

Nondestructive Pb Isotope Sampling and Analysis of Archaeological Silver Using EDTA and ICP-MS

Archaeologists have long employed lead (Pb) isotope analysis in efforts to identify the geologic sources of artifacts composed of or containing that metal. This paper describes a nondestructive, fast, and inexpensive method of Pb isotope sampling and analysis that involves ethylenediaminetetraacetic acid (EDTA) and inductively coupled plasma-mass spectrometry (ICP-MS). It has been successfully employed in provenance studies of lead-glazed ceramics¹ and lead metal artifacts.² It is used here in an attempt to determine the geologic sources of silver artifacts excavated at two sites of the Indus Civilization (ca. 2600–1900 BC) of Pakistan and northwestern India.

The element lead has four isotopes (²⁰⁸Pb, ²⁰⁷Pb, ²⁰⁶Pb, and ²⁰⁴Pb) that vary in absolute amounts, depending on the geologic age of the lead deposit and the conditions in which it mineralizes. The lead isotopes do not undergo physiochemical fractionation when an ore is smelted or when the extracted metal is fashioned into finished objects.³ Thus, an artifact containing lead from a single deposit will retain the original isotopic composition of that deposit. Although it is a potential problem that alloyed or recycled metal objects may contain lead derived from multiple sources, Pb isotope data are, nonetheless, extremely useful for archaeological studies attempting artifact-to-ore source correlation. This includes artifacts composed of silver, which is most commonly obtained through the cupellation (refinement through the oxidation of base metals) of argentiferous (silver-rich) lead ores.

Extracting lead from silver artifacts using EDTA

Silver ornaments from the Indus Civilization sites of Mohenjo-Daro and Allahdino were made available for this study by Dr. Fazal Dad Kakar (Director-General of the Department of Archaeology and Museums, Government of Pakistan) with the stipulation that the rare artifacts not be altered in any way. In order to extract lead from them for isotopic analysis, a solution was prepared that consisted of ultrapure water and 0.05% dissolved EDTA—a hexadentate chelating agent that forms coordinate bonds with lead atoms. The sampling procedure was simple (Figure 1). Each silver ornament was first cleaned in purified water, placed into a disposable plastic tray, and approximately 50 mL of the EDTA solution was poured into the tray immersing it (Figure 2). The artifacts remained in the sampling solution for 5 min while the trays were lightly agitated at 20-sec intervals. This short immersion time was usually sufficient to extract lead atoms in concentrations from 100 ppb to as much as 100 ppm—orders of magnitude more than minimally required for ICP-MS analysis. At that point, the lead-enriched solutions were poured into sample vials for return to the laboratory. The ornaments were rinsed in ultrapure water, allowed to dry, and then returned to their place of storage or display. Although this method is technically destructive in that Pb atoms form 1:1 bonds with the EDTA and are removed from sampled objects, the brief immersion time in the sampling solution did not result in any macroscopic alteration of the silver artifacts whatsoever.



Figure 1 The simple process of extracting lead from a silver ornament at the National Museum, Karachi, Pakistan, using an EDTA solution.

ICP-MS analysis: Precision and accuracy

The lead-enriched sample solutions were returned to the United States and analyzed at the Laboratory for Archaeological Chemistry (LARCH), University of Wisconsin-Madison, on a Thermo Finnigan MAT Element I high-resolution magnetic-sector ICP-MS (Bremen, Germany). For accurate counting statistics, 10⁷ counts per sec (approx. 10 ppb) were required against a background of approximately 10⁴ counts per sec. An EDTA-sampled solution of the NIST Common Lead Isotopic Standard (SRM 981) was assayed before and after each group run of five samples. Based on repeated measurements (n = 44) of this standard, the overall precision (Table 1)—an expression of analytical error based on the relative standard deviation (%RSD) of those measurements—was calculated to be under 0.2% for ratios constructed using the isotopes ²⁰⁸Pb, ²⁰⁷Pb, and ²⁰⁶Pb. It was significantly higher (0.86%) for ratios using ²⁰⁴Pb. Although considerably less precise than thermal ionization mass spectrometry (TIMS), which typically produces measurements with a precision of 0.005–0.01 %RSD,⁴ the ICP-MS has, nonetheless, provided values (for all ratios except those using ²⁰⁴Pb) for which it is possible to be confident to at least three significant digits. Furthermore, the frequently assayed NIST standard has been used to adjust (correct) measured isotopic values on the samples to more accurately reflect what their true values likely are. This was done by taking the average of the values measured for the two bracketing standards (one run before and one after five samples), calculating how that average varied from the NIST standard, and adjusting the measured values on the bracketed samples by the difference.

In order to gauge the accuracy of this technique and the corrections applied to the data it provided, one lead ore (galena) sample each from two isotopically well-characterized argentiferous lead occurrences in southern Rajasthan, India—the Zawar mines and the Rajpura-Dariba/Rampura-Agucha zone—were analyzed using the EDTA/ICP-MS method. The data were compared to the published⁵ TIMS produced values from those two ore fields. In both

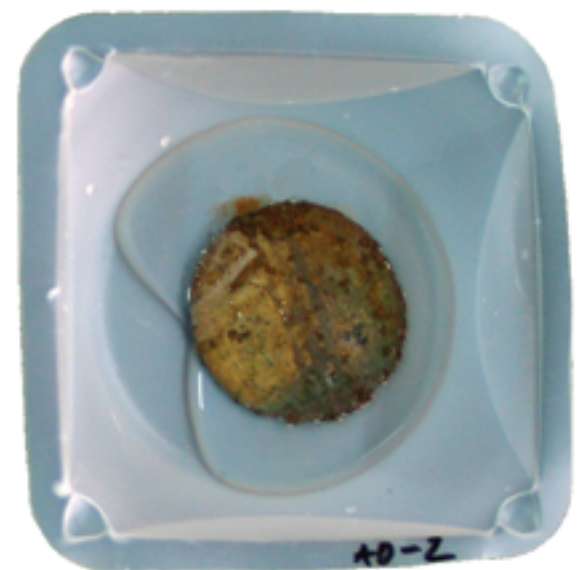


Figure 2 A silver bead from Allahdino immersed in EDTA sampling solution.

cases, the corrected EDTA/ICP-MS isotopic values for the geologic test samples closely matched those of the highly accurate TIMS method (Figure 3).

Results

Ten silver ornaments from Allahdino and five from Mohenjo-Daro were assayed using the EDTA/ICP-MS method described above. The results were compared to an extensive database⁶ of Pb isotope values for South Asian lead and lead-silver ore deposits. In Figure 4, the values for the 15 artifacts are plotted in relation to select ore fields using the ratios ²⁰⁸Pb/²⁰⁶Pb (y-axis) and ²⁰⁷Pb/²⁰⁶Pb (x-axis).

Most of the silver ornaments from Allahdino have Pb isotope values identical to argentiferous lead deposits located in Pakistan's southern Balochistan region, which happens to be the source area closest to that ancient site. The five artifacts from Mohenjo-Daro (as well as two from Allahdino) are not clearly analogous to any source in the database and, thus, may be composed of silver extracted from an as yet uncharacterized argentiferous lead deposit. They do, however, plot near datapoints for certain deposits in Oman and the southern Rajasthan region of India. Further characterization of those particular deposits could eventually expand the isotopic range of one or both enough to encompass the datapoints of the artifacts in question. On the other hand, it is possible that the ornaments were fashioned from metal derived from multiple sources that are unlike

Table 1 Overall precision of the EDTA/ICP-MS method			
Pb/Pb ratio	208/207	207/206	207/204
NIST standard	2.3696	0.9150	15.4970
Mean of 44 measurements of the standard	2.3724	0.9157	15.5544
SD of mean	0.004384	0.00175	0.13352
Precision (%RSD)	0.19%	0.19%	0.86%

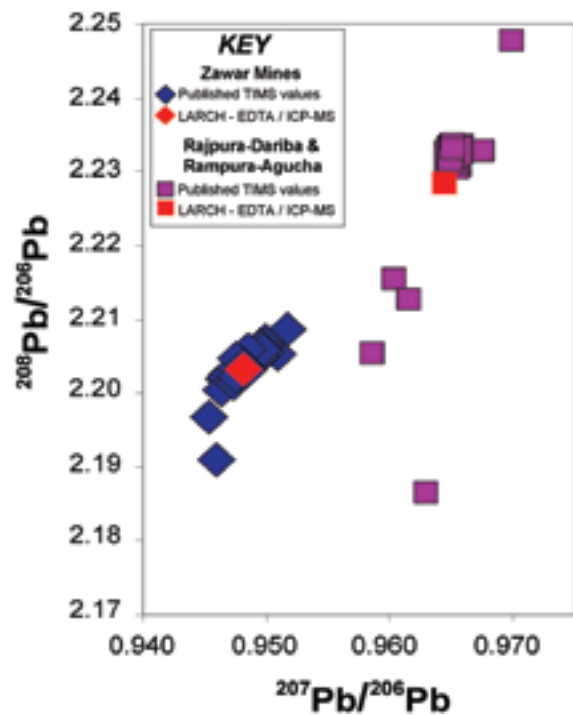


Figure 3 Accuracy of the EDTA/ICP-MS method.

isotopically. If so, then their measured values might reflect points on an isotopic “mixing line” between two (or more) sources rather than the characteristics of a single geologic deposit.

It is now possible to state, with a good degree of confidence, that ancient Indus Civilization peoples acquired some of the silver they used from sources in southern Balochistan, Pakistan. The provenances of a number of the ornaments examined remain unclear, however. This is not because the EDTA/ICP-MS method was used. The same provenance uncertainties and interpretive problems would exist even if the artifacts had been analyzed using TIMS. Those issues can only be clarified through new and/or additional characterizations of potential deposits and by developing a better understanding of the effects that alloying and source mixing might have had on the isotopic composition of silver artifacts.

Conclusion

Pb isotope sampling and analysis of archaeological silver using EDTA and ICP-MS is, for all practical purposes, nondestructive. No material need be chipped, scraped, or drilled from an artifact for sampling. Although Pb ions are physically removed from the surface of an object during immersion in the EDTA solution, this only takes place at an atomic level. Macroscopic alteration of artifacts is in no way evident. This feature is certain to appeal to excavators and museum curators who do not wish to see artifacts made from this precious metal defaced. Speed, ease, and cost of sample preparation and analysis are other advantages of the EDTA/ICP-MS method. In contrast to TIMS, samples need not be dissolved in hazardous acids, run through multiple purification columns, or painstakingly loaded onto filaments for analysis. EDTA-sampled solutions can usually be introduced directly into the ICP-MS. All of this keeps costs comparatively low. A final advantage of the method is that artifacts sampled for Pb isotopes in this way need not be removed from the location at which they are stored. A small kit containing purified water (for artifact cleaning before and after sampling), the nontoxic EDTA solution, disposable trays (for artifact immersion in the solution), and sample vials (for holding the sampled solution) can be taken directly to a site being excavated or a museum collection, and silver artifacts can be quickly and easily sampled.

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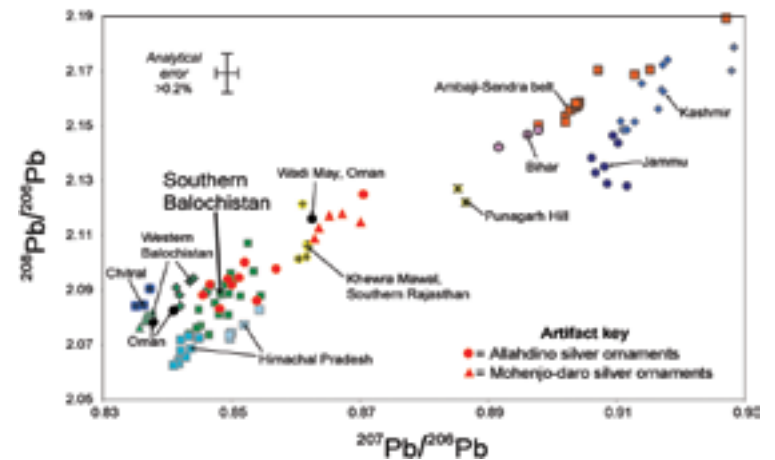


Figure 4 Pb isotope compositions of silver artifacts plotted in relation to select South Asian lead ore deposits.

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