



Application of LIBS and LA-ICP-MS analysis to Hellenistic tableware

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Abstract Greek and Hellenistic painted vases have attracted scholars of classical archaeology for centuries, either because of the artistic value of the painted decorations or because of the depicted scenes of ancient everyday life. Due to the application of thin slips on the surface, different methods are used for the chemical characterisation of the slips and the body of the same vase. The slips are commonly analysed by X-ray microanalysis, offering point-by-point analysis of mostly major elements, while different tools, such as X-ray fluorescence (XRF), inductively coupled mass spectrometry (ICP-MS), and instrumental neutron activation analysis (INAA), are used for bulk body analysis. This can cause difficulties in comparing the bulk composition and thus in determining the similarities and differences in the preparation process of the clay paste for the slips and bodies of an object. Given the artistic value of these objects, museum curators tend to be reluctant to provide samples for invasive characterisation. Micro-destructive laser ablation methods offer a robust solution to addressing both the relationships between ceramic body and surface treatment chemistry and destructive sampling. To provide a proof-of concept, we analysed slips and bodies of a small sample of Hellenistic fine wares from the Greek colony of Issa in modern Croatia with Laser-Induced Breakdown Spectroscopy (LIBS) and Laser ablation-ICP-MS. Results show remarkable diversity in the use of clay types and processing techniques.

1 Introduction

Hellenistic fine wares are renowned for their expert craftsmanship and technological sophistication. Chief amongst these are the shiny black surface treatments, variously referred to as glaze, gloss, and slip. The true magic of these surfaces, regardless of what we call them, is the expert manipulation of clay chemistry with precise control of kiln temperatures and redox conditions. These combined talents enabled potters to produce vessels with both black (reduced) and red (oxidised) surfaces from a single multiphased firing. Other surface colours including brown, red, grey, and white were also produced by Hellenistic potters, particularly those living in colonies away from the Athenian epicentre.

The wide distribution of Hellenistic pottery styles across the Mediterranean raises a number of intersecting questions concerning technology and exchange. Amongst these include:

- How diverse are Hellenistic slip recipes?
- How dispersed is the knowledge of multi-stage firing?
- What is the dispersion of slipped vessel production sites and the pottery they produced?
- How were suitable slip clays selected/prepared?
- Do body pastes and surface applications share a geological affinity?

Addressing these questions requires geochemical, mineralogical, and microstructural observations of vessel surfaces and bodies. Elemental analysis, in particular, has proved challenging, given the constraints imposed by micron scale surface thicknesses, heterogeneities of ceramic pastes, and the underlying assumptions of common characterisation methods. Common approaches to the elemental characterisation of ceramic surface treatments include X-ray microanalysis [1], [2], [3] and X-ray fluorescence [4]. These, however, fail to capture the measurement precision needed to consider provenance and can be difficult to apply separately to ceramic surfaces and bodies without measurement bias. Laser-based analytical methods, including Laser-Induced Breakdown Spectroscopy (LIBS) and Laser Ablation Inductively Coupled plasma Mass Spectrometry (LA-ICP-MS), offer both effective solutions to measurement bias and the added benefits of minimal sample preparation requirements ([5–9]). It is curious, however, that they are not applied with greater frequency to Hellenistic wares (but see [10]) where they could be used to shed light on the complex production and exchange networks of the Iron Age Mediterranean.

Following a brief review of Hellenistic ceramic technologies and pottery distribution, we describe the ongoing development of LA techniques applied to ceramic surface finishes at the UCL Institute of Archaeology's Wolfson Archaeological Science Laboratories.

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Fig. 1 Map showing the location of Issa within its Adriatic and Hellenistic context

As a proof-of-concept, LIBS and LA-ICP-MS are used to characterise the elemental chemistry of a small sample of Hellenistic fine wares from the Greek colony of Issa, on the island of Vis in modern Croatia (Fig. 1). The sample represents a diverse range of surface finish colours including black, brown, red, grey and white. Results show distinct differences between slip and body chemistry for darker coloured slips, though not for grey slips. Black and brown slip chemistries indicate at least three provenances of which one is consistent with Walton et al's [10] and two of which appear novel. Issa ceramic body chemistries, however, form a distinct group compared to those in Walton et dataset [10].

1.1 Review of Hellenistic firing technology and ceramic styles

Previous studies [3, 11–15] show that the black colour of slips results from the application of a thin, refined layer of clay rich in illite clay minerals and iron oxides. These sinter and vitrify in at lower temperatures and shorter time intervals than the clay used for the body. This slurry was applied to the vessels before firing, when pots were still moist, to prevent differential drying of the vessel

and coating [16]. Application could be made with a brush or by dipping the vessels into the slurry, and sometimes a combination thereof [17]. Once prepared they underwent a single firing with three stages (oxidising–reduction–oxidising). The chemical process can be explained by the decomposition of ferric oxide (Fe_2O_3), which is red, during firing under reduction conditions, to iron (II) oxide (FeO) and iron (II, III) oxide (Fe_3O_4), which are black [16, 18–20]. The firing temperature also played an important role, as all vessels with black slip were fired at maximum of 1000 °C [15, 18, 21]. On the other hand, the grey slips on surface were achieved by omitting the final re-oxidising phase, leaving the coloured of body and slip in same grey tone [14, 15].

Questions remain about the production of the colour and glossy appearance of the black surface finishes. Were the slips made from distinct clay choices [4], or of a common clay used to model a vase but refined by skilful levigation and settling [3, 13, 14, 21, 22]? If special clays were chosen, were they traded to other regions, or were the clays of similar geological species widely accessible? If special clays were not selected, were common ceramic clays further treated with vitriol or other weak acid to remove calcium carbonates [10], or altered with some other modification? Do slips vary depending on the skill and experience of the potters, kiln operators, and clay miners? Some regions, like Corinth, produced pots that failed to retain their slips well, resulting in brown or dull appearances on some vessels [23]. Bulk and trace elemental analyses can complement mineralogical and microstructural investigations to explore the relationships between technologies of clay processing, slip production, and provenance.

1.2 Elemental analysis of slips

X-ray microanalysis by scanning electron microscopy coupled with energy dispersive spectrometry (SEM–EDS) is one common approach that provides good major (> 1 wt%) and minor (> 0.1 wt%) elemental analysis of polished ceramic cross sections. The ~ 1 μm beam diameter is small enough to yield good data for homogeneous and low porosity surface treatments that tend to range between 5 and 100 μm . It is less effective, however, for the accurate analysis of ceramic pastes that tend to be composed of micropores and leading to low analytical totals. This proves consequential when functional differences between ceramic paste and slip are expected to be small and most provenance information is contained within trace element (< 0.1 wt%) compositions.

X-ray fluorescence (XRF) spectrometry (as handheld, bench-top, and floor instruments) is another common technique applied to ceramics and their surfaces. The generation of higher energy X-rays enables higher limits of detection and the measurement of trace elements but also tend to require larger analytical areas of several mm^2 and greater penetration depths (several mm for heavier elements). This precludes cross-sectional analysis of slips (10–100 μm thick) as well as accurate analyses of surfaces. XRF is most powerful when specimens can be homogenised into pressed powder pellets or fused glass beads. It is, however, possible to compare spectral differences between treated and untreated surfaces. Micro-XRF, using a spot size of ~ 20 μm , also provides an SEM–EDS like analysis of cross sections with similar performance across large areas.

Sampling surfaces by LA-ICP-MS or LIBS offers a solution to the problems of generating high-resolution data for ceramic surfaces and body pastes. With appropriate settings, it is possible to ‘excavate’ a line a few microns deep. This limits sampling to surface layers while generating high precision data that can cover almost the entire periodic table depending on technique and experimental parameters.

The procedure starts by focussing on the surface of specimen and selecting an ablation pattern. Once fired, the laser strikes the specimen and converts the surface material into a high temperature plasma. The plasma emits light as it cools with wavelengths characteristic of the atomic and ionic compositions of the material. Recording the intensity of these emissions enables compositional characterisation by LIBS. Particles condense as the plasma continues to cool and these can be conducted by a carrier gas (often helium) to another plasma source where they are again ionised and their isotopes sorted and counted according to by their mass. Integration of time resolved mass spectra provides the basis of measuring elemental composition by LA-ICP-MS. Both methods are capable of measuring large numbers of elements with sub-ppm limits of detection, but also come with distinct advantages and disadvantages.

LIBS can be operated with or without carrier gases with faster rates of data collection. A spectrum is collected for each laser pulse, and the same wavelengths of light are emitted regardless of gas (albeit with some variance in background levels and signal intensity). Ionic, atomic, and molecular emissions are generated spanning the entire periodic table but biased by the temperature of the plasma at the time of data collection. The emission spectra are sensitive to sample matrix and more complex than similar optical emission spectrographic techniques. This fact necessitates more time spent developing quantitative methods. Nonetheless, LIBS conducted in air is an inexpensive means of rapid chemical assessment that requires minimal sample preparation.

2 Experimental design

Twelve specimens of the Hellenistic fine tableware with different slips were supplied by the Archaeological Museum in Split and selected for analysis (Fig. 2). All materials were excavated from Martivilo, the western necropolis on Issa. Specimens include examples of Black Slip Ware, Brown Slip Ware, plain Grey Ware, Hellenistic Relief Ware with grey slip, Hellenistic Red Slip Ware, White Slip Ware and vases decorated in Gnathia style (Table 1).

A small section was removed from each using a fine bladed tile cutter and cleaned in an ultrasonic bath of Isopropanol. These were dried and mounted in the ablation cell with putty to achieve flat and level surfaces (to the degree possible).



Fig. 2 Photographs of analysed Hellenistic fine table ware. **A**—Black Slipped Ware (56016), **B**—Black Slipped Ware (67120), **C**—Gnathia ware (56508), **D**—Brown Slipped Ware (64891), **E**—Grey Ware (39081), **F**—Relief Hellenistic Ware (62052), **G**—Hellenistic Red Slipped Ware (39407), **H**—White Slipped Ware (67732)

Table 1 List of analysed samples of fine Hellenistic table ware from the Archaeological Museum in Split (AMS)

AMS ID	Type of ware	Shape
56016	Black Slipped Ware	Oinochoe
57962	Black Slipped Ware	Skyphos
39407	Hellenistic Red Slipped Ware	Table amphorae
67120	Black Slipped Ware	Oinochoe
56508	Gnathia Ware	Oinochoe
67127	Gnathia Ware	Oinochoe
64891	Brown Slipped Ware	Unguentarium
67732	White Slipped Ware	Oinochoe
67125	White Slipped Ware	Oinochoe
67643	Grey Ware	Kantharos
39081	Grey Ware	Kantharos
62052	Hellenistic Relief Ware	Bowl

2.1 Instrumentation and data acquisition

The instruments used to characterise the Hellenistic fine ware sample were an Applied Spectra, Inc J200 Tandem LA/LIBS unit equipped with a 213 nm Nd:YAG laser and 6 channel CCD spectrometer and an Agilent 7900 quadrupole ICP-MS.

2.1.1 LIBS

A 6-channel CCD spectrometer mounted within the LA unit was used to record atomic and ionic emissions between 190 and 1040 nm wavelengths after each pulse firing. (Detailed parameters are provided in Table 2.) Two sets of experiments were conducted, the first in concert with LA-ICP-MS in a He/Ar environment to facilitate direct comparison of slip chemistries between the two data sources and the second in air to explore changes in specimen chemistry from slip to body as well as assess the potential of LIBS as a rapid sorting tool. The first series of experiments consisted of ablating 3 lines of 1 mm length and 100 μm spot size across each slip. The second series of experiments consisted of ablating each specimen with a single line of 1 mm length and 100 μm spot size. Fifteen passes were made along each line at a higher repetition rate (20 Hz) and cell velocity (0.1 m/s) to create a rapid series of shallow ablations.

LIBS produces a spectra of intensities calculated in arbitrary units along the surveyed wavelengths, producing a graph of sharp peaks. The Clarity analytical software provides a starting point for peak identification using the TruLIBS database of atomic/ionic

Table 2 LA/LIBS-ICP-MS instrument parameters

Laser	ASI J200 Tandem LA/LIBS
Wavelength	213 nm Nd:YAG
Spot size	100 μm
Power	20%
Energy	0.25 mj
Repetition rate	10 Hz
Carrier gasses	He (chamber) + Ar (post-chamber)
Gas flow rate	0.7 L/min He + 0.7 L/min Ar
Warm up shots	Variable (30 and 100)
Experiment shots	Variable (560 and 589)
LIBS	6-Channel CCD spectrometer
Repetition rate	10 Hz (gas experiments), 20 Hz (air experiments)
Gate Delay	0.05 μs (gas experiments), 0.01 μs (air experiments)
Spectral generation	Accumulated
Wavelengths measured (nm)	Fe_238, Co_238.8, Fe_263, Mg_285, Si_288, Mn_294.9, Hg_296.7, Ni_356.6, Ti_368.5, Al_394.4, Ca_422.7, Sc_441.5, Ti_453.3, Ba_493.4, Mg_518.3, Pb_537.2, Cr_541, S_542.9, Sc_551, Ba_553.5, Na_589.5, Ca_612, Si_634.7, H_656.3, Li_670.8, K_766.5, Rb_780
ICP-MS	Agilent 7900
Dwell/integration time	0.01 ms
Sweep time	0.7070 / 0.7180 s
Background collection	30 s
Total acquisition time	2 min 1 s (1 line experiments) 4 min 30 s (3 line experiments)
Detection mode	Automatic
Isotopes measured	^7Li , ^9Be , ^{23}Na , ^{24}Mg , ^{27}Al , ^{28}Si , ^{29}Si , ^{31}P , ^{39}K , ^{43}Ca , ^{44}Ca , ^{45}Sc , ^{47}Ti , ^{51}V , ^{52}Cr , ^{54}Fe , ^{55}Mn , ^{56}Fe , ^{59}Co , ^{60}Ni , ^{63}Cu , ^{66}Zn , ^{71}Ga , ^{75}As , ^{79}Br , ^{85}Rb , ^{88}Sr , ^{89}Y , ^{90}Zr , ^{93}Nb , ^{107}Ag , ^{111}Cd , ^{118}Sn , ^{121}Sb , ^{125}Te , ^{133}Cs , ^{135}Ba , ^{139}La , ^{140}Ce , ^{141}Pr , ^{146}Nd , ^{147}Sm , ^{153}Eu , ^{157}Gd , ^{159}Tb , ^{163}Dy , ^{165}Ho , ^{166}Er , ^{169}Tm , ^{172}Yb , ^{175}Lu , ^{178}Hf , ^{181}Ta , ^{182}W , ^{185}Re , ^{197}Au , ^{205}Tl , ^{208}Pb , ^{209}Bi , ^{232}Th , ^{238}U
Calibration	
Method	Quadratic regression (LIBS) Ordinary Least Squares (LA-ICP-MS)
Internal standard	^{28}Si (LA-ICP-MS)
Quantification method	Sum normalisation (LA-ICP-MS)
SRMs	LIBS: NIST 610, NIST 612, NIST 614, NIST 679, USGS BCR-2G, USGS BIR-1G, BGS-111, BGS-112 (varies by element) LA-ICP-MS: NIST 610, NIST 612, NIST 614, NIST 679

emissions. Boundaries are chosen for the integration area of each peak and a nearby stable area selected for background removals. Other tools are available to model and remove areas with large backgrounds, though these have not been used in this study.

The use of LIBS in combination with LA-ICP-MS was used to provide a quick qualitative assessment of slip and body differences through comparison of raw spectra. Closer inspection of the data, however, reveals its potential value as a quantitative tool.

2.1.2 LA-ICP-MS

Two sets of experiments were conducted, the first in tandem with LIBS to investigate the slips in isolation and the second to provide repeat analysis of slips as well as the underlying body fabrics. The first series of experiments is described above. The second series consisted of ablating 3 parallel 1 mm lines across the slip followed by 2 additional passes to also reach the underlying body fabric. In cases where slip was still present after the third pass, the specimen position was shifted to enable ablation of a clean cross section.

The ICP was tuned before each run using the NIST 612 standard reference glass to optimise signal acquisition and limit the generation of spectral artefacts. Notably, the Th/U ratio was kept at ~ 1 to ensure low levels of fractionation, and the ThO/Th ratio kept $< 0.5\%$ to ensure low levels of oxide production in the plasma. Measured masses were selected to reduce influences from isobaric and polyatomic interferences as well as doubly charged ion species. Mathematical interference corrections were not used. Data were collected in the form of time resolved peaks of mass counts generated by ablating lines of 1 mm in length across the

sample material through a controlled number of laser pulses across a defined period of time. A gas blank was collected at the beginning of the experiment, followed by the ablation signal and eventual return to background. A plot of time vs sweeps—single counting periods of all isotopes within the analytical menu [24]—produces a short shallow signal (the background of the gas blank) and a ‘flat-topped’ peak from the ablation. A section of the background signal is averaged for each isotope and subtracted from the ablation signal. Integrated areas of the background-corrected mass peaks are the basis for calculating the chemical composition of a specimen using a calibration model.

All SRMs and ceramic specimens were placed in the J200 chamber and lines ablated as defined above. Single line ablations were divided into three equally sized areas for integration, while large sections of each of the three peaks for 3-line experiments were selected for integration. Care was taken to avoid the transient signal associated with the first 10 s of ablation in all cases. This practice reduces uncertainties in ablated material volume caused by changes in stage velocity and ensures a more stable flow of analyte into the plasma. Limits of detection were calculated following the procedure outlined by Longerich et al. [24]. In general, RSDs between integrated were less than 5, with notable exceptions for constituents near or below the limit of detection. Experimental parameters are provided in Table 2. All calibrations and quantifications were undertaken in R [28] using SRM data obtained from the GeoReM database [29] for NIST and USGS materials and certificates for the BGS materials.

2.2 Calibration

Quantification of the chemical concentration of an unknown specimen using any analytical technique requires comparison to one or more standard reference materials (SRMs) in which the chemistry is known or agreed. The mathematical relationship between accepted elemental concentrations for the SRMs and the analytical response is used as a calibration model to be applied to unknowns. Most techniques assume that sample specimens and SRMs are of similar chemical and mineralogical composition and introduced to the instrument in a similar form. The relationship material composition and detector response is known to be linear for ICP-MS as long as these assumptions are met. Atomic/ionic emission spectra generated by LIBS are more complex and can be modelled as quadratic relationships, of the form:

$$y = ax^2 + bx + c$$

where y wavelength intensities are created by the laser interaction with known independent standard reference materials concentrations (x). Intensities are measured as the integrated area under the peak identified with known emission lines. Because backgrounds are corrected, the calibration line is assumed to pass through the origin with offset c equal to 0. Resulting calibration lines were of variable quality with the accepted r^2 values ranging between 0.972 and 0.999. Some integrated emission peaks had to be abandoned for quantitative evaluation because of negative intensities (after correction) or failure to generate a predictable relationship. Examples of a good (Mg_518.3) and poor (S_542.9) calibration lines are provided as Figures S1 and S2 in supplemental data.

The characteristics of time-resolved peaks in mass spectra are influenced by electronic drift within instruments and subtle differences in matrix composition. Drift in laser energy and matrix composition have a direct impact on the amount of material ablated from a specimen and, therefore, chemical quantification. This can be corrected in part by selection of a suitable internal standard (IS)—some element that is a consistent matrix component of all SRMs and specimens being analysed. In the case of silicates, the most common choice of IS is silicon (Si) [25], though tests show that sodium (Na) and calcium (Ca) can also be effective choices [26].

The LA-ICP-MS calibration procedure used at the UCL Wolfson Archaeological Science Laboratory is a minor adaptation of that introduced by Neff [27].

- (1) Concentrations (x_{conc}) in the standard are divided by the concentration of the internal standard (IS_{conc}).

$$\text{Standardised concentration}(x_s) = \frac{x_{\text{conc}}}{IS_{\text{conc}}}$$

- (2) Background corrected element signal intensities (integrated isotope peak areas, y_{signal}) are divided by the signal intensities of the internal standard (IS_{signal}).

$$\text{Standardised signal}(y_s) = \frac{y_{\text{signal}}}{IS_{\text{signal}}}$$

- (3) Ordinary Least-Squares Regression of y_s on x_s for each element across all included SRMs generates a linear model for the relationship between the independent variable x_s and the dependent variable y_s of the form:

$$y_s = Kx_s + C$$

where K is the slope, and C is the y-offset. Background correction of x_s should ensure that any best-fit line passes through the origin and in practice the regression is forced to have y-offset (C) of zero. The quality of the calibration line may be judged by its coefficient of determination (r^2) and its fit with hypothesised matrices.

Graphs of all calibrated constituents are created to facilitate rapid inspection of line quality [26]. Standards that fail to provide a linear alignment due to matrix-related problems are removed. Note, however, that this criterion of exclusion only reflects the relationship to hypothesised unknown specimen matrices and is not carried out for the purpose of inflating r^2 values.

(4) Specimen concentrations (x_{conc}) are calculated by algebraic manipulation of the equation in step 3, above, and multiplication of both sides by the IS_{conc} :

$$\begin{aligned} x_s(IS_{\text{conc}}) &= \frac{y_s}{K}(IS_{\text{conc}}); \\ \frac{x_{\text{conc}}}{IS_{\text{conc}}}(IS_{\text{conc}}) &= \frac{\frac{y_{\text{signal}}}{IS_{\text{signal}}}}{K} IS_{\text{conc}} \\ x_{\text{conc}} &= \frac{y_s}{K}(IS_{\text{conc}}) \end{aligned}$$

(5) If IS_{conc} is known either by independent measurement (e.g. X-ray microanalysis or X-ray fluorescence) or by assumption (in the case of minerals and geological glass), then the appropriate values may be inserted into the equation.

Where IS_{conc} remains unknown, then we can follow 25, 28 and Neff [27] in assuming: (a) that all elements in the sample are being measured, and (b) that all or most constituents of geological rocks and similar synthetic materials (e.g. ceramics and glass) are present as oxides. Because the concentration of constituent x in a material represents a proportion of x to the total concentration of all constituents, then it is logical to conclude that its respective slope standardised signal (y/K) is a proportion of the total slope standardised signal.

$$\frac{x_{\text{oxideconc}}}{\sum_{i=1}^m x_{\text{oxideconc}(i)}} = \frac{\frac{y_{s-\text{oxide}}}{K}}{\sum_{i=1}^m \frac{y_{s-\text{oxide}(i)}}{K_i}}$$

Elemental concentrations in SRMs can be converted to appropriate oxides by stoichiometry prior to regression and oxide concentration ($x_{\text{oxide conc}}$) can be calculated as a proportion of the total of all oxide signals and normalised to 100% (or 1 million ppm).

$$\begin{aligned} \frac{x_{\text{oxideconc}}}{1,000,000\text{ppm}} &= \frac{\frac{y_{s-\text{oxide}}}{K}}{\sum_{i=1}^m \frac{y_{s-\text{oxide}(i)}}{K_i}} \\ x_{\text{oxideconc}} &= \frac{\frac{y_{s-\text{oxide}}}{K}}{\sum_{i=1}^m \frac{y_{s-\text{oxide}(i)}}{K_i}} \times 1,000,000\text{ppm} \end{aligned}$$

(6) The sum normalisation procedure described in (5) requires that those constituents whose measured compositions are less than the limit of detection be excluded. This necessitates that close inspection of the initial results and removal of those isotopes that fail to meet the criterion.

This study makes use of the sum normalisation procedure described above to generate concentration data for all specimens analysed. Calibration curves for all included constituents were high quality, with most $r^2 > 0.99$.

2.3 Data analysis

Data acquired from all LIBS and LA-ICP-MS experiments were investigated using principal component analysis (PCA) to identify and describe patterns of variability. Raw data were transformed to centred log-ratios (CLR) to overcome the constant-sum constraint [30] Specific questions being explored include:

- chemical relationships between slip and body clays
- diversity of slip recipes found in the Issaeon sample
- Comparison of sample slip and body fabric chemistries to the small sample from the collection of the J. Paul Getty Museum [10].

3 Results

Data quality for LIBS and LA-ICP-MS data was explored with clay SRMs NCS DC 60102 and NCS DC 60105 (Table S1) using the suggested values from Hunt et al. [31]. These reference materials were selected because of their similar matrix to the specimens under investigation, range of recorded elements, and absence from the calibration profile. They were not selected for calibration because of the lack of certified values despite the multi-instrument work by Hunt et al. [31]. Measured accuracies were poor for both LIBS and LA-ICP-MS across both reference materials, though precision was reasonable and consistent (RSDs: ~10–20% for NCS DC 60605 and ~5% for NCS DC 60602). Best overall results obtained by both techniques were for the higher iron srm, NCS DC 60102. Calibrated LIBS data are provided in Table S2 and calibrated LA-ICP-MS data in table S3. Data were generally consistent between LIBS and LA-ICP-MS.

3.1 Data analysis

The chemistry of each slip was measured multiple times during the investigation. A PCA of the repeated LIBS measurements (excluding the white slipped sample 67732) shows a clear coherency amongst individual slips and the development of a clustered

Fig. 3 PCA plot of LIBS analyses of ceramic slips excluding 67732 (white-slipped sample) arising from CLR transformed element data

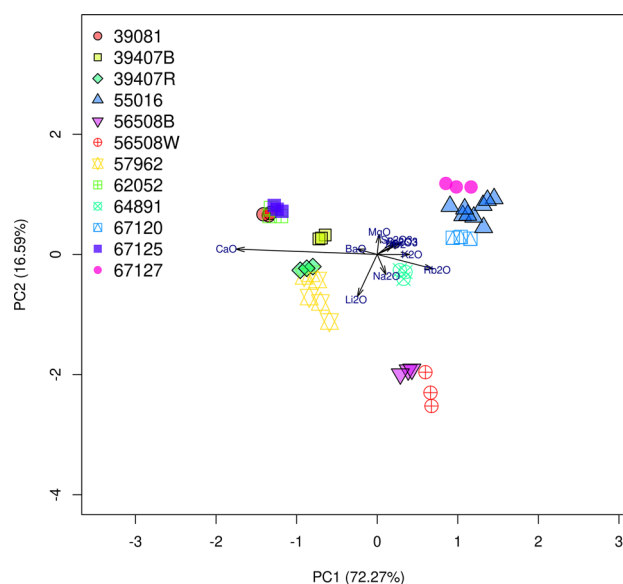
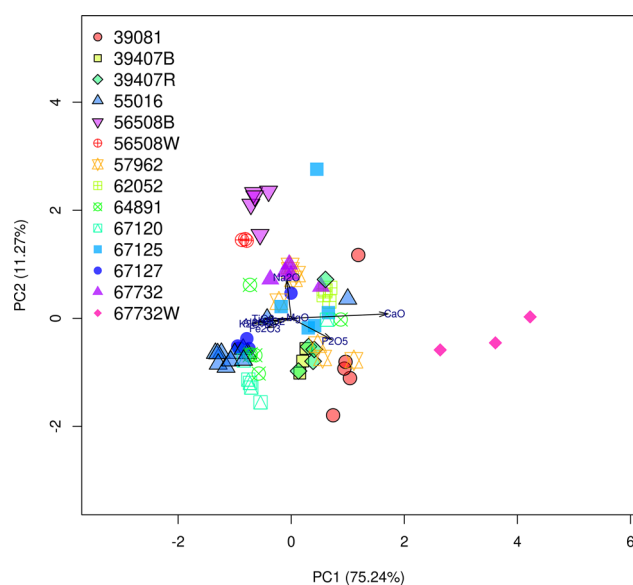


Fig. 4 PCA plot of all LA-ICP-MS analyses of ceramic slips and bodies arising from CLR transformed major element data



distribution (Fig. 3). Because the LIBS results anticipate those of the LA-ICP-MS analyses with fewer measurable elements, we constrain further reporting until more detailed method development can be undertaken.

A PCA of all slip and body major element chemistries measured by LA-ICP-MS shows a clear difference between the single white slip analysed (67732W) and all others (Fig. 4). Once removed, a complex pattern emerges that is difficult to disentangle (Fig. 5). Darker slips have a different relationship to their underlying body fabric compared to those with red (39407) and white (67125) slips. The former appear to be depleted in CaO and enriched in Fe_2O_3 , Al_2O_3 , K_2O , and TiO_2 , while the latter show less variance. A similar pattern is observed in trace element distributions in which darker slips are depleted in SrO relative to body fabrics (Fig. 6). No observable patterns are present based on slip colour (excluding white).

An exploration of slips alone using trace elements shows strong coherency amongst analyses of the same specimen, but no clear evidence of grouping beyond what might be expected by chance (Fig. 7). In other words, the clustered distribution visible in the PCA plot is, in part, an artefact of including repeated measures. This picture changes, however, when the black and brown slips (55016, 56508B, 57962, 64891, 67120, and 67127) are compared with published analyses [10] of black slipped wares from the core Hellenic region. Observation combined with average-linkage hierarchical cluster analysis led to the removal of 2 outlying specimens from the legacy data (79.Ae.17.6 and 83.Ae.430). PCA following this removal indicates the presence of a main group containing specimens from both Issa and the Hellenic core, and two outlier groups of containing only Issaeen specimens (Fig. 8). This pattern can also be attested by average linkage cluster analysis (Figure S3), but a larger sample size is required to assess its validity.

Fig. 5 PCA plot of LA-ICP-MS analyses of ceramic slips and bodies arising from CLR transformed major element data. Excludes 67732-white slipped specimen

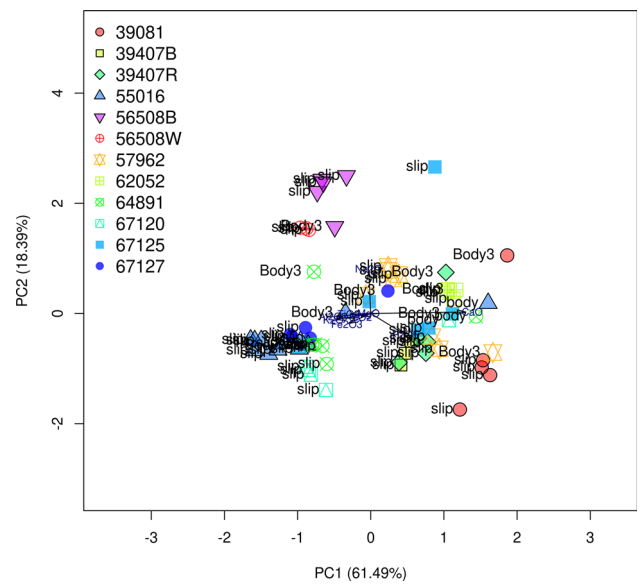
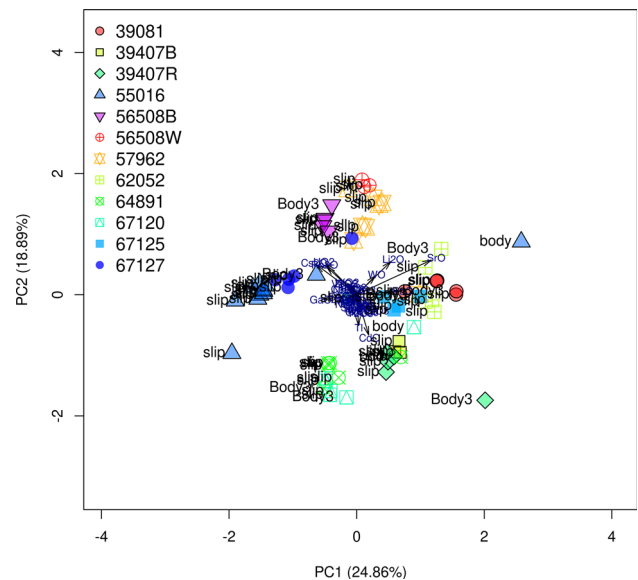


Fig. 6 PCA plot of LA-ICP-MS analyses of ceramic slips and bodies arising from CLR transformed trace element data. Excludes 67732-white slipped specimen



A final PCA was conducted on body chemistries of the Issaeon and Hellenic Core datasets. In this instance, all Issaeon specimens formed a visibly distinct cluster that tends to be enriched in Sc and rare earth elements (Fig. 9).

Plots of rare earth elements normalised by the upper continental crust (values from [32]) reveal a similar pattern of variation amongst individual black/brown slips as well as relationships between slips and their underlying body fabrics (Fig. 10). The structure of these plots differs from those reported by Walton et al. [10], notably by possessing stronger negative Eu anomalies and less consistent negative Ce anomalies.

Fig. 7 PCA plot of LA-ICP-MS analyses of ceramic slips arising from CLR transformed trace element data. Excludes 67732-white slipped specimen

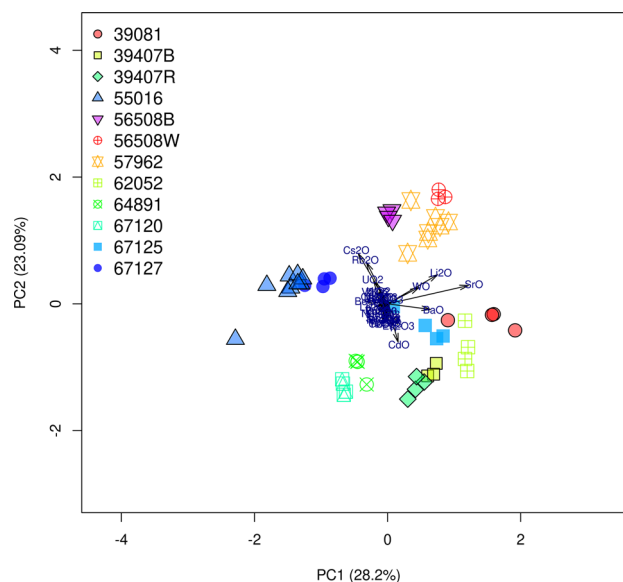
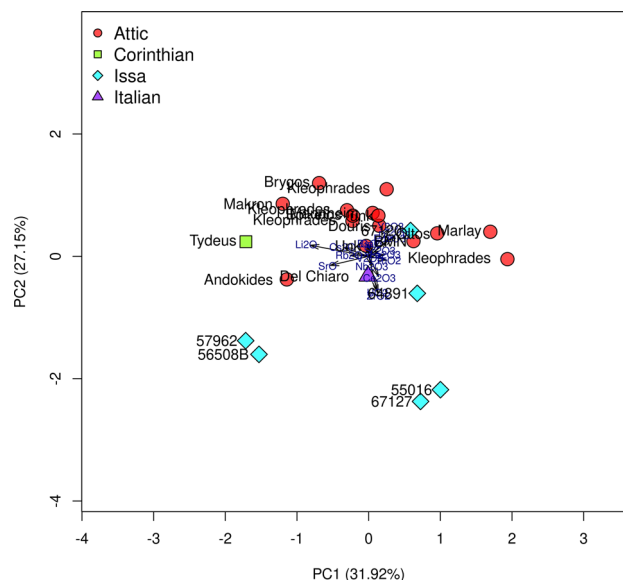


Fig. 8 PCA plot comparing black and brown slips in the Issaeon sample to data collected in [10] from black slipped specimens analysed from the J. Paul Getty Museum. All data have been subjected to CLR transformation

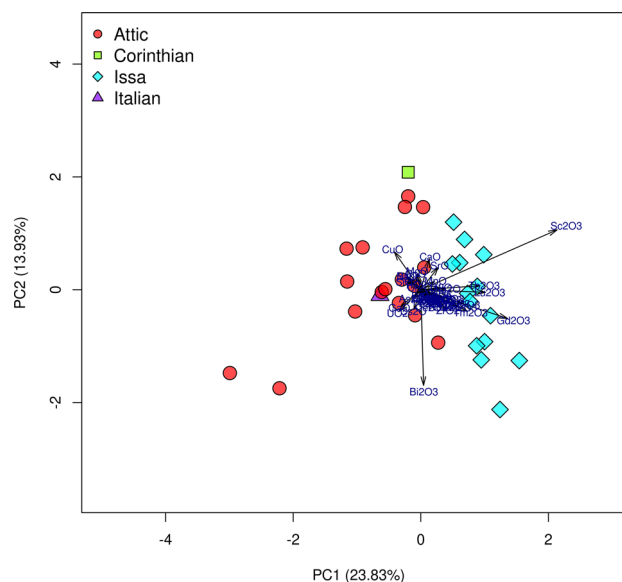


4 Discussion

Results indicate substantial variation in slip and body chemistries. The Issaeon ceramics were formed of distinct clays and covered with slips representing at least 4 different chemistries (including the CaO rich slip). One group of the dark slip varieties share affinity with slips analysed from the core Hellenic world, while the other two appear distinct. This leads to four possible models for slips present at Issa:

1. All Hellenistic fine wares in Issa were imported from the Hellenic core
2. Ceramics fine wares were fired using local clays for bodies and at least some imported Illitic clays for slip
3. Hellenistic fine wares in Issa were made from local clays for bodies and slips prepared from the same
4. Hellenistic fine wares in Issa were made from local clays for bodies and different local clays for slips.

Fig. 9 PCA plot comparing black and brown slipped ceramic bodies in the Issaeon sample to data collected by Walton et al. [10] for black slipped specimens analysed from the J. Paul Getty Museum. All data have been subjected to CLR transformation



Given the complexities of the Hellenistic world, it is possible that each of these models holds true for different cases. Model 1 can be rejected based on prior work indicating local provenance or clays for ceramic production at Issa [33]. Model 2 also seems unlikely given the magnitude of the undertaking (see also comments in [10]). The abundance of suitable clays for making slips also makes this an unlikely scenario. Models 3 and 4 have the best support from the data presented. The MUQ-normalised REE plots suggest that similar clays were used for both bodies and slips for 3 black slipped specimens (56508B, 64891, and 67127), while others (55016, 57962, 67120) indicate either distinct processing techniques (variation in levigation practice or application of vitriol [10]) or different clays. Variation in the trace element composition of slips and bodies, as a proxy for technological recipes (including raw material provenance and their processing), complements the REE plots by showing at least 3 slip chemical groups and a single body compositional group. Though not highlighted above, our LA-ICP-MS analyses also show elevated Zn in slips relative to bodies (Table S3) in agreement with [10]. The relationship between Zn concentrations and REE distributions in the Issaen sample is unclear and calls for evaluation with larger sample sizes. More than anything else, these results paint a picture of remarkable diversity which we have only begun to decipher. Taking a larger view, it is possible that the same situation is true across the entire Mediterranean.

5 Conclusions

The application of LA methods, though in increasing frequency amongst ceramic analysis within archaeology, remains scarce with respect to Hellenistic pottery and other Mediterranean wares. The effectiveness of these methods for conducting in-depth elemental analysis on ancient Greek pottery surface treatments holds great promise if applied to sufficient sample sizes. In limited application, as reported here (and [10]), LA methods raise more questions than answers. Applied to hundreds or thousands of sherds, they may shed light on crucial aspects of pottery production, including provenance, application techniques, and firing processes for slips and decorative elements.

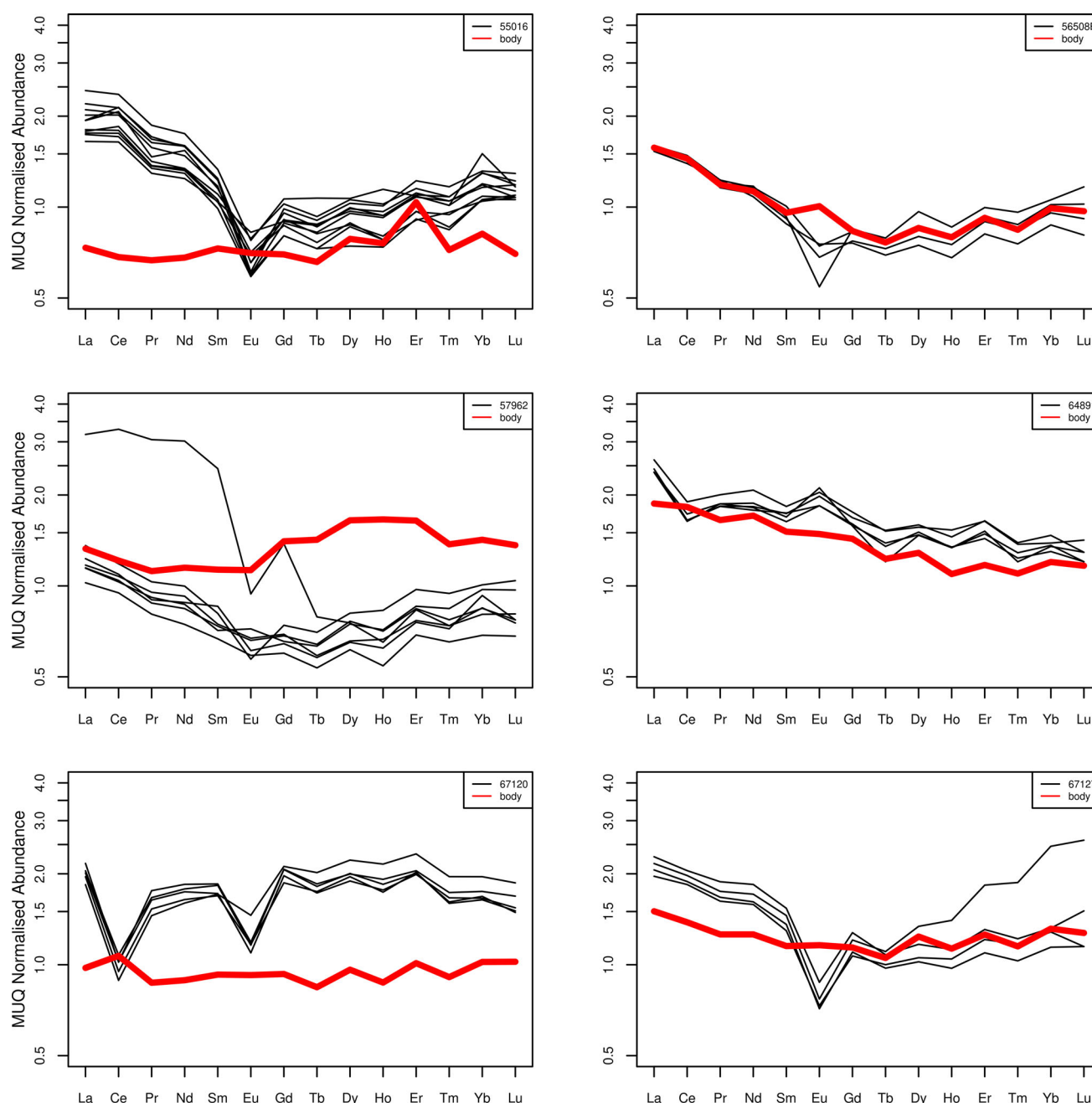


Fig. 10 MUQ normalised REE plot of black and brown slips in the Issaeen sample

We envision a future where LA methods become a standard in archaeological ceramic analysis. To achieve this vision, it is imperative for researchers to embrace these techniques and embark on projects of much broader scope than those undertaken at present. The optimistic outlook is that these advanced methods will pave the way for ground-breaking discoveries and a deeper understanding of Mediterranean cultural heritage.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1140/epjp/s13360-024-05558-5>.

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Data Availability Statement The authors declare that all data created for this paper are available within the supplementary information files. Additional LA-ICP-MS data for Athenian black slips were obtained from the supplementary information files created by [10] in the online version of their article <https://doi.org/https://doi.org/10.1111/jace.13337>.

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