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An Advanced Method of Laser Ablation MC-ICP-MS for Provenance Studies in Archaeometallurgy: Chalcolithic Metal Objects from Israel as a Case-Study

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Introduction

One of the main issues faced in archaeometallurgical research focuses on the provenance of ancient metals. Together with chemical composition, lead isotope ratios can be very useful in such studies. As lead fractionation does not occur during pyrotechnological processes (Barnes et al. 1978; Gale and Stos-Gale 1982) and lead isotope ratios are constant at all stages of ore treatment, smelting and refining, it is possible to compare lead isotope ratios in ores, slags and metal objects in order to define the sources of the ores from which the metal objects could have been produced.

The usefulness of lead isotope ratio studies to distinguish sources of ore depends on the precision of the technique by which the ratios have been measured. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) has considerably facilitated analytical measurement procedures by eliminating tedious sample separation (necessary when using Thermal Ionization Mass Spectrometry—TIMS), especially when analyzing heavy metals. It thereby enables rapid sample preparation. Furthermore, the introduction of the Multiple Collector ICP-MS (MC-ICP-MS) has significantly improved the precision of isotope ratio measurements (Halliday et al. 1998; Platzner, Ehrlich and Halicz 2001).

Conventional analyses using ICP-MS are usually based on the dissolution of part of, or, if the object is small, the entire sample. Moreover, when the sample is strongly corroded with traces of small remnants of pure metal, lead from the environment may also be dissolved with the sample, causing the results to be unreliable. The Laser Ablation (LA) technique (sample evaporation by focused laser beam) requires no dissolution and does minimal damage to the sample. The laser beam diameter is at least 10 μm; thus, even if most of the sample is strongly corroded, it is in many cases possible to target the beam on fresh metal.

When dissolved samples are analyzed for lead isotope ratios, high precision and accuracy may be obtained by spiking the samples with thallium (Tl). The spiking procedure enables the correction of the mass fractionation of the instrument and effectively eliminates the effects of plasma fluctuations and matrix (Ehrlich et al. 2001). However, when using laser ablation, the sample is analyzed in a solid state, making the correction of these factors problematic.

Kent (2008), who studied the homogeneity of glass NIST (National Institute of Standards) standard reference materials (SRM) 610 and 612, using LA-MC-ICP-MS, showed significantly better accuracy and precision for lead ratios corrected for mass bias by the sample-standard-sample bracketing method, as opposed to normalization using thallium present in NIST SRM 610. Unfortunately, the bracketing method corrects only mass bias and drift of mass spectrometer, but not the effects of matrix and of fluctuations in the plasma. Bracketing mode measurements are also time-consuming. On the other hand, thallium correction is only possible for solid samples containing thallium in relatively high concentrations with known isotope ratios.

Horn, Rudnick and McDonough (2000) described a method for correcting the mass discrimination of the LA Quadrupole (Q)-ICP-MS using combined solution nebulization and laser ablation sample introduction, the mixing for which was performed in a chamber attached directly to the end of a demountable torch. Noble et al. (2008) and Shepherd et al. (2009) described another method of mass bias correction using thallium solution aspirated through a desolvating nebulizer and passed through the laser ablation cell. Utilizing this method, the combined overall uncertainties (2σ) over a five-year period were: for $^{206}Pb/^{204}Pb$ ± 0.113%; $^{207}Pb/^{204}Pb$ ± 0.087%; $^{208}Pb/^{204}Pb$ ± 0.095%; $^{207}Pb/^{206}Pb$ ± 0.070%; and $^{208}Pb/^{206}Pb$ ± 0.033%.

LA-MC-ICP-MS has been used by Ponting, Evance and Pashley (2003) for lead isotope analysis of Roman silver coins. In the study, the external reproducibility using simultaneous thallium aspiration was better than when using conventional TIMS analysis: for $^{207}Pb/^{206}Pb$ ± 0.015% (2σ) compared to ± 0.04% in TIMS.

Lead isotope ratios in silver and copper artifacts were determined with MC-ICP-MS using LA and bulk dissolution, without the separation of lead from the matrix (Baker, Stos and Waight 2006). The results obtained by LA are comparable within the error to those of conventional TIMS analyses. Inaccurate LA analyses on low-lead copper reflect erroneous mass bias corrections from the use of a non-matrix matched standard. However, Baker, Stos and Waight suggested that in most cases, silver and copper objects may be analyzed using bulk dissolution or LA-MC-ICP-MS.

LA-Q-ICP-MS was used by Resano et al. (2008) for analyzing ancient Spanish lead-glazed ceramics. The raw ratios of the samples were corrected for mass discrimination using the ‘‘bracketing’’ method. In this manner, it was feasible to obtain internal precision in the range of ± 0.15–0.25% for the most abundant lead isotope ratios.

In the present study, we describe an advanced method of lead isotope ratio determination using MC-ICP-MS, based on the simultaneous introduction of thallium solution and a laser-ablated sample to the plasma.

INSTRUMENTATION, METHOD AND SAMPLES

Lead isotope ratio determination was executed using the LA LSX-213 system (Cetac Technologies, Omaha, Nebraska, USA) coupled with MC-ICP-MS (NU Instruments, Wrexham, UK) and an Aridus desolvation system (CETAC Technologies). The laser system employs a built-in Nd:YAG laser, with a final output wavelength of 213 nm. The spot size on the sample may vary, ranging from 10 to 200 µm. The helium carrier gas from the laser ablation cell was mixed with the argon gas stream from the Aridus using a glass coaxial bulb mixer. This device, compared to a T or a Y connector, maintains a more laminar gas flow and is less affected by pressure differences between the two gas flows. We found that the helium flow of 600 mL min^{-1} combined with 500 mL min^{-1} argon flow was optimal for maximum lead beam intensity.

Thallium solution was continuously introduced through the Aridus desolvation system, along with the sample aerosol from the laser ablation system. The experimental scheme used for the measurements was the same one used in Halicz and Gunter (2004). The operating conditions are shown in Table 1.

The precision and accuracy of the results were checked using homogeneous glass standards: NIST SRM 610 and 612, containing 426 and 38.6 ppm lead respectively. For each analytical batch, multiple analyses of these standards were conducted daily to monitor instrument performance. For the clarification of long-term stability, lead isotope ratios were measured over a four-month period. A comparison of lead isotope ratios was undertaken using earlier results for NIST SRM 610 solution, obtained using the same MC-ICP-MS coupled with an Aridus desolvation system (Platzner, Ehrich and Halicz 2001), which reduces polyatomic interferences,

Table 1. Operating Conditions for LA-MC-ICP-MS Analyses

MC-ICP-MS Operating Conditions	
RF power	1.1 kW
Reflected power	<7 W
Cones	Nickel (NuPlasma Type B)
Accelerating voltage	4000 V
Analyzer vacuum	2×10^{-9} mbar
Plasma gas-flow rate	13 l min^{-1}
Auxiliary gas-flow rate	0.90 l min^{-1}, optimized daily
Ion lens settings	Optimized for maximum intensity
MC-ICP-MS Acquisition Settings	
Dwell time	10 ms
Number of readings	15, one block
Laser Operating Conditions	
Laser wavelength	213 nm
He carrier gas	600 ml min^{-1}
Energy	585–735 V depending on concentration
Pulse repetition rate	10–20 Hz depending on concentration
Spot size	50–200 µm depending on concentration
Aridus Operating Conditions	
Spray chamber temperature	105°C
Desolvation temperature	165°C
Sweep gas	Ar, ~2.5 l min^{-1} optimized daily
Tl liquid uptake	100 µL min^{-1}

particularly from oxides and hydrides in the plasma.

In order to test the effectiveness of the methods proposed above, Chalcolithic copper-based artifacts found in the Peqi‘in and Qurunṭul caves (Segal 2002; Segal and Goren 2009) and previously analyzed using conventional Q-ICP-MS, were re-analyzed using LA-MC-ICP-MS. In addition, Chalcolithic copper objects from the Camel Site, whose chemical and metallographical composition had previously been studied (Segal and Rosen 2005), were analyzed here for lead isotope composition using LA-MC-ICP-MS.

RESULTS AND DISCUSSION

Lead isotope ratios in glass standards and their standard deviations (2σ), measured using LA-MC-ICP-MS with and without thallium correction, are presented in Table 2. Each given result is the average of five one-day measurements using the same operating conditions. The results clearly indicate that standard uncertainty for various isotope ratios with fractionation correction is up to twice as good than without it. The results obtained with thallium correction correspond well with the recommended values within the 2σ, whereas

Table 2. Comparison of Results for Five One-Day Replicates of NIST 610, with and without Tl Correction

Pb Isotope Sample No.	208/204	2σ	207/204	2σ	204/206	2σ	208/206	2σ	207/206	2σ
NIST 610, No Correction										
1	38.319	0.008	15.933	0.004	0.057601	0.000009	2.20737	0.00012	0.91779	0.00006
3	38.345	0.020	15.940	0.008	0.057589	0.000028	2.20823	0.00014	0.91798	0.00008
2	38.324	0.007	15.935	0.004	0.057604	0.000012	2.20744	0.00012	0.91783	0.00006
4	38.320	0.008	15.933	0.002	0.057604	0.000010	2.20735	0.00014	0.91777	0.00004
5	38.322	0.008	15.933	0.004	0.057602	0.000012	2.20733	0.00012	0.91779	0.00006
Average	*38.326*	*0.021*	*15.935*	*0.006*	*0.05760*	*0.00001*	*2.2075*	*0.0008*	*0.91783*	*0.00016*
2SU	0.005		0.001		0.000003		0.0002		0.00004	
% (2SU)	0.025		0.018		0.010		0.016		0.008	
NIST 610, With Correction										
1	36.877	0.008	15.480	0.004	0.058723	0.000012	2.16557	0.00013	0.90904	0.00008
2	36.886	0.018	15.480	0.006	0.058723	0.000028	2.16606	0.00016	0.90915	0.00008
3	36.889	0.007	15.485	0.004	0.058710	0.000014	2.16574	0.00012	0.90905	0.00006
4	36.877	0.012	15.480	0.004	0.058728	0.000018	2.16563	0.00014	0.90905	0.00004
5	36.896	0.008	15.487	0.004	0.058714	0.000012	2.16583	0.00014	0.90914	0.00006
Average	*36.885*	*0.015*	*15.482*	*0.006*	*0.05872*	*0.00001*	*2.1658*	*0.0004*	*0.90909*	*0.00010*
2SU	0.004		0.001		0.000003		0.0001		0.00002	
% (2SU)	0.020		0.018		0.010		0.008		0.005	
Recommended[i]	36.964	0.044	15.504	0.018	0.05867	0.00006	2.168	0.002	0.9096	0.0006
GSI[ii]	36.965	0.016	15.507	0.008	0.05864	0.00004	2.1677	0.0008	0.90944	0.00022

[i] From http://georem.mpch-mainz.gwdg.de
[ii] Data obtained using conventional MC-ICP-MS method (Platzner, Ehrlich and Halicz 2001).
SU = standard uncertainty, 2σ = standard deviation.

the systematic error for non-corrected data reaches up to ± 3.7% for some isotope ratios. The error of one measurement varies from ± 0.004 to 0.008% (2σ). The standard uncertainty of the average (2σ) of the five replicates without correction; for example, for $^{207}Pb/^{206}Pb$, it is 0.008% while with correction it is ± 0.005%.

The dependence of isotope ratio precision on lead concentration was examined using NIST 610 and 612 glass standards. It is clear that the precision is better with increasing concentration. The results of the long-term stability test are shown in Fig. 1. Comparison of the results for NIST 610 measured over the course of four months showed that standard deviation (2σ) for various lead isotope ratios is 5–9 times better with thallium correction than without it. Standard uncertainty of the average (2σ) during this period was: $^{208}Pb/^{204}Pb$ ± 0.042%, $^{207}Pb/^{204}Pb$ ± 0.016%, $^{204}Pb/^{206}Pb$ ± 0.020%, $^{207}Pb/^{206}Pb$ ± 0.018% and $^{208}Pb/^{206}Pb$ ± 0.027%.

ARCHAEOLOGICAL IMPLICATIONS

In applying the method described above to Chalcolithic copper artifacts found in Israel, lead isotope ratios measured using LA-MC-ICP-MS in samples from the Peqi‘in and

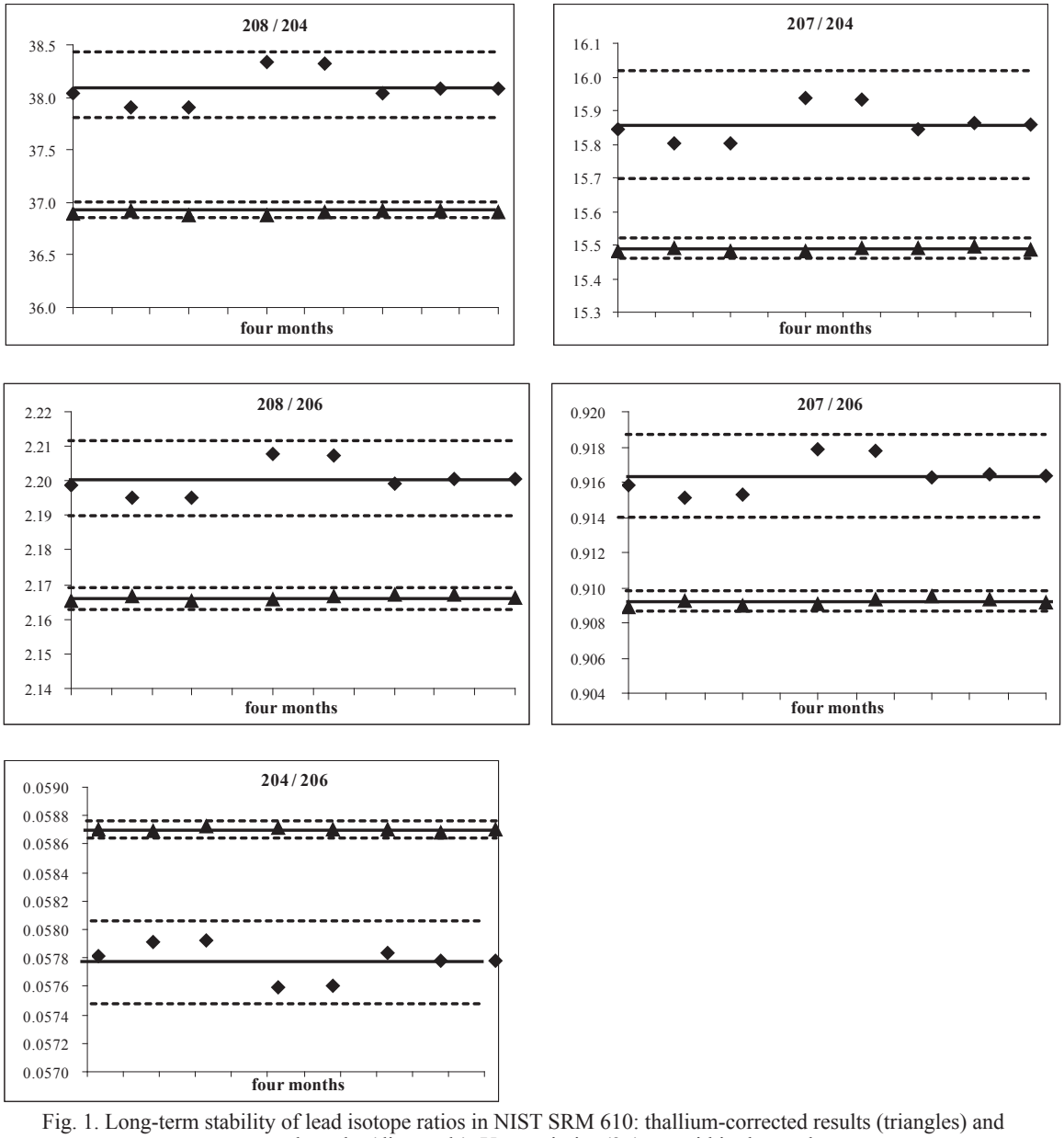

Fig. 1. Long-term stability of lead isotope ratios in NIST SRM 610: thallium-corrected results (triangles) and uncorrected results (diamonds). Uncertainties (2σ) are within the markers.

Qurunțul caves were compared with earlier results (Segal 2002; Segal and Goren 2009) obtained using the conventional Q-ICP-MS method (see Table 3). Figure 2 shows that correlation of the ratios is well within the error bars. The standard deviation reached using the new method is better than that of Q-ICP-MS and comparable with results from conventional MC-ICP-MS. Ratios for 204Pb/206Pb are not represented because of the very low lead concentration in the samples and, as a result, a high standard deviation of the Q-ICP-MS measurements.

Data for the objects from the Camel Site are presented in Table 4 and Fig. 3. In order to compare these data with the relevant ores

Table 3. Comparison of Results for Samples from Peqi'in and Quruntul Caves Obtained Using Conventional and LA-MC-ICP-MS

	LA-MC-ICP-MS	Q-ICP-MS	LA-MC-ICP-MS	Q-ICP-MS
	Pb208/206		Pb207/206	
Peqi'in Cave				
Mace	2.084(4)	2.088(6)	0.850(1)	0.853(3)
Mace head	2.088(3)	2.090(5)	0.8486(2)	0.849(3)
Axe	2.106(1)	2.109(6)	0.8591(3)	0.859(3)
Chisel	2.079(1)	2.079(6)	0.8352(1)	0.835(3)
Qurunțul				
Axe	2.086(2)	2.092(5)	0.8591(1)	0.860(2)

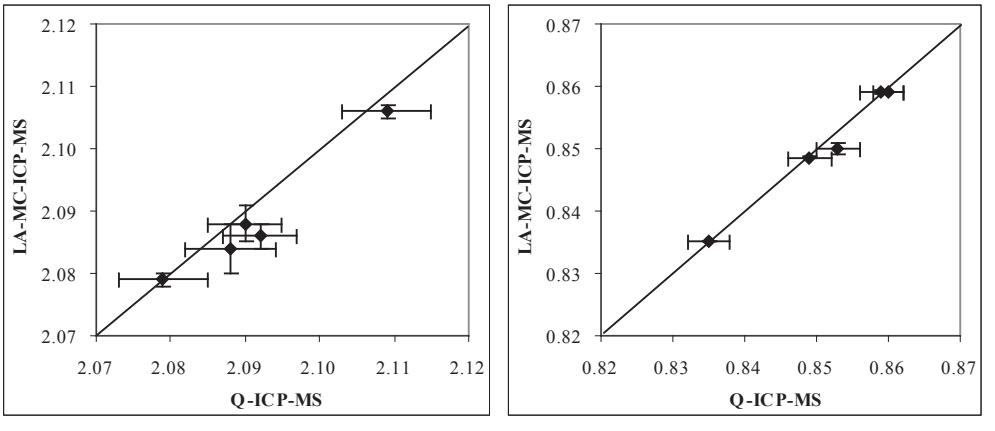

Fig. 2. Comparison of results for Peqi'in and Qurunțul artifacts obtained using LA-MC-ICP-MS and conventional Q-ICP-MS.

(see Fig. 3:a), the results of lead isotope ratios for ores in Feinan (Hauptmann et al. 1992), Timna (Gale et al. 1990) and Sinai (Hauptmann, Begemann and Schmitt-Strecker 1999) were also plotted. In addition, new ratios for the Timna ores—dolomites, shales and sandstones—recently defined in the Geological Survey of Israel using MC-ICP-MS, were also plotted (Asael et al. 2008; Segal et al. 2011). As Hauptmann et al. (1992) concluded, two types of copper ores—massive brown sandstones (MBS) and dolomite limestone shales (DLS)—were used in antiquity at Feinan. Feinan DLS ratios coincide with those of the Timna ores, whereas ratios for Feinan MBS are distinctly different.

Copper objects from the Camel Site fall within the Feinan field, with the exception of one point (lump, L30c-1) that is located within the Timna-Sinai ore field. This exceptional lump, contrary to the rest of the samples, contains 17% sulfur, with its chemical composition typical of copper sulfide prills in smelting slag. The lump was most likely lost during the smelting process. Two additional lumps, Q30b-2 and I32c, seem to have been the result of casting, as indicated by their purity. A square-sectioned awl (P30a) made of arsenical bronze revealed rather high

Table 4. Lead Isotope Ratios for Copper Objects from the Camel Site

	Point No.	Pb 204/206	σ	Pb 208/206	σ	Pb 207/206	σ
Q30b-1 Heavily Corroded Awl	3	0.05923	0.00017	2.109	0.003	0.8638	0.0011
P30a Square-Sectioned Awl	5	0.05575	0.00003	2.1178	0.00004	0.8688	0.00006
Q30b-2 Lump/Prill	5	0.0553	0.0004	2.0979	0.0007	0.8555	0.0001
I32c Lump	5	0.0571	0.0006	2.10742	0.00013	0.86355	0.00013
L30c-1 Cu Sulphide Lump	5	0.0569	0.0015	2.10082	0.00009	0.86646	0.0001

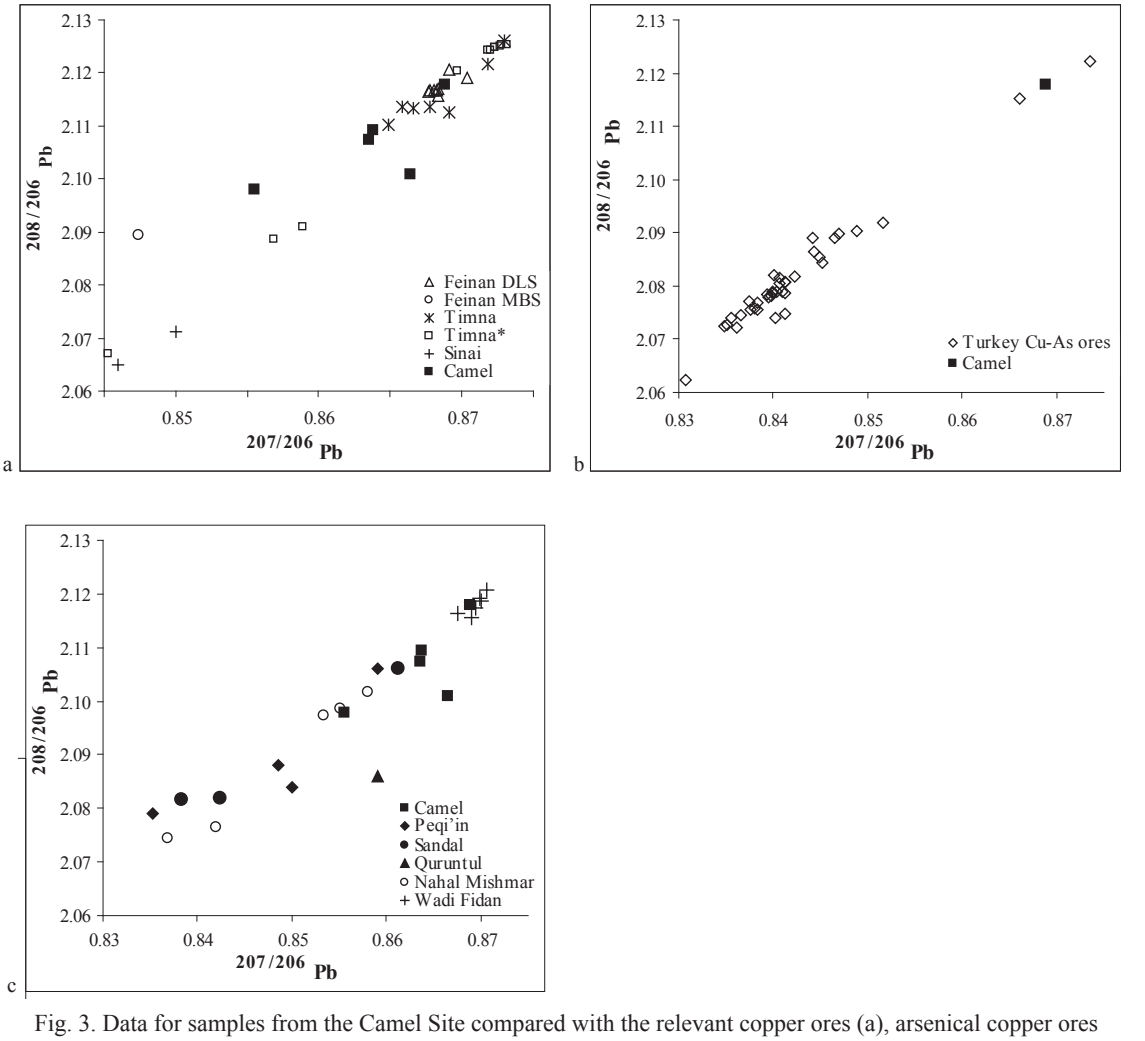

Fig. 3. Data for samples from the Camel Site compared with the relevant copper ores (a), arsenical copper ores from Turkey (b) and Chalcolithic objects (c); errors are within the markers;
*data obtained by GSI (Asael et al. 2008).

lead isotope ratios. In this case, the Feinan DLS is indistinguishable from the Timna ore; thus, the awl seems to have been manufactured using Feinan DLS or Timna ores.

The possibility of the utilization of arsenical copper ores, located in the region of Anatolia, was also considered for awl manufacturing. Figure 3:b shows the ratios of the arsenical copper bronze awl together with those for Turkish arsenical copper ores (Seeliger et al. 1985; Wagner et al. 1989; Hirao, Enomoto and Tachikawa 1995; Sayre et al. 2001). The ratios for the awl fall between two points of Anatolian ores, both located in the Horzum-Adana region. Figure 3:c shows that the data for the Camel Site artifacts fall within the same field as the Chalcolithic copper objects from Peqi‘in (Segal and Goren 2009), the Cave of the Sandal (Segal, Kamenski and Merkel 2002) and Naḥal Mishmar (Tadmor et al. 1995). The arsenical bronze awl perfectly matches the Wadi Fidan objects (Hauptmann et al. 1992). The copper sulphide lump and the Qurunṭul axe are exceptional and fall within the range of the Timna-Sinai ores.

CONCLUSIONS

This study presents the analysis of copper artifacts by the advanced method of lead isotope ratio measurement using LA-MC-ICP-MS and based on simultaneous correction of mass fractionation, matrix and time drift. The precision (2σ) of one-day results (N = 5) for NIST SRM 610 is within ± 0.005–0.02% for various isotope ratios, far better than without correction. Standard deviation (2σ) of a single measurement varies from ± 0.004–0.008%. Long-term standard uncertainty (2σ for various lead isotope ratios), over a four-month period is ± 0.016–0.042%, which is 5–9 times better with fractionation correction than without it. The results for the NIST SRM obtained with thallium correction are in accordance with the recommended values, within a 2σ error, whereas systematic error for non-corrected data reaches up to ± 3.7% for some isotope ratios.

The results obtained showed that the method presented here may be useful for archaeometallurgical provenance studies. The lead isotope ratios obtained through LA-MC-ICP-MS correlate well with analyses previously performed using solution. This precise method enabled the study of the provenance of small and corroded artifacts found at the Camel Site. The new data for copper objects from this site show that of the five objects analyzed, three matched the Feinan MBS field. Of the other two objects tested, the arsenical bronze square-sectioned awl falls within the field of both the Feinan DLS and Timna ores; however, ratios of arsenical copper ores from Horzum-Adana in Anatolia also match the object. The copper sulfide lump matches the Timna-Sinai ore field. With the exception of the copper sulfide lump, all of the artifacts from the Camel Site are similar to those from the Sandal and Peqi‘in caves, Naḥal Mishmar and Wadi Fidan.

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