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HISTORICAL METALLURGICAL ACTIVITIES AND ENVIRONMENT POLLUTION AT THE SUBSTRATUM LEVEL OF THE MAIN MARKET SQUARE IN KRAKOW

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Abstract: The main purpose of the interdisciplinary research described in the present paper is to determine the characteristics of ground environment changes in the Main Market Square area, and to compare these with analyses of metal artefacts. The elemental composition of metal artefacts and the degree of contamination of archaeological layers make it possible to consider both as specific indicators, including being geoindicators that are helpful in establishing the chronology of layers. Metal-artefact samples come from archaeological layers originating from different parts of the Great Weigh House. Layers were sampled, both in this region and also in a neighbouring area at the entrance to Bracka Street — trench A. They were collected from an area of archaeological excavations, which were carried out in the years 2005–2010, reaching down to a depth of 4 meters. All artefacts come primarily from cultural layers and structures - probably linked to workshops in the early medieval settlement which functioned in the area of the Main Market Square in the 12th and early 13th century. However, archaeological analysis of historical material allowed us to more precisely date metal artefacts to the turn of the fourteenth and fifteenth centuries, which was confirmed by analysis of the radiocarbon age of a sample from Room R of the Great Scales, from layer 109. Average concentrations (mg/kg) of Pb of 128454 and Cu of 108610 were determined in this sample to the AAS, which significantly exceeded of the most concentration values characteristic of the layers from the Great Weigh House.

Keywords: Krakow, archaeological layers, metallurgical artefacts, historical contamination, lead and copper.

1. INTRODUCTION

Historical metallurgical activities in Krakow

Within the borders of present-day Poland, the first metal artefacts appeared in the middle Neolithic period (*ca.* 4000 BC) (Gedl, 1982). There are also clear traces of copper smelting and casting, parts of clay crucibles, tuyere fragments and copper objects from this period. Smelted copper was hammered into bars, bands and wires, which were then used for the production of adornments and, more rarely, tools. The oldest artefacts were made from 99% pure copper, with traces of antimony, iron, lead and silver.

The first bronze objects appeared in the vicinity of Krakow as imports from the West between 1800–1600

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BC. Bronze smelting skills were learnt from trans-Carpathian contacts with the Mierzanowice culture, which led to bronze production becoming more common about 1300 BC (Górski, 2012). The average copper content in bronze objects from that time found within one of the studied sites is 88%, while tin accounts for 11%; the remaining part is made up of antimony, arsenic, silver, lead and other tramp elements (impurities) resulting from metallurgical processes.

The Iron Age started about 650 BC on the territory of present-day Poland (Gedl, 1982). Metal processing at that time consisted of bronze working, which was already at a specialized level, and also the first attempts at making and working the new metal — iron. Bronze continued to be made from imported copper and tin.

Celts settling in the area of present-day Nowa Huta towards the end of the 4th and the beginning of the 3rd century BC precipitated a breakthrough in the field of smelting and working metals, since they had knowledge of the smelting of both non-ferrous metals and iron, and of metallurgy and casting of bronze, silver and gold using imported materials. An example of a Celtic bronze artefact, a torque, was cast from leaded tin bronze (Cu 79%, Sn 12%) with a significant addition of lead (Pb 6%), which was added intentionally as a technological component. An addition of silver is also characteristic (Ag 1.5%), having either prestigious or symbolic significance.

In the first centuries of the Common Era (1–400), the settlement area in the Krakow-Miechów-Proszowice triangle came under the influence of the Roman Empire. In the loess areas near Krakow, there are traces of smelting activities dating from that period. The presence of iron smelteries and smithies in the Krakow area leads us to believe that a range of metal objects from the Roman period comes mostly from local production. Metals and alloys were used mainly for making weapons and weapon parts, as well as for making tools.

Archaeological research on the Main Market Square conducted over many years attested to well-developed metallurgical, casting and smithy activities, whose beginnings can be traced to the 10th or the beginning of the 11th century. According to Radwański (1975), 'in the area of […] St. Wojciech's (St. Adalbert's) Church there might have existed workshops where non-ferrous metals were worked. This fact is attested to by the presence of casting crucibles with traces of silver and bronze, found in the cultural layers under the early medieval utility levels of this Church (4 items), in the furnace in the Cloth Hall, trench I and in the *ex-situ* deposit within the cemetery by the Church.' One particular crucible was made of clay and was used to melt small amounts of silver and other metals and their alloys, which is evidenced by traces of silver and bronze discovered in it and identified by spectral analysis. This is a direct proof of casting activities in the old Krakow and its surroundings. Before the mid-13th century there were already workshops in Krakow, satisfying local needs. Krakow was a major centre of production and trade. Here, amongst many other professions, were metalworkers — makers of ornaments and jewellery, everyday objects and church equipment from non-ferrous metals: goldsmiths, bell-founders, tinsmiths, coppersmiths, brass-makers and others. As concerns metal crafts, Krakow held a high position among Polish towns. In this town, with its rich economy and material and artistic culture, crafts developed quickly, especially during the Middle Ages and Renaissance (Bodnar *et al.*, 2005; Głowa and Garbacz-Klempka, 2010; Głowa *et al.*, 2010).

The current status of Krakow historical layers research and their indicative role in archaeological research

Technological, metal and chemical analyses (similar to analyses applied in modern casting and metal science) play an important role in the study of our ancestors' activities. Identifying the (historical) range of application of metals creates a basis for assessing the technical capabilities (of a given society) and — especially — for determining the origin of raw materials. Interdisciplinary research in the area of historical metallurgical activities has also been conducted with a view to understanding (historical) water supply, waste water and waste management issues, and also the supply routes of raw materials (Cembrzyński, 2011; Plaza, 2015; Piekalski, 2004; Sowina, 2009, 2016). Identification of these kinds of infrastructure makes it possible to recreate technology and other processes connected with production, *i.e.*, raw material supply, metal processing and casting, and the creation of the final product.

Research on the casting technology and metal analyses of the metallurgical artefacts from the Main Market Square were carried out in the context of the functioning of the buildings housing the Great Scales and the role of Krakow, which was known as the 'House of Copper' (Garbacz-Klempka and Rzadkosz, 2009, Garbacz-Klempka *et al.,* 2012; Garbacz-Klempka *et al.*, 2015; Rzadkosz *et al.,* 2012; Stos-Gale and Gale, 2010; Wyrozumski, 2007).

Metals show a tendency to accumulate in the environment, and above-normal concentrations of different compounds clearly point to the presence of a 'source' — for example, a manufacturing or trading site or an area susceptible to a surface run-off of contaminated waste. In the case of investigations conducted in the area of archaeological sites, the presence of high concentrations of metals points to interesting areas that are rich in cultural meaning, which may contain metallogenic objects (Monge *et al.*, 2015; Boroń, 2013; Dąbrowski and Hensel, 2005; Gaydarska and Gurova, 2008; Kafkala *et al.,* 2011; Molenda, 2001; Wardas *et al.,* 2008; Wardas-Lasoń and Lasoń, 2013; Waters, 1992). Metal accumulation within earth layers can be viewed as a special artefact, constituting a precise indicator as to how a site was used. Locating metal accumulation within the layer profile, and estimating the thickness of layers rich in metals, the degree of contamination and the elemental content — all these can be used as date markers and indicators of the development of specific crafts, or even of people's wealth, if we consider the presence of products or materials that have been imported from distant places. Both metal archaeological objects and historical layers, together with contaminants present in the ground, constitute evidence of a town's history.

Many multifaceted studies have been carried out on a significant number of slag samples and earth from historical layers from the Krakow area, which have resulted in numerous publications. They have focused on, among other things, parts of the medieval sewage system in Krakow, which to some extent acted as a protective measure against anthropogenic modification of the environment. Environmental contamination with metals in the medieval period in the area of Okół settlement, the towns of Krakow and Kazimierz, and their suburbs was compared. Environmental changes linked to manufacturing activities based on metals were investigated on the basis of material excavated from the area of Krupnicza St, demonstrating the possibility of applying geoarchaeological methodology (Buśko *et al.,* 2009; Garbacz-Klempka *et al.,* 2012; Sokołowski *et al.,* 2008; Wardas *et al.,* 2008). The greatest anomalies were discovered in the Main Market Square in Krakow. The metal enrichment index was used in researching utility levels in the area of the Rich Stalls. This could help, for example, to characterise the kinds of goods that were traded, supplementing the information obtained from historical studies of the artefacts found there. Metal concentrations in the earth of historical layers of the so-called 'Cloth Hall Cross', which is at the point of intersection of Szewska and Sienna (streets) with Św. Jana and Bracka (streets), created a basis for investigating the origin and migration paths of contamination. The presence of such high concentrations of lead and copper in Krakow layers, and especially in water sediments of medieval moats, created an opportunity to use this geoenvironmental marker to map medieval watercourses (Łyskowski and Wardas-Lasoń, 2012). An especially important aspect of the research was studying the modern consequences of environmental contamination from the past, in the context of today's geoenvironmental conditions in Krakow (Kasprzak *et al.,* 2013; Motyka *et al.,* 2012).

Historical layers of Krakow were also researched by scientists from other fields, and the results strongly point to the fact that the underground infrastructure of historical towns is an especially valuable element of cultural heritage (Buśko and Komorowski, 2007; Buśko *et al.,* 2009; Buśko and Głowa, 2010; Kmietowicz-Drathowa, 1974; Lityńska-Zając, 2005; Mueller-Bieniek, 2010; Poleski, 2013; Zaitz, 2012).

Archaeological geochemistry can be very helpful for assessing the influence of historical human activities on their, and also our, environment, and the boundaries of a contamination circle can indicate the limits of a site. Another branch of science that facilitates determination of the origin of stratification — and also the destruction or levelling off of layers — is geoarchaeology, which can indicate the role of natural processes, which are connected, for example, with the building up or eroding of strata during great floods.

2. THE AIM OF THE PRESENT RESEARCH

Archaeological research was carried out on the Main Market Square in the years 2005–2010, by the Archaeological Research Group Market Square (Schejbal-Dereń and Dereń, 2010, 2011; Szejbal-Dereń and Garbacz-Klempka, 2010), yielding new discoveries in the field of casting (new types of moulds, *etc.*). Moreover, the collection of historical objects and materials connected with ornament-making workshops was enlarged: casting crucibles, slags, raw materials and casting moulds, which constitute important sources relating directly to goldsmithing activities. Based on the analysed objects, it can be concluded that there were already workshops in the early Middle Ages, where casting techniques were used for the production of body and clothes adornments. Many artefacts were found (both imported and made locally), cast from bronze, copper, tin, lead, silver and gold. The historical artefacts found at the Main Market Square are linked to a broad spectrum of activities, amongst which the ones connected with using metals and alloys for the production of ornaments and everyday objects seem to be especially important. The group of found objects includes numerous cast rings.

These relics come primarily from cultural layers and structures — possibly workshops connected with the early medieval settlement — functioning in the area of the (present day) Main Market Square in the 12th century and the first half of the 13th century. Most of the slags, metal (copper and lead) lumps and crucible fragments were found in buildings used for economic purposes — the precise function of which was not determined — but a casting mould was discovered in the utility levels of a dwelling, dated to the first half of the 13th century.

Objects and study area

It should be emphasized that all the material analyzed during the research (*i.e.* the earth from individual layers of archaeological strata and the deposits from the place where the loaf of lead was found, coming from the trench A, as well as the deposits of the rooms of the Great Weigh House, where metal slags were present) was taken only from those areas where it was possible to clarify dating. The age and diagnosis of the layer stratigraphy was confirmed based on the analysis of historic ceramic material. (Schejbal-Dereń and Dereń, 2010, 2011). The metallic objects from the Great Weigh House have been made available for research by the Archaeological Research Team of the Main Market Square.

The Great Weigh House (GWH) was located in the south east part of the Main Market Square and it functioned as the Scales Office from about 1300 AD (Komorowski and Sudacka, 2008). It was a mortared building, with its entrance from the side of St. Wojciech's Church. The artefact samples come from archaeological layers originating from different parts of this building – GWH (**Fig. 1**). Layers were sampled, both in this region and also in the neighbouring area at the entrance to Bracka Street – trench A (**Fig. 2a–d**). The results presented in this article are based on the content analyses of metal artefacts and physicochemical earth markers from the places where the artefacts were discovered. They were collected from an area of archaeological excavations reaching down to a depth of 4 metres below the Main Market Square in Krakow.

The main purpose of the ongoing interdisciplinary research is to determine the characteristics of ground environment changes in the Main Market Square area (see **Fig. 1**), and to compare these with analyses of metal artefacts found in archaeological layers in the area near the Great Weigh House, which is the historical area where metals were used.

Samples of earth (geoartefacts) and metal artefacts were collected by the authors during archaeological work, making it possible to carry out an interdisciplinary analysis of the chemical composition of metal objects and the state of contamination of the site of exploration (**Fig. 1, 2**). Furthermore — and most importantly — the site of collection had an unequivocal archaeological context. Mini profiles of archaeological layers were collected from the sites of exploration where the artefacts were found (see **Fig. 2a–b**) (these layers were ascribed heights above the mean sea level using geodesic techniques). In other regions, where sequences of intact layers were present which were dated to the Middle Ages (which were significant for analyses of changes of the degree or spreading of contamination), profiles or a collection of samples (in the direction of run-off) were collected from the bottom to the top (see **Fig. 2c–d**). The area where the loaf of lead was found was a special place — the lead was sampled with the aim of assessing the degree of contamination of the substrate exposed to prolonged contact with the metal (see **Fig. 2**).

The present research was aimed at determining the degree and nature of the influence of human metallurgical activities on changes in physicochemical parameters of soil and earth in archaeological strata, especially within production and utility levels. At the present stage of the investigation, the primary objective was to answer the question as to whether, in the Middle Ages, there was a melting shop in the area of the Main Market Square in Krakow, and what kind of effect it had on the earth and sediments.

Interpretation of the stratification process and standardisation of terminology relating to this process.

The nomenclature connected with interdisciplinary studies of archaeological sites needs to be clarified and precisely defined — this especially concerns the terminology used by archaeologists in such interdisciplinary studies (Rosenbaum *et al.,* 2003). In historical urban soils, the thickness and vertical profile of layers can indicate the nature and degree of human pressure. Archaeological layers in historical towns with significant profile differentiation are an example of so-called urban soil. Urban soil lies over virgin ground. Sometimes, primitive soil can be found between the virgin ground and the urban soil. It (urban soil) consists of anthropogenic layers — in built-up areas these are ekranosols (covered soils) of the deposit type. In the case of archaeological layers — as in the case of urban soils — soil scientists, archaeologists and geochemists indicate the necessity of including them in systematic soil science classification and of introducing their own terms. Gołembnik (2012) suggests using three terms — deposit, layer and stratum — relating to archaeological strata in a specific and defined way (as opposed to the rather loose and ambiguous way in which they were used before):

- deposit — an entity with a specified boundary, with uniform or mixed content, distinguished by its stratigraphic context — created as a result of a homogenous activity or event;
- strata — a continuous sequence of distinguishable deposits, formed as a consequence of repeated activities of a similar nature, or a series of consecutive events conditioned by a similar cause occurring in the same, specified place (shown by an initial stratigraphic analysis, consisting in revealing entities [deposits] in sequences or stratification continuity, or pointing out disturbances in this stratification continuity — if there is a sudden unusual event that has no direct relationship with the context or if destruction/damage occurs [e.g. a fill or redeposit — namely an entity — over the secondary deposit — *ex situ*], by using the term 'strata' in archaeology instead of the term 'sediment' proposed by Gołembnik (2012), a conflict of meaning with sedimentology terminology can be avoided);
- stratum — spatially defined entity of homogenous content, distinguished by stratigraphic context, physical features and cultural content of illegible, primary character.

Thus in this article, when describing the anthropogenic origin of the substrata of the Main Market Square in Krakow, the terms 'deposit', 'strata' and 'stratum' will be used — when we have in mind their successive formation as a consequence of their self-accumulation, or intentional accumulation of matter (including waste) as a conse-

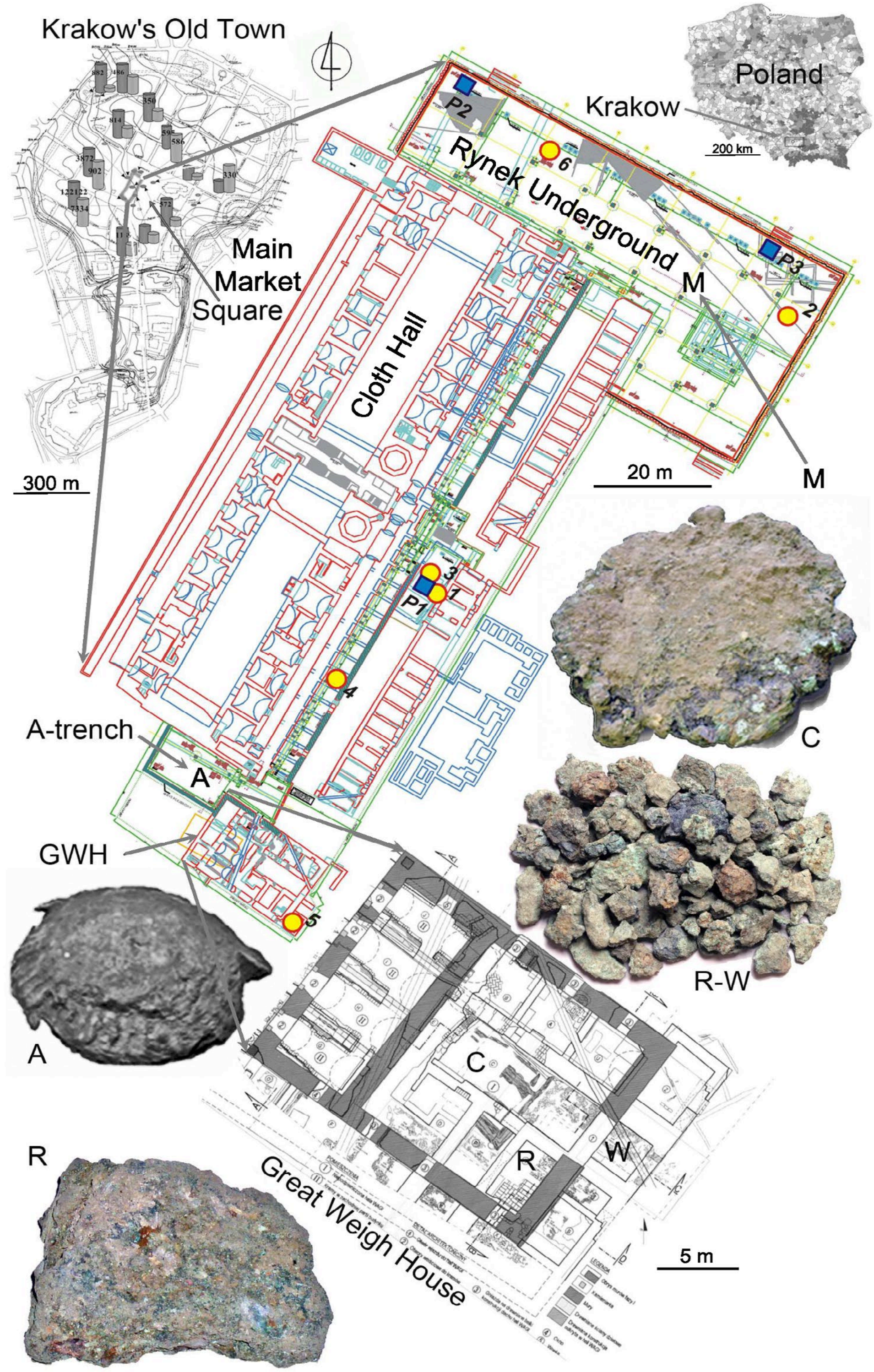

Fig. 1. *The finding place and appearance of the historical slag examined: the slag was found in room R and W, the lead in trench A (Szejbal-Dereń and Garbacz-Klempka, 2010):*
The map of the Old Town in the top left hand corner according to Radwański (1975) — sampling sites [associated with previous studies (Wardas et al.*, 2008; Wardas and Such, 2009)] of copper and lead contamination of historical layers are indicated by cylindrical bars [left and right hand bars show concentrations in mg/kg of copper and lead respectively];*
Diagram M shows the Rynek Underground according to Kadłuczka (2004): sampling sites (P1–P3 and 1–6) [associated with previous studies]; chemistry of groundwater (Czop et al.*, 2010), including studies of copper and lead contamination (Motyka* et al.*, 2012).*
(A — trench A; GWH — the Great Weigh House; C R W — rooms)
Inset — photographs of samples taken from various sites as labelled.

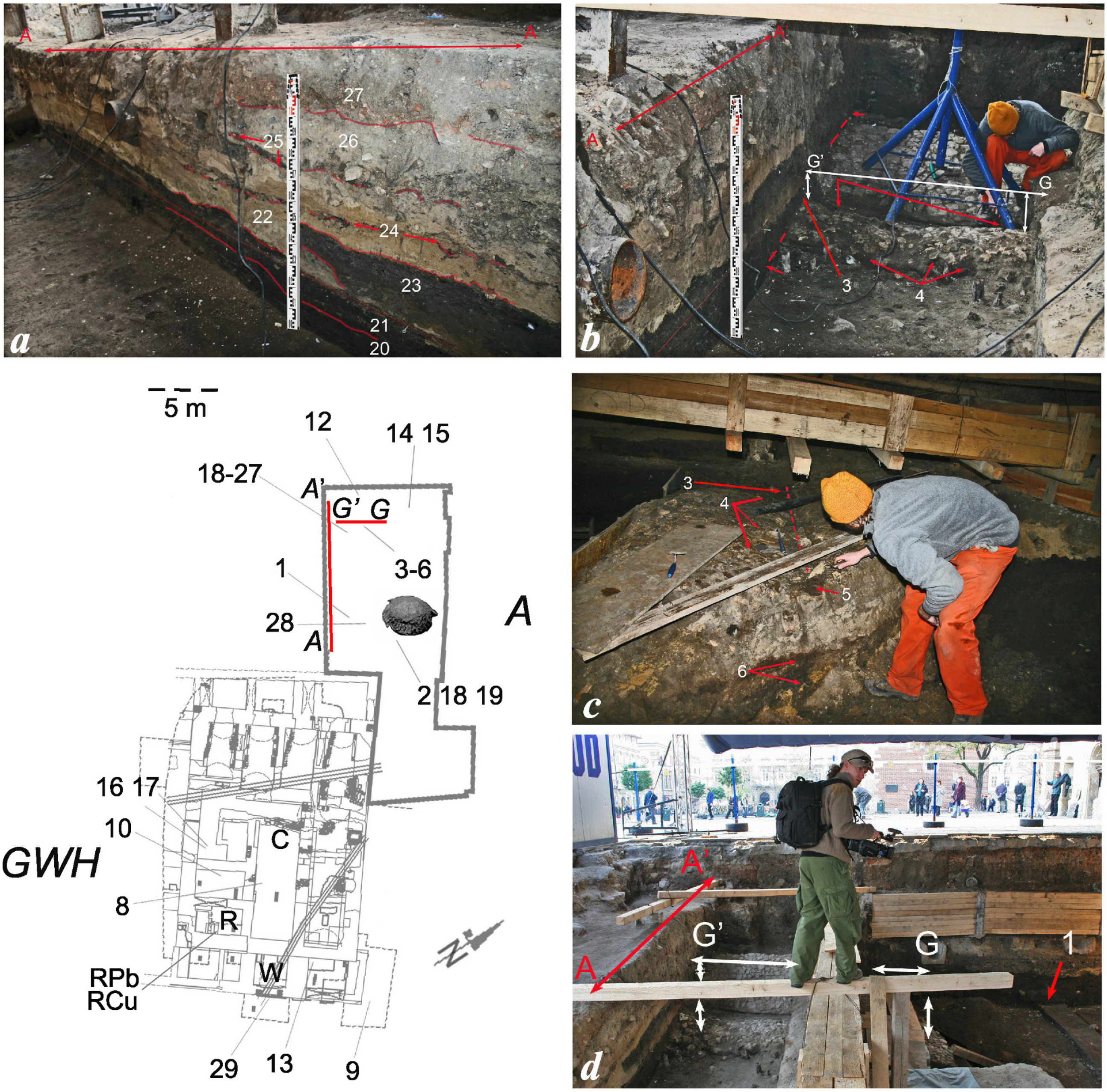

Fig. 2. *Sites of collection of earth and deposit samples (waste water sediments) in an area where a lead slab known as the 'loaf' was found as well as in other Great Weigh House rooms (Szejbal-Dereń and Garbacz-Klempka, 2010). Locations of the sampling points are indicated: 1–29, RCu, RPb; Photographs: a) A-trench cross-section AA' of the south wall; b) A-trench sampling of wastewater sediments from the gutter; c) A-trench site sampling of the ground of the gutter profile; d) a general view of the sampling site in trench A. (GWH: the Great Weigh House; A: trench A).*

qunce of the functioning of the town. The term 're-deposit', on the other hand, will be used for both fills and mounds created by human activity occurring at similar times.

The same importance is attached to determining the utility level, *i.e.*, the continuous sequence of micro-deposits which indicate areas of short or long-term strengthening of the utility level surface, e.g., hard, durable levels with a cobbled surface, or less durable ones – functioning as a dirt road, or dirt floors, which are floors made from hard earth. A considerable content of anthropogenic material can point to high levels of craftwork or the presence of bloomeries and metalwork (metal melting shop) activities. In historical towns, both depositional and post depositional processes occurred differently in different zones, e.g., the zones could be isolated or exposed to atmospheric conditions. Quite often, it was necessary to level off the ground, and this in turn resulted in a complete disappearance of some utility levels. It should be remembered that contaminated deposits could have been moved in a completely accidental way to areas not connected with the genesis of their transformation, where secondary processes of re-emission could create a false picture (Baltacov, 2008; Charzyński, 2006; Charzyński *et al.,* 2013).

Methods

The historical material comes from precisely dated archaeological layers, which correspond to a period of development of the (metal) market from the late 10^{th} century until the end of the Middle Ages. Dating of sample from the Great Weigh House by the ^{14}C method was carried out by the Poznań Radiocarbon Laboratory under the guidance of Prof. Tomasz Goslar, using the accelerator technique (AMS). Calibration was performed using OxCal v4.2 (Bronk Ramsey and Lee, 2013) and IntCal13 calibration curve (Reimer *et al.,* 2013). The analysis was designed to confirm the thesis about a common time horizon selected for analysing material. One metal object from the area of the Great Scales (room R, layer 109 — sample labelled R113C01, earth sample labelled RCu) was chosen for analysis, as it was representative of a large number of the found objects.

Research aimed at characterising historical metallurgical activity connected with the Great Weigh House operating on the Main Market Square in Krakow consisted in conducting parallel investigations and determining the relationship between the conditions of relics and physicochemical ground properties (grain-size distribution, pH value, Eh potential, electrolytic conductivity EC, humidity and roasting loss LOI). The weight percentage of certain elements — mainly Pb, Cu and Ni — was determined in the relics, as was the level of contamination (by these metals) of earth samples obtained from rooms connected with the Great Weigh House (**Figs. 1**, **2**). Special attention was paid to the presence and chemistry of micro-artefacts and ecofacts, the latter being depositions of organic or environmental remains. Markers which would determine the way of bonding of metals and their susceptibility to migration were sought in the grain, chemical and phase content.

Analyses of the historical material were conducted in the Laboratory for Metal Artefacts Research, at the Foundry Faculty of AGH, the University of Science and Technology in Krakow. Non-destructive methods were applied — mainly optical and scanning microscopy, X-ray fluorescence spectroscopy (XRF), and also (in selected instances) the method of X-ray fluorescence analysis in micro-areas. The research was conducted with the help of a SPECTRO MIDEX spectrometer and a JEOL JSM 5500 scanning microscope with an energy dispersive analyzer (EDAX). Quantitative point analyses were conducted with ZAF correction.

Environmental samples were examined in the Absorption Laboratory of Atomic Spectroscopy at the Faculty of Geology, Geophysics and Environmental Protection (AAS SOLAAR M6). The detection limits for the flame AAS method (with deuterium background correction) for the equipment and methodology applied (digestion with HNO_3/H_2O_2 — by the EPA 3050 method, using about 1.0000 g of dry sample) are as follows (mg/kg): Fe — 6, Mn — 3, Zn — 1, Cd — 1, Cu — 2,5, Ni — 6, Pb — 5, and Cr — 5. To determine inorganic anions, ion chromatography was applied (IC DIONEX DX-100; the detection limits for the anions are (mg/l): fluorides and phosphates < 0.01, chlorides < 0.2, nitrates < 0.3, and sulphates < 0.4), and physicochemical markers were determined using standard methods, following the same procedures as in the case of archaeological layers, which ensured comparability of the results (Wardas *et al.,* 2008; Garbacz-Klempka *et al.,* 2012).

In order to standardise the measurement of physicochemical indicators and concentrations of anions, samples were disintegrated, and aqueous extracts were prepared (ratio of solid phase to distilled water 1:3), which eliminated the influence of different moisture levels of samples. Grain fractions were extracted wet, on polyethylene sieves. The organic matter content was determined by applying the method of roasting losses, roasting the samples at a temperature of 600°C for 12 hours. Standard methods were applied to measure the pH value — active acidity, Eh potential and electrolytic conductivity. Reagent blanks, soil (HRM — home reference material) and sediment (Sediment river 1646) standard reference materials were used to assess the accuracy of the analytical method. The relative standard deviations for all measured metal concentrations were less than 8% for the AAS method. The results for metals showed good consistency with certified values, and recoveries were satisfactory. The content of metals was checked with an ICP-MS (ELAN 6100) and ICPOES (Optima 7300 DV) spectrometer in an accredited hydrogeochemical laboratory (Certificate number AB 1050). The estimated relative error of the mean value was less than 2%. To sum up, all the materials were examined using uniform methodology, and validation was carried out by analysing reference materials at intervals of 10 samples.

3. RESULTS AND DISCUSSION

The historical, copper-based alloy that was analysed is difficult to classify according to present-day norms. The proportions of different components seem to be similar in specific artefacts, but certain items with compositions that are significantly different from median values can be singled out (**Table 1**, **Fig. 3d**). And so, with average copper content (%) at 75 and zinc at 16, the percentage of copper varies from 62.42–88.57 and that of zinc: 10.01–23.46. The tin content (%) is low, on average 3.39, although in one case the percentage of this element ex-

Table 1. *XRF analyses results for the chosen copper alloy rings (Głowa and Garbacz-Klempka, 2010).*

The analysed area symbol	Element content (% wt.)						
	Cu	Zn	Sn	Pb	Sb	As	Ag
P001 / plate	62.42	14.96	19.42	1.88	0.04	0.33	0.05
P002 / plate	76.44	18.92	1.68	0.79	0.17	0.34	0.13
P003 / plate	72.22	23.46	0.41	0.46	0.07	0.09	0.12
P004 / plate	77.10	20.30	0.08	0.41	0.33	0.10	0.07
P005 / ring	79.31	10.62	4.22	1.88	0.14	0.02	0.16
P006 / plate	78.99	18.13	1.25	0.82	0.00	0.00	0.10
P007 / plate	73.94	15.32	8.33	1.50	0.00	0.09	0.09
P008 / plate	88.57	10.01	0.29	0.30	0.17	0.08	0.10
P009 / plate	66.23	16.69	10.90	2.43	0.13	0.41	0.13

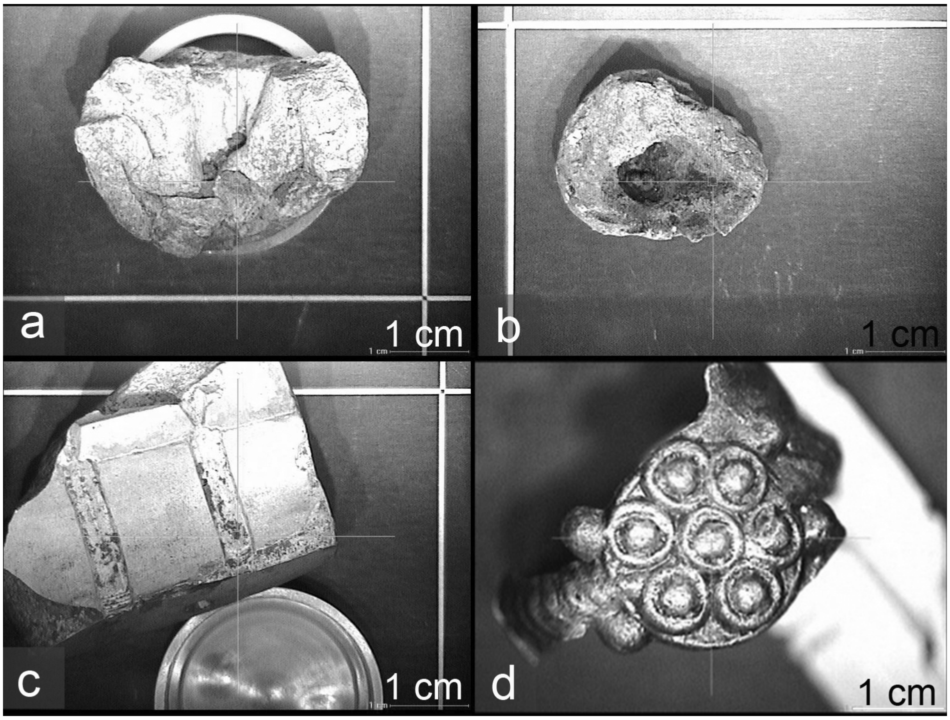

Fig. 3. *a–b) Medieval crucibles from the Main Market Square during spectral analysis; c) 13th century stone casting mould for a part of a ring from the Main Market Square; d) 14th century ring from the Main Market Square in Krakow; spectrometer images (Głowa and Garbacz-Klempka, 2010).*

ceeds 19.42. The artefacts contain little lead (%) — on average 1.07 (the maximum value is 2.43). There are traces of other elements, namely, arsenic, antimony and silver. The closest modern equivalents to the historical alloys used in Krakow are, according to the CDA (Copper Development Association), modern copper-tin-zinc and copper-tin-zinc-lead alloys with the following reference numbers ascribed to them: C84200, C84400, C84410, C84500, and C84800. They belong to the group of brasses, a kind of casting copper used nowadays (Kulig, 2007).

A series of metal analyses of the artefacts from the Main Market Square showed that a typical material used for the rings made in Krakow was an alloy containing about $75.00 \pm 0.05\%$ copper, and $15.00 \pm 0.01\%$ zinc, with the addition of tin ($4.00 \pm 0.06\%$) and lead ($1.00 \pm 0.05\%$), and with traces of antimony, arsenic and silver (Ag $0.10 \pm 0.01\%$), the latter elements being impurities remaining from the smelting of copper from ore. This material is sometimes referred to as artistic bronze, although in the technical literature it is called brass – with a colour that is close to gold. Apart from its aesthetic value, it also has very good casting properties, which must have been known to the craftsmen of old. Despite metallic zinc not being known at the time, it was obtained by melting pure copper with zinc ore, which was described precisely by Monk Teophile in the 12th century ('...stone of yellowish colour and sometimes red, which is called (…) calamine, is mixed next with very fine coal and addition of copper … this mixture is called brass.'). An analysis of guild documents indirectly points to the kinds of materials used by particular metal guilds in Krakow, but their precise characteristics can only be determined by thorough research (Garbacz-Klempka *et al.*, 2015; Szejbal-Dereń and Garbacz-Klempka, 2010).

The most numerous group in a series of historical rings from the Main Market Square was made from copper alloys. From the technological point of view, this kind of alloy has better qualities than pure copper. The presence of zinc in the alloy lowers its melting point, which creates better conditions for carrying out melting, and facilitates its working in the craftsman's shop. The main advantages of brass are its ease of working (including chasing and polishing) and soldering. It is hard to overestimate its aesthetic values: its colour and lustre after polishing. It is also resistant to corrosion. This technique made it possible to create ornamental items with complicated shapes, using clay or stone moulds. As a result of archaeological excavations at the Main Market Square, casting crucibles and fragments of three stone casting moulds, including one used for ring making, were found (see **Fig. 3a–c**). The results of specialist analysis of medieval ornaments from the Main Market Square attested to the use of the casting method for producing these artefacts in the early medieval period.

Archaeological analysis of historical material allowed for more precise dating of the metal artefacts (a sample from Room R of the Great Scales, sample R3 from layer 109) to the turn of the fourteenth and fifteenth centuries. However, ongoing archaeological research does not rule out that the material was created in the late fifteenth century.

Because the structure of the investigated slag samples (metallurgical semi-finished products) revealed the presence of charcoal, they can be used for dating. Thus, the time horizon of the 109 layer can be verified, from which the earth sample (RCu and RPb) came. Among a number of metal artefacts to determine the age by analysis of the radiocarbon age, one object R3 was selected. It was representative of a large group of the finds collected by the Archaeological Research Team of the Main Market Square.

The result of radiocarbon dating 295 ± 30 BP after calibration gives the range of 1490–1660 cal AD (2σ = 95.4% confidence interval) or 1520–1650 cal AD (1σ = 68.2% confidence interval). The calibration results indicate, therefore, that the slag and the formation of the 109 layer in room R should be attributed to 16–17th century. According to written sources, it was the period of most intense activity of Great Scales, the functioning of the lead depot in the House of Lead near the Great Weigh House that survived until the Swedish "deluge".

At places metal constituents penetrated into the well preserved structure of the wood cell walls (see **Fig. 4**). Charcoal was a basic fuel in metallurgy, both in copper smelting and in recovering metallic components, such as silver, from copper. Coal became part of the slag structure, so its presence should be connected with metallurgical processes. The above findings may therefore indicate that as late as in the 17th century there was a melting shop on the Market, which, due to its production volume could be considered as metalworks. Because of the presence of slag and metal scraps the impact of its operation is "stamped" on historical layers in the area near GWH, and trench A, which maybe was the main lead storeroom. As a result of different migration forms, contaminants are also observed throughout the Old Krakow area.

Earth samples from room R, from layer 109, were analysed for Pb and Cu (%) and average concentrations were extremely high: 12.84 ± 0.54; 10.86 ± 0.22 (sample RCu) and 16.51 ± 0.57; 0.73 ± 0.01 (sample RPb). Average concentrations (g/kg) of Pb at the level of 3.10 ± 0.21, and Cu at the level of 0.22 ± 0.01 were determined for a sample from another room. These significantly exceeded both the values of the local geochemical background, which are Pb: 8–25 and Cu: 2–30, and the legally prescribed limit values for soil and earth (above which they are considered to be contaminated), which are for Pb — 100 and Cu — 70, and also the environmental standards for water sediments (including residues extracted from dredging water reservoirs), where the values are Pb — 200, and Cu — 150 (Kabata-Pendias and Mukherjee, 2007).

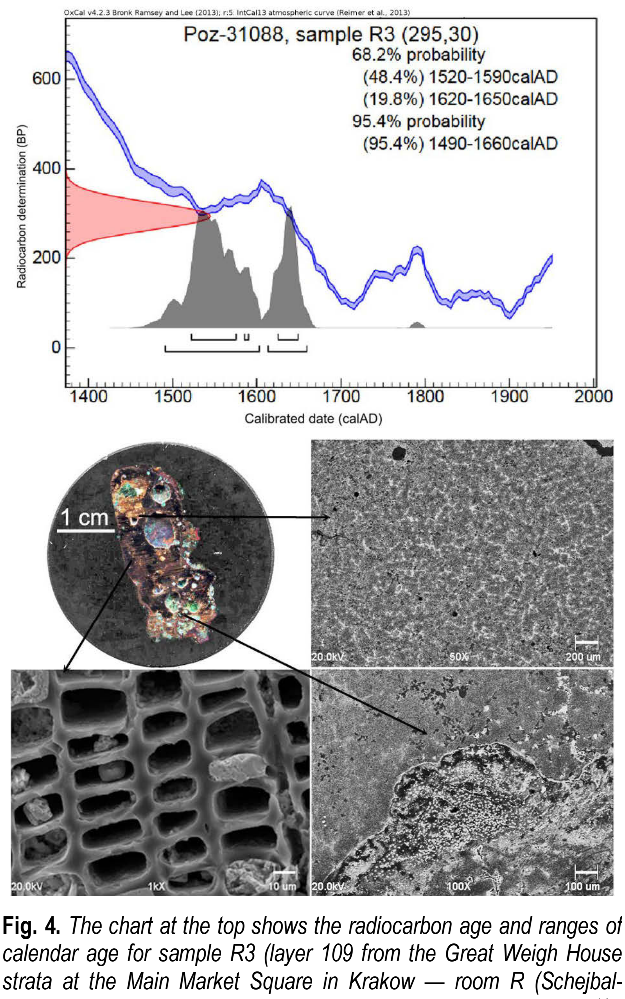

Fig. 4. *The chart at the top shows the radiocarbon age and ranges of calendar age for sample R3 (layer 109 from the Great Weigh House strata at the Main Market Square in Krakow — room R (Schejbal-Dereń, Garbacz-Klempka 2010)) on the basis of radiocarbon ^{14}C dating; the photographs below show14th / 15th century metal artefact R3 — the first image is of the whole object and the remaining three are close-ups of the surface (using SEM).*

The earth layers which yielded all the artefacts came from the Great Weigh House area and the neighbouring trench A, and they were characterised by greatly varying values of physico-chemical markers. Moisture fell within the range 0.981–29.672 (wt%) and loss on ignition representing the organic substance content ranged from 0.573 to 9.900 (wt%). The content of fluorides in water extracts (1:3), which represents the content of easily soluble salts, was between 0.3–3.9 (mg/l); for chlorides it was 24.5–495.0; for nitrates: 0.7– 201.5; for phosphates: 0.01–6.10; and for sulphates: 5.6–233.0. The salinity of most of the samples exceeded 1.00 mS/cm, reaching up to 3.00 mS/cm. The ground was characterised by active acidity within the pH range 6.23–7.30. In samples obtained from both places, the grain-size fraction (0.18–1 mm and < 0.18 mm) dominated, usually totalling over 75 wt%.

Geochemical research on the Main Market Square and many others areas was aimed at emphasizing the role of metals as markers in archaeology, with the lead and copper content in the historical grounds being recognised as especially relevant. The artefacts analysed were highly corroded cakes of copper or archaeological objects of another kind with a porous structure (see photos in **Fig. 1**). Chemical analysis of the metal artefacts found in the layers of the excavated part of the Great Weigh House (see **Figs. 1, 2** and **5**), in room R, showed predominant copper content (**Fig. 5e**). In another room (labelled W), some of the artefacts showed a higher content of lead than copper (**Fig. 5f**).

The earth forming the strata on the eastern side of the Main Market Square, not being directly influenced by the functioning of the Great Weigh, contained (mg/kg): Cd — 2.0 ± 0.2, Cr — 17.5 ± 1.0, Ni — 7.3 ± 1.0, Cu — 80.4 ± 4.0, Pb — 291 ± 20, Zn — 82.9 ± 7.0, Mn — 412 ± 38 and Fe (%) — 1.69 ± 0.10 (average values from about 50 samples, 5 profiles). On the opposite side of the Cloth Hall, in the western part of the Main Market Square, the average concentration values in mg/kg were (based on 45 samples,7 profiles): Cd — 1.63 ± 0.15, Cr — 12.5 ± 1.0, Ni — 8.5 ± 0.8, Cu — 54.92 ± 2.00, Pb — 301 ± 10, Zn — 81.7 ± 6.0 Mn — 102.0 ± 9.0, and Fe (%) — 0.53 ± 0.04 (see **Fig. 1**).

Analysis of these results shows that, with the exception of Cu and Pb, the determined metals do not exceed environmental standards for soil and earth. Hence, when researching strata material from the Great Weigh House areas and trench A, special attention was paid to these elements, assuming that the main causal activity was the processing of Cu and Pb and its conversion into marketable portions. Because of higher Ni concentrations, this element was also included. In the chart (**Fig. 5d**), the concentration changes are presented in the order in which the samples were obtained from the Great Weigh House areas and from the neighbouring trench A, located at the exit of Bracka St.

It can be clearly seen that, generally speaking, within Trench A, the strata are less contaminated with Cu and Pb than in the case of the Great Weigh House samples. However, the degree of contamination is much more uniform in Trench A. Maybe the Great Weigh House rooms were used for different purposes, hence such vast differences — even in the range of 1500. Also, there is a high concentration of Ni (about 400 mg/kg) — significantly different from concentrations typically found in the historical layers of Krakow.

This value was confirmed in the metal analysis of the artefacts (see **Fig. 5e–f**). In sample W3, X-ray microanalysis confirmed that although there is a pure copper matrix (99.84 ± 0.07%), locally there is also an intermetallic phase consisting of iron, copper, magnesium and nickel. Based on X-ray fluorescence spectroscopy, it was shown that in the sample examined, the highest concentrations are of arsenic (26.11 ± 0.03%) and copper (25.27 ± 0.02%), with a significant concentration of nickel (17.87 ± 0.01%), iron (15.55 ± 0.01%) and antimony (7.00 ± 0.09%).

It was interesting to trace lead accumulation changes within buildings serving as warehouses for the Great Weigh House. These buildings were located at trench A, at the Bracka Street exit (see **Fig. 2**). Due to the fact that the lead slab was discovered there, earth (sediment) samples were taken from the top and bottom levels of layer 118, adjacent (from the outside) to the wall of an unidentified room or building, in a place susceptible to leachate accumulation (**Fig. 5c**). Also, the layer profile labelled AR-2W was sampled, starting from its first layer up to the level of the modern fill (**Fig. 5a**). The above mentioned wall was intersected, at right angles, by a communication route with a pavement and gutter, where samples of waste sediments and earth were taken (see **Figs. 2b–c, 5c**). The chart shows, based on the example of lead and copper, the contamination level of the earth and sediments.

Within the profile (see **Fig. 5a**), up to the level of modern fills, contamination is present even in the sandy substratum at an average level of 500 mgPb/kg; in the case of copper, the level of 120 mg/kg also points to the storage of raw material (copper) here. Lead contamination is definitely higher — also within the cobbled area and the gutter. Maybe the raw materials (copper and lead) were stored (separately) in storage rooms in this area, to which they (mostly lead) were transported by road.

The Great Weigh samples from the investigated rooms were analysed from the perspective of their deposition level, and in this way a simplified timeline of (the variability of) contamination was obtained for the Main Market Square substratum in this area, as the historical layers were created. In this way, it was ascertained that from layer 207.90 to 208.30 m AMSL, copper content increases 200 times, and lead — as much as1000 times. This increase is especially noticeable in the level determined at 208.30 m AMSL (**Fig. 5b**).

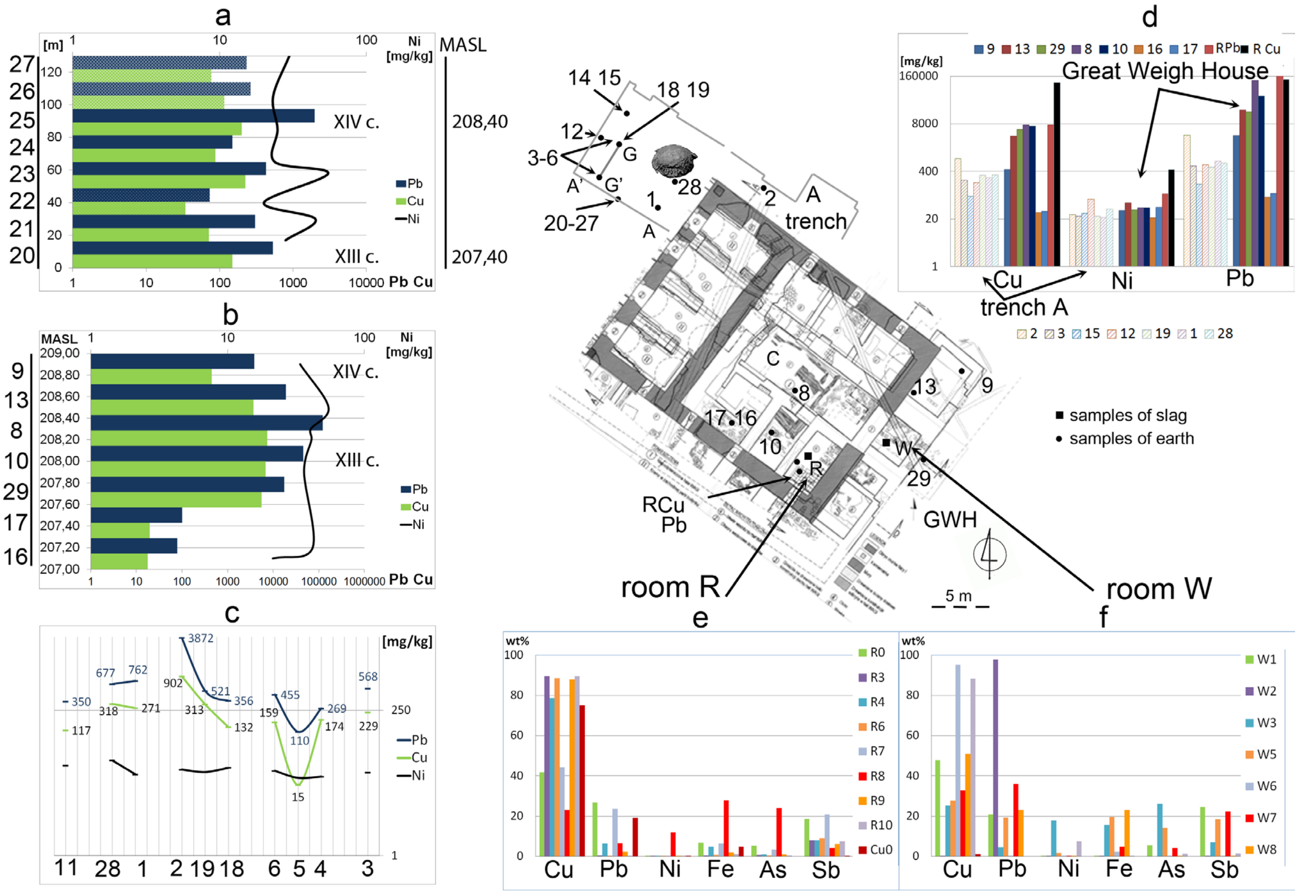

Fig. 5. *The graphs show elemental content (%wt.) of various samples (as labelled) taken from locations indicated on the plan in the centre (Szejbal-Dereń and Garbacz-Klempka, 2010).*
a) shows a vertical profile of the sequence of layers (fraction < 0.18 mm) in trench A (samples 20–27) showing Pb Cu and Ni levels as labelled; in sample 22 levelling sand is present in samples 26 and 27 there are — modern fills; the additional y-axis shows MASL and estimated age.
b) shows Pb Cu and Ni concentrations in samples taken from utility levels in the GWH.
c) shows Pb Cu and Ni concentrations in sediment samples from potential leaching areas taken from the GWH and trench A (except for sample 11): Sample 11 was taken from a trench on the north side of the Cloth Hall – M; Sample 28 was taken from the bottom of the wooden trough in trench A; Sample 1 was taken from the top of the wooden trough in trench A; Samples 219 and 18 were taken from the site of excavation of the lead slab; Samples 3–6 were taken from the gutter (Sample 11 has been included for comparative purposes — revealing similar elemental concentrations).
d) A comparison of concentrations of Cu Ni and Pb between samples taken from trench A and the Great Weigh House.
e) A comparison of element concentrations in metal artefacts taken from Room R in the Great Weigh House (individual samples are not indicated on the plan in the centre).
f) A comparison of element concentrations in metal artefacts taken from Room W in the Great Weigh House (individual samples are not indicated on the plan in the centre).

Analysis of concentration changes and their indiscriminate dating and matching with the history of this place and town is not, of course, recommended, because the deposit growth was uneven in particular rooms and resulted from the designation and specific usage of a given room. Also, the metal accumulation may have resulted from the same causes, but should not be translated into the same mechanism in a broader perspective. Nevertheless, the degree of contamination of the deposits, layers and re-deposits shows that the Great Scales were not only used for weighing the raw materials, but also that some metal melting took place there for a considerable period of time.

Earlier research showed that this contamination could have caused some hydro-chemical anomalies in the underground waters of the Main Market Square, which had been noted earlier by Kleczkowski (1967). It is difficult, however, to trace the migration paths of these metals, because at the solid ground level, directly beneath a very contaminated layer, there are only slightly increased values. In the Great Scales area, the values for Cu and Pb are respectively, 30 and 70 mg/kg (Pawlikowski *et al.*, 2008). The recognised sewage systems mainly disposed of meteoric and sewage waters, rather than serving to protect from anthropogenic modification of the environment. They also spread metals in an uncontrolled way in the Main Market Square environment and other lower areas situated within the water runoff from the medieval utility levels (pavements, abode flooring, floors), as well as along the town streets and other communication routes.

A special role was played here by gutters and waste water troughs — which enabled horizontal transportation of pollutants — and also other structures (e.g. walls) that cut through layers made from compact loam and organic formations, which facilitated the seeping of pollutants into the ground. Pollutant migration could take place both at the time the pollutants were created (generally speaking, when the metals were produced, worked with and traded), and in later centuries, when metal particles were deposited in the earth, and then processes of resorption and remobilisation took place slowly.

During the earth and construction works connected with alterations to the Great Weigh House, the contaminated earth could have been used for filling cellars and for levelling ground. That is how in modern fills, contamination can appear that is not caused by a continuation of the activity that actually generated it, but by the shifting of contaminated earth from some older layers.

So it follows that in research assessing metal concentrations in earth, aimed at evaluating the level of contamination of the old Krakow environment, samples should be taken exclusively from old and preserved utility levels, namely from abode flooring, cobbled areas and floors and the waste layers resting on them. The research conducted so far has yielded interesting results, confirming the very important role of copper in the development of medieval Krakow; this will broaden the scope of knowledge concerning the use of semi-finished metal, copper and bronze objects, as well as finished, cast artefacts in metal production and trade in Europe. Also, it is worth remembering that in the Main Market Square area, starting from a depth of 80–100 cm (see **Fig. 5a**), there are medieval strata present, formed in the 15th or even 14th centuries. Thus, everything that was present and recorded within these layers is connected with that period, including the heavy metal contamination determined there.

4. CONCLUSIONS

In the Middle Ages, (besides lead) copper and tin became the basis for making alloys in casting workshops. Written sources and also research results undoubtedly point to large scale metal production conducted in medieval Krakow. Finds of melted copper fragments and copper raw material in the form of a round slab in the vicinity of the Great Weigh House (see **Fig. 1**) show that there must also have been a melting shop — a non-ferrous metal works. The slab found here has an irregular shape, and — below a thick layer of earth and corrosion products — a fracture with a characteristic red-brown colour has appeared, which indicates that the metal was not only weighed but also divided here.

It is worth remembering that the Great Weigh House institution was connected with trade. Its activity was based on a special charter or privilege, granting the town a monopoly in this respect. Greater trade turnover in a given town was connected with the obligation to weigh the goods there. The weighing was connected with special fees, and often also additional levies, which benefited the town. Copper, similarly to lead and iron, was weighed on the Great Scales, which were hundredweight scales.

During the period when the Great Scales functioned, there was exceptional contamination of the layers formed around them. In the Great Weigh House, irregular, porous lumps of copper were found, resulting from the processing of this metal, which must have been carried out in this place. This is attested to by the fact that parts of furnaces were discovered in the actual Weigh House itself. The great number of small, green particles, which are shreds (and also larger fragments) of oxidised copper, distributed within a 30-cm earth layer — accompanied by occurrences of lead — constitute material proof of the weighing, heating, dividing and marking (and — what follows — distribution) of copper.

A slab of copper from the Great Scales (which are also known as the Lead Scales) in Krakow assumed the shape of a hollow in the earth in which it lay, and so it must have been created there, *i.e.* next to the Scales, maybe from scrap material resulting from pieces that were cut off from larger slabs, mixed with inclusions and shavings of lead and copper.

The lower (but still high) copper and lead concentrations in its immediate neighbourhood, especially in buildings in the area of Bracka Street, probably testify to their auxiliary function: the warehousing of raw materials. The finds of coloured metal lumps — especially a lead slab weighing 693 kg, which is a unique find because of its size — come from this area. Other areas of the Main Market Square were probably polluted by the spreading of contamination on shoes or by means of transportation used at that time.

1) Studies of the effects of metallurgical processes in the area of the Great Weigh buildings on the Market Square in Krakow have shown that metal artefacts and geoartefacts in the form of contaminated earth and water sediments constitute good material for interdisciplinary analysis.
2) Metal science and geochemical methods have shown that both metals and geochemicals may act as indicators, on the basis of which one can identify the history of changes in the technology of making metal objects, including pressure on the natural environment – mainly soil and earth.
3) Metal processing during the weighing and packing of lead and copper led to the accumulation of waste materials in the substrate, which, through contact with the ground caused permanent contamination of suc-

cessive levels. These levels formed a considerable thickness of the archaeological layers.

4) The elemental composition of metal artefacts and the degree of contamination of archaeological layers can both be considered as specific indicators, including geoindicators that are helpful in establishing the chronology of the layers.

The present paper has attempted to demonstrate that metal artefacts and the chemical composition of the archaeological layers in which they were deposited can fulfil the role of geoindicators. Interdisciplinary studies by archaeologists, metal scientists and geochemists enable the full characterization of layers, including determining their origin, and even sometimes chronology. The state of preservation of artefacts in the ground — when analysed in comparison with the ground's physicochemical properties — also serves as an indicator of the best methods of preservation of archaeological sites.

In the light of the latest archaeological researches on the Main Market Square in Krakow, the role of this city in the copper trade has become more evident (Buśko *et al.,* 2009; Garbacz-Klempka and Rzadkosz, 2009; Schejbal-Dereń and Garbacz-Klempka, 2010). Copper came to Krakow mainly from Koszyce. Round or oval ingots, formed in Hungarian smelters, were weighed and divided on the Market Square in Krakow, from where they were sent on. Krakow gained the privilege of a right to store copper in 1306, which enabled it to mediate in the Hungarian copper trade, which ran through Gdańsk to Flanders and England (Kutrzeba, 1902; Wyrozumski, 1992, 2007). Krakow's significance was confirmed by its membership in the Hanseatic League, the most powerful trade organization of the Middle Ages (Kutrzeba, 1902; Wyrozumski, 2010). Among Hanseatic towns, Krakow was known as Kupferhaus, which means Copper House (Rzadkosz *et al.,* 2012; Wyrozumski, 1992; Wyrozumski, 2007).

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APPENDIX

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