Archaeological and Anthropological Sciences (2020) 12: 165
https://doi.org/10.1007/s12520-020-01148-5

BRIEF REPORT

Lead isotope ratios and the provenance of medieval silver

A comment on "Archaeometric studies on early medieval silver jewellery from Central and Eastern Europe" by Ewelina Miśta-Jakubowska, Renata Czech Błońska, Władysław Duczko, Aneta M. Gójska, Paweł Kalbarczyk, Grzegorz Żabiński, Krystian Trela. Archaeol. Anthropol. Sci. 11 (12), 6705–6723.

Ernst Pernicka[1]

Received: 29 April 2020 / Accepted: 30 June 2020 / Published online: 14 July 2020

The material presented in this article is certainly interesting and the authors present data and interpretations concerning the technology that was used to produce silver jewellery in the Middle Ages in western Poland, with an emphasis on the granulation technique and on the provenance of the silver. They claim to have identified three different joining techniques, namely "(i) spilled granulation ornaments, (ii) non-oxidised spherical granules and (iii) oxidised soldering area with spherical granules". From the images provided, it seems that the first technique relates to soldering with metallic solder and the second to reaction soldering with copper salts. But it is unclear what the authors mean with "the use of non-metallic soldering". In the discussion on the soldering techniques, they refer to the measured oxygen contents but do not discuss the possible influence of corrosion. It is also not made sufficiently clear why linear discrimination analysis had to be used to determine the compositional difference of the base metal and the soldering regions.

While this result is certainly consistent with many previous studies and insofar unspectacular, the part on provenance analysis is fundamentally flawed. First, it is a general consensus that leads isotope ratios to have to be measured with the highest possible precision due to the substantial overlaps when more than a few ore deposits are considered as potential sources. Nowadays, precisions of less than 0.03% are standard and are routinely obtained with multi-collector ICP mass spectrometers. However, the authors used a single-collector quadrupole mass spectrometer coupled with laser ablation with a relatively long wavelength (266 nm) for their study. This has two major disadvantages: The precision of measurement for lead isotope ratios is usually in the order of a few per mill. The authors state a precision between 1.02 and 1.16% (percent!) for measurements of the NIST 981 reference material and between 5 and 7% for the measurements of the artefacts. This is more than a factor of 30 less precise than is nowadays considered as useful and achievable in the NIST 981 reference material. But the range measured in the artefacts covers most lead isotope ratios found on Earth and, accordingly, no discrimination between different ore deposits is possible. Furthermore, the laser used for ablation is more prone to isotope fractionation than lasers with shorter wavelengths, but this possible complication is not discussed at all.

The key problem of this article is the assumption that the large variations that were observed in repeated measurements of the same sample is due to inhomogeneity of the lead isotope ratios within the sample. It is suggested that recycling and mixing of silver were common in the Middle Ages and therefore, "one can expect more than one value of individual isotopic ratios in one and the same artefact". So far, it has been generally assumed and actually repeatedly confirmed that melting of a metal effectively homogenizes the chemical composition as well as the lead isotope ratios. Depending on the alloy composition on solidification, there may arise compositional inhomogeneities on the microscale but this would not affect the lead isotope ratios. Since the silver analysed in this study also contains copper, one could consider a possible influence of lead introduced by the addition of copper but this again would refer to the bulk composition and not to inhomogeneities on the microscale in a single artefact. This has been confirmed in many replicate measurements in many publications. Since medieval silver was always produced from argentiferous lead ores, it usually contains between 0.1 and 1% lead so

This paper is a commentary to https://doi.org/10.1007/s12520-019-00935-z.

✉ Ernst Pernicka
ernst.pernicka@ceza.de

[1] Curt-Engelhorn-Zentrum Archäometrie, Mannheim, Germany

that the possible influence by the addition of a few percent copper seems to have only a minor effect.

Although it is a moot point to discuss the provenance of the silver with such imprecise data, the authors nevertheless compare their results with published lead isotope ratios of ore deposits and artefacts but do not present their own data in any of the conventional lead isotope diagrams. Only diagrams of principal components and canonical variables are shown. Two three-dimensional plots with kernel density estimates of the lead isotope ratios of two artefacts show a range of more than 10% in the $^{207}Pb/^{206}Pb$ ratio and as much as more than ca. 30% in the $^{208}Pb/^{206}Pb$ ratio within one artefact! In one artefact, lead isotope ratios for $^{207}Pb/^{206}Pb$ of ca. 0.85 and for $^{208}Pb/^{206}Pb$ of ca. 2.8 were plotted. This combination of lead isotope ratios has never been reported and it is unlikely that it exists on Earth. However, the reader cannot check the consistency of the data and the conclusions drawn from them.

The major research question concerning the provenance of medieval silver in eastern and central Europe is the amount of silver that was traded from central Asia as indicated by many silver coins from mints in central Asia and Iran found in silver hoards as described in this article. It is also known that silver from regional sources may have been used, for which there is historic evidence available for their exploitation in the Middle Ages. This question has been repeatedly addressed and an initial systematic attempt to apply scientific methods to find an answer by Ilisch et al. (2003) was unsuccessful, because the chemical composition of silver bears little information on its geological source (e.g. Pernicka 2014). A major step forward was the dissertation by Stephen Merkel (2016) who introduced lead isotope studies in this field and also characterized a number of important lead-silver mining regions in Central Asia.

However, one prerequisite is obvious: For the discussion of the provenance of silver objects, it is only useful to compare lead isotope ratios of objects with those of lead-silver ores. In their discussion, the authors refer on page 6714 to Ettler et al. (2015), Merkel et al. (2013) and Hatz et al. (1991) for comparative data of silver deposits. However, of these three publications, only one (Hatz et al. 1991) reports lead isotope data from Germany but not from Freiberg, which is mentioned as one major source in the conclusions. However, it is well known that the silver mines in the Saxo-Bohemian Ore Mountains were opened only in the twelfth century and could not have provided the silver of the objects analysed that are dated to the tenth and early eleventh centuries. Ettler et al. (2015) report on lead isotope ratios in copper slag from an archaeological site in the Czech Republic which is also dated to the twelfth century and is not even related to silver production in any way. Merkel et al. (2013) report on the analyses of lead slag of uncertain date from Afghanistan.

In their discussion, the authors use data from 17 ore regions and deposits as well as archaeological sites for comparison. The selection of these sites and regions appears rather arbitrary and reveals a complete lack of knowledge of the relevant ore deposits. The sites and regions named include large areas that may comprise many different deposits like Afghanistan, Uzbekistan and Slovakia (Tatro veporic unit, Gemeric unit and Slovakian neovolcanites) and mining regions like Oberlausitz, Harz (with the mines at Rammelsberg and Bad Grund), Freiberg, Kutna Hora, Pribram and Horbach, for all of which the beginning of mining is attested later than the tenth century with the exception of the Harz Mountains. There are also three archaeological sites included in the comparison that have nothing to do with silver production or silver metallurgy and all are not contemporary. These are Na Slupi in Bohemia (Ettler et al. 2015), a late medieval settlement where copper slag was found, Buchberg in Austria, an Early Bronze Age copper smelting site in the Inn valley and Gammersham, an Early Bronze Age site in southeastern Bavaria where a hoard of so-called Ösenringe was found that consist of unalloyed copper (Höppner et al. 2005). There is no metal deposit in its vicinity and the metal may derive from the Inn valley. Obviously, this list of regions and sites for comparison with the lead isotope data in this article is largely taken from the three publications mentioned above, namely Ettler et al. (2015), Merkel et al. (2013) and Hatz et al. (1991) but the original sources (Höppner et al. 2005 for Buchberg and Gammersham and Niederschlag et al. 2003 for Freiberg, Harz and Oberlausitz but mainly copper ores) are not cited. In summary, it does not make any sense to compare lead isotope ratios of medieval silver objects with Early Bronze Age copper metal of copper mines.

Despite the use of sophisticated data analysis with kernel density estimates, it is no wonder that the result of the lead isotope study in this article is inconclusive. Yet, the authors claim that "... the isotopic composition in individual groups results from the fact of mixing of the raw material from Central Asian (Afghanistan and Uzbekistan), German (Freiberg) and Polish ores". This would mean a further complication, because the end members of the presumed mixing line(s) are unknown and the interpretation is open to any speculation. However, this implicit conclusion is contradicted by the next sentence that "in all Slavic groups ... there is a preponderance of Freiberg silver over that from Uzbekistan and Afghanistan...", despite the historical fact that the first reported find of silver near Freiberg was in 1168 and real mining did not begin before the end of the twelfth century. Finally, the authors present a bold estimate that in the (typologically defined) Scandinavian group, "the share of European deposits is 32%, while nearly 70% of metal seems to have come from Asian sources". These statements and conclusions as summarized in their Table 5 are completely unfounded.

In their reply (Mišta-Jakubowska et al. 2020), the authors do not answer the major critical points. They repeat their claim that lead isotope ratios may not be homogenized on melting of a metal and cite Merkel (2016) and Baron et al. (2009) in

support. However, the latter article has only shown that products obtained from silver production may have heterogeneous Pb isotopic compositions at the furnace scale, while the individual samples of slag, lead "smoke" (volatilised lead oxide) and especially lead metal were quite homogenous. Merkel (2016) does not report at all on inhomogeneities of lead isotope ratios in single artefacts. Quite to the contrary, seven repeat analyses of silver coins resulted in the same ratios within experimental uncertainty. Last but not the least, the authors fail to acknowledge that it does not make sense to compare medieval silver artefacts with Bronze Age copper artefacts and metallurgical remains. They do not comment on the fact that their claim that Freiberg in Saxony was a major source for the investigated objects is clearly disproven by historical knowledge.

Funding information Open Access funding provided by Projekt DEAL.

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