Gold parting, iridium and provenance of ancient silver: A reply to Pernicka

Jonathan R. Wood, Michael F. Charlton, Mercedes Murillo-Barroso and Marcos Martinón-Torres

UCL Institute of Archaeology

Abstract

We present a detailed response to Professor Pernicka's critique of our paper entitled "Iridium to provenance ancient silver". We have concluded that Pernicka's hypothesis, which suggests that elevated levels of iridium in ancient silver artefacts is a consequence of silver deriving from the cementation (parting) process, does not account for the available evidence and that his critiques of the analyses we presented seem misplaced. We offer a simpler solution and show that the structure of our transformed data is founded on logical reasoning which is borne out by the empirical results. Essentially, this response supports our view reported in the original paper that the variation in iridium in ancient silver is largely geological rather than a consequence of de-silvering gold.

Key words: iridium; silver; log-ratios; cementation; geological variability; lead isotopes

Introduction

We realise that our paper "Iridium to provenance ancient silver" offers new ideas that need discussion and we are very grateful to Professor Pernicka for his critical insight. In fact, we are pleased that our assessment of data which has been in the archaeological literature for about 30 years, has prompted him to re-evaluate his position on iridium and the significance of gold parting more explicitly than in his recent review articles on provenancing of ancient silver and gold (Pernicka, 2014a; Pernicka, 2014b).

At its core, our paper is an empirical reassessment of some of the compositional data in the literature where iridium was reported. Our aim was to show that there is structured *variation* in the gold and iridium levels in ancient silver which can, with due critical consideration, be used to investigate the provenance of the silver. We are very grateful for Pernicka's detailed geological analysis of platinum group elements (PGE), and we recognise its merit. However, what our reanalysis of the legacy data shows is that both gold and iridium are useful for discriminating silver objects, regardless of the mechanism – and this is unchallenged by his comment.

Iridium and gold-silver parting

Pernicka has attempted to explain some of the iridium concentrations we presented as a consequence of argentiferous gold being de-silvered using the cementation parting process that was initiated at Sardis, the Lydian capital, in the sixth century BC. In his view, the only way to explain high iridium levels in archaeological silver would be as a result of contamination from the gold during this reaction, by (partial) chlorination of the iridium and subsequent deposition in the cement together with the silver chloride. This is an interesting proposal and Pernicka may be correct, but his hypothesis is at present unsubstantiated by the data, and it makes more assumptions than ours. The initial discussion of the NAA elemental analyses conducted on the silver from Sardis maintained that the silver most likely derived from cerussite ores in Anatolia and stated explicitly: "silver metal could in theory have been recovered from the cementation process… However, there is no evidence either directly or from archaeological finds or literary sources or indirectly from elemental compositions of Anatolian silver, that silver was produced in this manner" (Meyers, 1983: 188). The evidence subsequently presented by Ramage and Craddock (2000) showed that parting did take place, and highlighted that the main evidence for recovery of silver from parting vessels and furnace fragments were the numerous small hollows scooped in the dust at the site, some of which had high lead in the clay linings (Craddock, 2000a: 208-209). We are not saying that silver recovery from parting vessels did not happen in antiquity, but we are questioning whether the evidence supports its existence at

the scale required by Pernicka to supply the corpus of Byzantine and Sasanian silver we reanalysed. The reason we focus on Sardis in this reply is that silver recovered there is potentially recovered from parted gold (which is why we excluded it from our reanalysis), and gold and iridium data are available (Meyers, 1983). Thus, we can use this silver to evaluate Pernicka's hypothesis.

Let us start with some implications of Pernicka's hypothesis as they relate to mining activity, the composition of silver, and technological trajectories. As we noted in our Table 1 (Wood et al., 2017), 75% of our Near Eastern silver group has elevated iridium levels. If we believe Pernicka's claim that all of this silver was generated by parting, then it would follow that only the remaining 25% of Near Eastern silver was produced by mining (even less if we adopt his suggestion of 33ppb Ir as the cut off, rather than our median value of 44ppb). Considering that there is three times as much gold than silver in alluvial gold, but that silver is a much more common metal than gold, this seems a lot of silver coming from parting compared to mining, and such intensity should leave an observable archaeological trace.

Furthermore, Pernicka claims that silver obtained from the parting process "should contain in the order of 1% gold". If we assume that the nine Sardis silver objects analysed (eleven measures in total) derive from cementation parting, it is worth noting that they have only moderately high levels of gold (mean=0.26 wt%, s=0.14), i.e. lower than the gold levels of the Sasanian and Byzantine silver (mean=0.6 wt%, s=0.17) and well below Pernicka's indicative figure. This would imply that the parting process was less efficient in later periods than at its inception. While possible, this pattern suggests a trend opposite to most technological systems and requires an alternative sociocultural explanation. For now, we believe our hypothesis of a unique, as yet unidentified Ir-rich silver deposit offers a more elegant and parsimonious explanation of the observed phenomenon.

Pernicka correctly points out that the lead isotope analysis (LIA) signature from silver recovered from parting vessels would be influenced by exogenous lead used in the process. As far as we know, no LIA analyses have been conducted on the Sardis silver, so it is not possible to determine whether

there are any mixing lines (as we have done using Pb crustal ages and the iridium concentrations of the silver objects in our paper, which we attributed to exogenous lead during smelting). The iridium range for silver objects at Sardis analysed is between 0.78ppb-280ppb, providing a wide spread of data which lays below the Sasanian objects in the log-ratio plot (Figure 1, below). If Pernicka's interpretation is correct that the iridium is enriched together with silver in the cementation material, then the spread of iridium values would presumably be due to variations in the amount of iridium forming a chloride during cementation and ending up as traces in the silver. Without more data or an understanding of how iridium partitions during cementation, this is difficult to ascertain. However, the evidence currently available would seem to argue against his proposal. First, it is not clear whether iridium would form a chloride under such conditions. According to Ogden (1977), PGE inclusions in gold are not affected by the modern chlorination refining process, and experiments suggest that only some inclusions are attacked by chlorine at temperatures over about 650°C. However, iridium chloride decomposes to metal with continued heating (Leddicotte, 1961: 6) with a decomposition temperature of 763°C or lower (Newkirk and McKee, 1968), i.e. below 800°C, the holding temperature proposed by Pernicka for cementation. This suggests that conditions were not favourable for iridium chloride to be stable during the cementation process, if it formed at all. In a review of the behaviour of PGE inclusions in gold during parting, Craddock (2000: 239) noted that these are largely unaffected by solid-state cementation, and cited iridium in particular as an element whose presence decreased the susceptibility of PGE inclusions to halogen attack. As he notes, the survival of iridium-rich PGE inclusions in Lydian coins made of refined gold corroborates the fact that elements such as iridium would generally not be affected by salt cementation. In sum, while we acknowledge the worth of Pernicka's hypothesis, it seems unlikely that partitioning of iridium during the cementation process would explain all the high iridium concentrations in archaeological silver. In fact, high levels of iridium (up to 900ppb) and other PGE have been reported for South American silver coins (Guerra, 2004), which derive from silver mines rather than de-silvered gold. We would

also like to highlight that high levels of gold have been found in Bronze Age silver thought to derive from cerussite ores (e.g. Meyers, 2003: Table 3), i.e. predating the inception of cementation parting.

This leads us to maintain our view that variation in the iridium levels of ancient silver is in many cases a consequence of geological variability of the ore from which the silver derived. Even if human technological processes such as mixing may be at play and obscure these patterns, the evidence makes it unlikely that iridium content is primarily a side-effect in silver recovered from cementation parting.

Lead isotope data, log-ratios and correlations

Pernicka also takes issue with our use of Pb crustal ages based on lead isotope data, as it "does not provide any additional information" (Pernicka 2017). It is perhaps necessary to reiterate the point made in the original paper, where we clearly state that this approach "is not considered as a replacement for traditional lead isotope plots (which may allow variability in specific ratios to identify differences between objects and ores) but as an alternative that allows presenting on one plot the variability within lead isotope measurements alongside trace element data." (Wood et al. 2017:5). As a matter of fact, we use this not only in conjunction with elemental concentrations but also with the traditional lead isotope plots that Pernicka favours (e.g. Wood et al. 2017: Figure 11). Significantly, Pernicka uses the Orrescii coins as a case in point to argue the alleged flaws in our approach, but he is compelled to concede that his conclusion is the same as ours: that the signature of these coins is different from that of the Laurion ores (Wood et al. 2017: 6). If anything, the agreement between his conclusion and ours validates our approach, with the advantage that ours considers both isotopic and trace element data, as recommended by most studies on metal provenance (e.g. Pernicka 2014a). To say it once again: we are not advocating the replacement of traditional LIA plots. What we do argue is that using the crustal age on the same plot as compositional data is a way to visualise patterns that may not be otherwise apparent, as demonstrated in our paper.

We also appreciate that we could have used several parameters to represent the skewed distribution of the iridium levels in our geographically and chronologically disparate data set. We chose the median to represent the data because it is a more robust measure of central tendency amongst skewed distributions and in the presence of outliers. Pernicka suggests using the log-scaled distribution but he also rightly points out that it makes very little difference.

Perhaps more importantly, we believe Pernicka is wrong in his dismissal of our use of log-ratio plots as a "flawed application of statistical packages". His argument is that the correlations we observe in ratios "are to be expected" and that "plotting the silver versus gold… will always result in a **spurious** correlation" (Pernicka, 2017; his emphasis). He then refers to his Figure 2 (a plot of silver versus gold, which is incorrectly captioned as double logarithmic), presumably as proof of this correlation. Eyeballing this graph might lead one to the false impression that it does show a correlation, but a more objective calculation of the correlation matrix shows that this is not the case. Tables 1 and 2 show correlation matrices of all the raw, transformed and ratio measures for the entire dataset and for the Sasanian subset, respectively. They clearly demonstrate that there is no such correlation between gold and silver. Conversely, elemental ratios and, especially, log-ratios, are strongly correlated – i.e. exactly as we claim in our original article.

While the above demonstrates, in practice, the usefulness of our approach, in our paper we also lay out the fundamental principles that justify its use: namely, that this plot is a way of handling the constant sum constraint. The rationale has been made many times (e.g. Aitchison 1986) that the resulting linear and clustering patterns (like the Sasanian Royal silver) are more meaningful, at least with respect to provenance, than auto-correlated raw compositional data. Furthermore, as also mentioned in our paper, a further reason for using log-ratios is that they deal with *relative* rather than absolute magnitudes and variations of the components. We believe that this is a more consistent way of dealing with compositional data, especially when it is highly unlikely that the amounts of all components are known.

Two predictions derived from regionalised variable theory are: 1) that features of local geological formation processes will be positively correlated with one another and; 2) the functions that define the correlated phenomena will differ between locations as a consequence of varying geological histories. We argue that the data which lies on lines on these log-ratio plots reflects this regionalised tendency, i.e. silver from the same deposit. We appreciate that this may be debatable, but less so than Pernicka's claims. If most of the gold in the silver was "a remnant of the cementation process" (Pernicka 2017), variations in the degree to which gold was purified (and, presumably, in the extent to which iridium would contaminate the silver) would affect the log-ratio plot. We can again use the Sardis data for illustrative purposes, assuming that it derives from parted silver (Figure 1): on the log-ratio plot, this dataset appears scattered and does not lay on a particularly straight line; this raises the question of why Sasanian data is relatively linear if most of it is also supposed to derive from parted silver. In other words, we are not claiming that there is no parting in the silver we re-analysed, but we question its prevalence and maintain that the variation in iridium levels is more likely to be geological, even though the mechanism for its enrichment in the silver metal is unspecified.

Concluding remarks

Overall, we really appreciate that Pernicka has taken time to re-evaluate our reanalysis of the iridium data from the archaeological literature. We tend to side with the view in our paper, that the variation in iridium is largely geological rather than a consequence of de-silvering gold, and that it can be useful as a complementary proxy for provenancing. Pernicka's attempt to find a metallurgical mechanism to explain the elevated gold and iridium levels in Sasanian and Byzantine silver is worthy of further consideration, and it should warrant additional research. We are very happy that we have contributed to providing a forum for this open exchange of ideas.
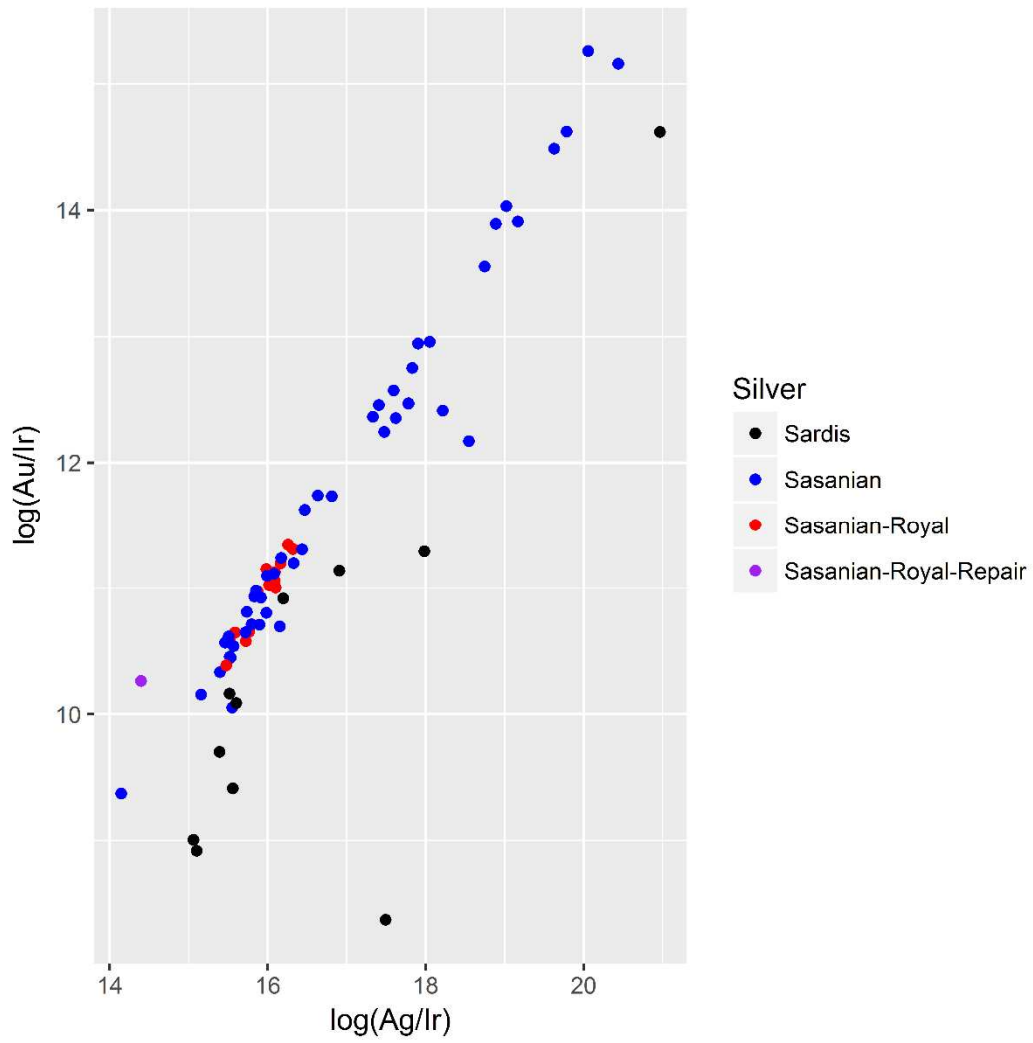
Figure 1 Log-ratio plot showing the compositional data from the Sasanian silver (Harper and Meyers, 1981) and the silver recovered at Sardis (Meyers, 1983).

	Ag	Au	Ir	Ag/Ir	Au/Ir	log (Ag)	log (Au)	log (Ir)	log (Ag/Ir)	log (Au/Ir)
Ag	**1.00**	0.07	-0.08	0.09	0.17	1.00	0.04	-0.12	0.17	0.17
Au	0.07	**1.00**	0.34	-0.45	-0.14	0.08	0.86	0.50	-0.49	-0.19
Ir	-0.08	0.34	**1.00**	-0.21	-0.27	-0.07	0.27	0.69	-0.69	-0.70
Ag/Ir	0.09	-0.45	-0.21	**1.00**	0.61	0.08	-0.66	-0.69	0.69	0.51
Au/Ir	0.17	-0.14	-0.27	0.61	**1.00**	0.15	-0.14	-0.68	0.68	0.75
log (Ag)	1.00	0.08	-0.07	0.08	0.15	**1.00**	0.04	-0.11	0.15	0.15
log (Au)	0.04	0.86	0.27	-0.66	-0.14	0.04	**1.00**	0.58	-0.58	-0.22
log (Ir)	-0.12	0.50	0.69	-0.69	-0.68	-0.11	0.58	**1.00**	-1.00	-0.92
log (Ag/Ir)	0.17	-0.49	-0.69	0.69	0.68	0.15	-0.58	-1.00	**1.00**	0.92
log (Au/Ir)	0.17	-0.19	-0.70	0.51	0.75	0.15	-0.22	-0.92	0.92	**1.00**

Table 1. Correlation matrix for Ag, Au, Ir and relevant ratios and log-ratios for the entire dataset used in Wood et al. (2017). Correlation coefficients ≥0.65 are highlighted.

	Ag	Au	Ir	Ag/Ir	Au/Ir	log (Ag)	log (Au)	log (Ir)	log (Ag/Ir)	log (Au/Ir)
Ag	**1.00**	0.25	-0.31	0.27	0.26	1.00	0.21	-0.29	0.35	0.34
Au	0.25	**1.00**	0.21	-0.05	0.07	0.27	0.97	0.23	-0.21	-0.05
Ir	-0.31	0.21	**1.00**	-0.43	-0.41	-0.28	0.23	0.79	-0.80	-0.77
Ag/Ir	0.27	-0.05	-0.43	**1.00**	0.97	0.24	-0.06	-0.80	0.80	0.81
Au/Ir	0.26	0.07	-0.41	0.97	**1.00**	0.23	0.06	-0.78	0.78	0.81
log (Ag)	1.00	0.27	-0.28	0.24	0.23	**1.00**	0.23	-0.26	0.32	0.31
log (Au)	0.21	0.97	0.23	-0.06	0.06	0.23	**1.00**	0.24	-0.22	-0.06
log (Ir)	-0.29	0.23	0.79	-0.80	-0.78	-0.26	0.24	**1.00**	-1.00	-0.98
log (Ag/Ir)	0.35	-0.21	-0.80	0.80	0.78	0.32	-0.22	-1.00	**1.00**	0.98
log (Au/Ir)	0.34	-0.05	-0.77	0.81	0.81	0.31	-0.06	-0.98	0.98	**1.00**

Table 2. Correlation matrix for Ag, Au, Ir and relevant ratios and log-ratios for the Sasanian silver data used in Wood et al. (2017). Correlation coefficients ≥0.65 are highlighted.

References

Aitchison, J. (1986) *The statistical analysis of compositional data*. London: Chapman and Hall.

Craddock, P.T. (2000a) Reconstruction of the salt cementation process at the Sardis refinery. In: Ramage, E. and Craddock, P.T. (eds.) *King Croesus' gold: Excavations at Sardis and the history of gold refining*, British Museum Press, London, 200-211.

Craddock, P.T. (2000b) The Platinum Group Element inclusions. In: Ramage, E. and Craddock, P.T. (eds.) *King Croesus' gold: Excavations at Sardis and the history of gold refining*, British Museum Press, London, 238-244.

Guerra, M. F. (2004) The circulation of South American precious metals in Brazil at the end of the 17th century, *Journal of Archaeological Science*, 31, 1225-1236.

Harper, P. O. and Meyers, P. (1981) *Silver vessels of the Sasanian Period Vol.1 Royal Imagery*, The Metropolitan Museum of Art, Princeton University Press.

Leddicotte, G.W. (1961) The Radiochemistry of iridium, National Academy of Sciences, Nuclear Science Series, NAS-NS345, US Atomic Energy Commission.

Meyers, P. (1983) Elemental composition of silver objects found by the Princeton expedition. In: Waldbaum, J.C., *Metalwork from Sardis*, Harvard University Press, Cambridge, Massachusetts, 185-191.

Meyers, P. (2003) Production, distribution, and control of silver: Information provided by elemental composition of ancient silver objects. In: van Zelst, L. (ed.) *Patterns and Process: A Festschrift in Honor of Dr. Edward V. Sayre,* Smithsonian Center for Materials Research and Education, 271–288.

Newkirk, A.E. and McKee, D.W. (1968) Thermal decomposition of rhodium, iridium and ruthenium chlorides, *Journal of Catalysis*, 11, 370-377.

Ogden, J. M. (1977) Platinum group metal inclusions in ancient gold artifacts, *Historical Metallurgy*, 11, 53-72.

Pernicka, E. (2014a) Possibilities and limitations of provenance studies of ancient silver and gold, In: Meller, H.H., Risch, R. and Pernicka, E. (eds.) *Metals of power – Early gold and silver*, Tagungen des Landesmuseums fur Vorgesschichte Halle, 11, 153-164.

Pernicka, E. (2014b) Provenance determination in archaeological metal objects, In: Roberts, B.W. and Thornton, C.P. (eds.) *Archaeometry in global perspective: Methods and synthesis*, Springer.

Pernicka, E. (2017) Provenance and recycling of ancient silver. A comment on "Iridium to provenance ancient silver" by Jonathan R. Wood, Michael F. Charlton, Mercedes Murillo-Barroso, Marcos Martinón-Torres. J. Archaeol. Sci. 81, 1-12. *Accepted by Journal of Archaeological Science*.

Ramage, A. and Craddock, P.T. (2000) *King Croesus' gold: Excavations at Sardis and the history of gold refining*, British Museum Press, London.

Wood, J.R., Charlton, M.J., Murillo-Barroso, M. and Martinón-Torres, M. (2017) Iridium to provenance ancient silver, *Journal of Archaeological Science*, 81, 1-12.