ore samples from Upper Silesia have similar data to the Cu ore from Lower Silesia. The same situation is for coal samples. Due to the fact, that these deposits were not used in the first half of the thirteenth century we can exclude them.

The conclusions regarding the elemental composition were also confirmed by the microscopic observation of the find. The analysis of unetched surface of the ingot sample with a metallographic microscope resulted with an observation of a metallic network as the dominating structure. Moreover, places with visible metal discontinuity and non-metallic structures were also observed. Further observation, conducted in a larger magnification and with a scanning electron microscope (Fig. 6), showed that within the metallic phase are located agglomerations and individual platelets/grains,[2] as well as voids/pores within the metallic structure, so-called shrinkage porosities. In order to better recognise the presence of grains/platelets, an EDS spectrometer was used which further confirmed their different chemical composition. In the metallic phase the strongest signals come from lead, which constitutes the vast majority. Apart from it, carbon and oxygen were also recognised (Fig. 6, spectrum 3). Outside the regular metallic structure lead was identified as well, but also large amounts of carbon and silicon, which may also come from lubricants used in polishing the sample (Fig. 6, spectrum 4). The last analysed areas were the platelets (grains) suspended in the metallic phase. Their semi-quantitative elementary analysis, presented as spectrum 5 (Fig. 6), showed 88% Pb and 12% S, which after calculation into atomic fraction tells us the grains contain almost equal masses of lead and sulphur. This leads to a hypothesis of presence of lead sulfide (PbS—galena),

[2] Platelets are visible as flat objects through a BSE detector, but become grain-like when an SE detector is used, which better shows the sample's topography.

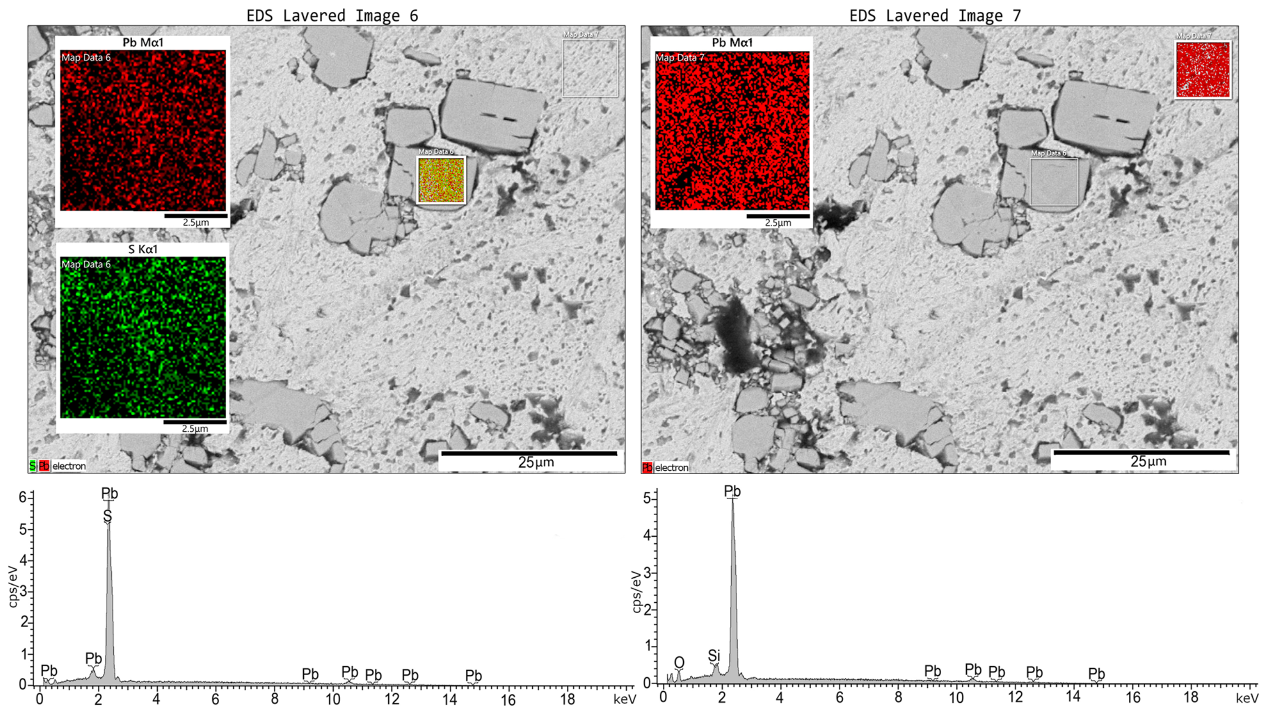

Fig. 7 SEM images (mag. 1500×), maps and EDS spectra of a lead ingot after etching

which can probably be identified as unreduced lead ore. The presence of galena in the lead loaf sample were confirmed in the finds from the site in Stare Bukowno studied by Karbowniczek et al. [71].

Further archaeometric analysis was conducted on a sample which was simultaneously polished and etched in order to more clearly expose the light-grey grains set in metallic structure. Their elementary analysis, conducted as a map of elementary layout, showed that those grains contained exclusively lead and sulphur, as visible in Fig. 7. The remaining analysed fragments of the ingot had similar elementary composition to that determined prior to etching (with a slightly larger content of silicone noted occasionally, due to silicate dispersion used during sample etching).

Aside from the analysis of the metallic structure, an archaeometric study connected with the recognition of the state of the preservation as well as the confirmation of the archaeological context of the ingot found in Wrocław was also conducted. A macroscopic analysis of the uncleaned surface showed, apart from charcoal bits, the presence of multicoloured deposits which were then analysed separately. The most commonly occurring white residue was recognised as carbonate products resulting from calcium and lead corrosion: calcite ($CaCO_3$), cerussite ($PbCO_3$) and hydrocerussite ($Pb_3(CO_3)_2(OH)_2$), as indicated by the O-H stretching vibrations located at 3421 cm^{-1}, as well as a series of vibrations of a carbonate group: a strong 1419 cm^{-1}, responsible for asymmetric C-O stretching vibrations, symmetric C-O stretching vibrations within 1053 cm^{-1} or out-of-plane bending vibrations (873 cm^{-1}) and in-plane bending vibrations (a sharp band at 682 cm^{-1}). The vibrations stretching the lead-oxygen bonds near 405 cm^{-1} were also unmissable [58]. The sample also contained trace amounts of organic substances. An X-ray diffraction of the sample confirmed the initial identification of the components from the white sample as hydrocerussite, calcite and silica, SiO_2 (Fig. 8).

There were only a few brown and blue coloured deposits on the surface. The latter ones were identified by FT-IR and XRD as iron phosphate, mainly vivianite($Fe^{2+}{}_3(PO_4)_2 \cdot 8H_2O$). The sample also featured another type of iron phosphate—blue-grey strengite ($FePO_4 \cdot 2H_2O$)—and calcite. Orange-brown deposits from the surface turned out to be a mixture of silica and aluminosilicates, such as muscovite ($KAl_2(AlSi_3O_{10})(OH)_2$) and pegmatite. The presence of those substances clearly indicates that the ingot was contaminated by mineral compounds present in the soil during its deposition underground. Our research confirmed that the ingot is slightly corroded and has typical oxidation products- lead compounds (cerussite and hydrocerussite), aluminosilicates, silica and calcite as

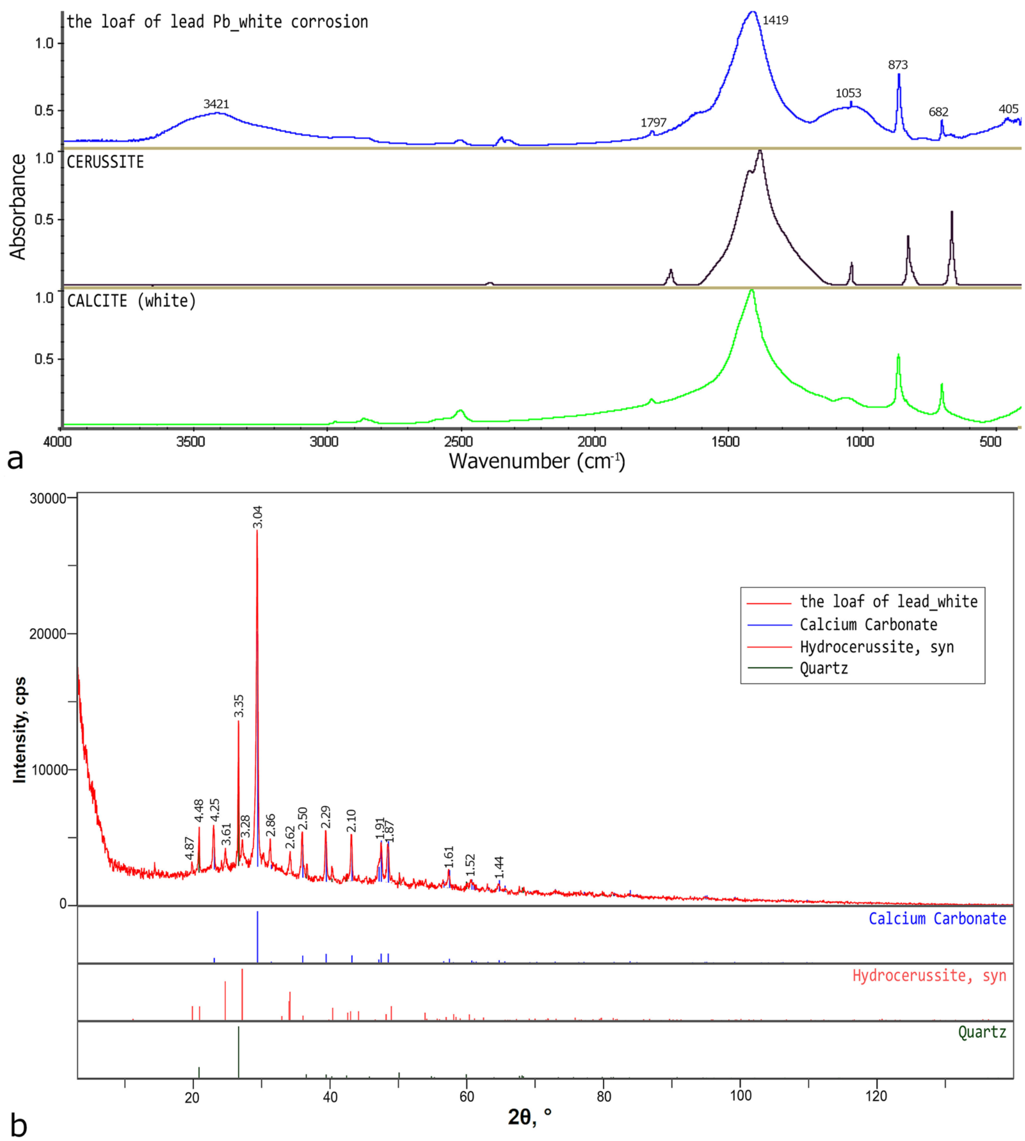

Fig. 8 FTIR spectrum (**a**) and XRD diffractogram (**b**) of a white corrosion sample. Numbers indicate peak position (**a**) and d-values in Å (**b**)

well as iron compounds (e.g. vivianite), which are present in the urban soil.

The analyses of Pb isotopes of lead objects indicated that the "Polish" lead was used in quite distant places in the Early Middle Ages. A pectoral cross (№ 482/394) found on site Gniezdowo 2 in Suzdal Region (Kievan Rus), and dated to the tenth–thirteenth century, was identified as made of Olkusz's lead (isotopic composition was similar to ingot from Wrocław) [72]. Analysis of slags from Prague Na Stupi, dated to the twelfth century indicated usage of "Polish" lead in silver refining [67]. These two examples present a final destination of lead, not the exact trade connection. Lead obtained from ores could be de-silverised on spot, or transported to another mining centre, where after refining of silver it could be traded on the local market. In this context the ingot from Wrocław, as well as from Kraków, can be seen as direct evidence of trade. In the first place, archaeometric analysis clearly states that the ingot containing pure lead originated from the Olkusz region. Its presence in the thierteenth century context in Wrocław proved a view of lead trade in that period established based on written records [11]. The ingot is much smaller than the one from Kraków, and not stamped. Its smaller size and deposition on a plot near New Market may suggest that it was a bulk product meant for the local market, to supply many local crafts using lead in their work.

One can claim that Wrocław ingot proved a known fact that lead was transported from Olkusz district. Such tautology is a typical accusation in historical archaeology [73]. Nevertheless, it gives us new solid data for further comparative analysis of lead origins. Since the isotopic analyses in East-Central Europe, and especially in Poland, are still developing, the ingot shows us the potential and need for further studies of lead trade.

Conclusions

Two ingots of lead described above—from Wrocław, 4 St. Catherine Street and from the Main Market Square in Kraków—were helpful in achieving the goal described at the beginning of the article. The dating of both finds suggests that they were created within a span of roughly 100 years.

Non-destructive and relatively less-invasive archaeometric analysis of the lead ingot from Wrocław revealed its chemical and structural composition. Three different methods of chemical analysis confirmed that the main component is lead, which constitutes over 99% Pb of the whole mass. A few other elements were recognised in a significantly smaller amount: tin (0.15% Sn), silver (0.008% Ag). Other elements are present in a roughly 100-times smaller amount and are typical trace elements with concentration equal to a ppm or its fraction. The results were compared- but not the same- with the study of the lead ingot from Cracow. However done isotopic analysis clearly revealed the shared origin of both ingots in the mines around Olkusz. Comparing the contents of both ingots shows differences in concentration of particular elements, which can also be explained by the heterogeneity of both artifacts and the minimal amount sampled for invasive analysis. Moreover, through the analysis post-production residue was identified, such as shrinkage porosity, non-metallic inclusions and grains with recognised equal weight amounts of lead and sulphur, which may suggest leftovers of unreduced lead ore (galena, PbS). Aside from that, the analysis of the ingot's surface yielded information on foreign substance residues, stuck to the surface during the time the ingot spent buried underground. Those include mineral substances, mainly silica (SiO_2) and calcite ($CaCO_3$), as well as oxidised metals such as iron (Fe).

The research allowed for determining the properties of lead (Pb) extracted in the Middle Ages from the deposits in Silesia and Lesser Poland, especially from the mines around Olkusz. The composition of both ingots, created within a period of roughly 100 years, is almost identical. The results open a perspective for further research of the range of wholesale trade and used of lead in twelfth-fourteenth century Central Europe and beyond. The opportunities to analyse those issues, earlier limited by the written sources available only from the fifteenth century onwards, were significantly broadened.

Abbreviations

XRD: X-ray diffraction; ED-XRF: Energy-dispersive X-ray fluorescence spectrometry; FT-IR: Fourier transform infrared spectroscopy; SEM–EDS: Scanning electron microscope, coupled with an energy-dispersive spectrometer; ICP-OES: Inductively coupled plasma-optical emission spectrometry; SDD: Silicon drift detector; MC ICP-MS: Multicollector inductively coupled plasma mass spectrometry.

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Author contributions

BM—conceptualization, methodology, formal analysis and interpretation of XRF, FT-IR, XRD, SEM–EDS, microscope pictures data and interpretation of the ICP-OES results; writing of the original draft, PD—analysis and interpretation archaeological context of examined lead deposit from Wrocław, writing of the original draft. PC—establishing a historical and archaeological context of lead trade in Europe, and contribution to the writing of a whole paper. MM—investigation of the Pb isotopic composition. JP—conceptualization, methodology, development of article structure, research questions and historical conclusions, writing of the original draft. All authors read and approved the final manuscript.

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Availability of data and materials

The datasets used and/or analyzed during the current study are available from the authors on reasonable request.

Declarations

Competing interests

The authors declare no competing interests.

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