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Chapter 15

Selected Applications of Laser Ablation Inductively Coupled Plasma–Mass Spectrometry to Archaeological Research

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Use of inductively coupled plasma-mass spectrometry (ICP-MS) coupled to a laser-ablation sample introduction system (LA-ICP-MS) as a minimally destructive method for chemical characterization of archaeological materials has gained favor during the past few years. Although still a relatively new analytical technique in archaeology, LA-ICP-MS has been demonstrated to be a productive avenue of research for chemical characterization of obsidian, chert, pottery, painted and glazed surfaces, and human bone and teeth. Archaeological applications of LA-ICP-MS and comparisons with other analytical methods are described.

In recent years, laser ablation (LA) systems coupled to state-of-the-art inductively coupled plasma-mass spectrometers (ICP-MS) have gained increased popularity in archaeological science for chemical analyses of a variety of inorganic and organic matrices. In archaeology, LA-ICP-MS has facilitated research concerning provenance, trade, and technology through the analysis of metals, rocks, ceramics, pigments, and other archaeological materials (1–10). In addition, analyses of human teeth and bone by this technique have been used to make inferences regarding nativity (11, 12) and diet (13). LA-ICP-MS also has been used in attempts to identify chemical signatures in archaeological wood samples that might be useful for dating prehistoric volcanic eruptions (14, 15).

As an ICP-MS sample introduction technique, laser ablation provides a viable alternative for ICP-MS characterization studies that traditionally have required digestion of solid samples using a combination of heat and/or strong acids—a time consuming and unpleasant task. Laser ablation was first applied to ICP in the late 1970s (16), but it was not until the mid-1980s that a laser ablation system was coupled to an ICP mass spectrometer (17). The coupling of laser-ablation with ICP-MS has resulted in the development of extremely sensitive microprobes capable of determining most elements of the periodic table. LA-ICP-MS offers several advantages over other analytical methods, including low detection limits, rapid analytical time, low cost per sample, high sample throughput, and minimal damage to the sample. The range of materials that can be characterized by LA-ICP-MS (rocks, ceramics, glasses, pigments, fauna and other organics) and types of analyses (bulk, surface, and microprobe) are unsurpassed by most other analytical techniques. The fact that in situ analyses can be conducted by LA-ICP-MS suggests less chance of contamination resulting from sample preparation in that the sample remains intact within its original matrix until the analysis. Although potential problems exist with data calibration, spectral interferences, and fractionation, these problems can be ameliorated such that any negative impacts to the analysis are minimized. LA-ICP-MS has tremendous potential for providing chemical characterizations of archaeological materials, permitting questions regarding prehistoric production, trade, interaction, and manufacturing technology to be addressed. The examples presented below illustrate a few of the potential applications of LA-ICP-MS to archaeological characterization studies.

Analytical Methods

Data for all case studies presented below were generated using a VG Axiom (high-resolution, double-focussing, single-collector) ICP-MS coupled to a Merchantek Nd:YAG 213–nm wavelength laser ablation unit. The laser can be targeted on spots as small as 5 μm in diameter. The small spot size and the high

sensitivity of magnetic-sector ICP-MS to a wide range of major, minor, and trace elements make LA-ICP-MS a very powerful microprobe. Moreover, laser ablation is virtually non-destructive to most samples considering that the ablated areas are often indistinguishable with the naked eye. Unlike instrumental neutron activation analysis (INAA), X-ray fluorescence (XRF), or ICP-MS of solutions which produces a bulk elemental characterization of the entire matrix, LA-ICP-MS provides a point specific characterization of the ablated area of the sample. Relatively homogeneous samples, such as obsidian and to a certain extent cherts, paints, and glazes, are ideally suited for LA-ICP-MS given that spatial variation is minimal in these materials. ICP-MS can generate compositional data for 50–60 elements, whereas, other techniques typically generate compositional data for about 30 (or less) different elements. Some elements such as lead and phosphorus which cannot be measured by INAA but can be measured by LA-ICP-MS may prove important for separating materials into different compositional groups. For many elements LA-ICP-MS has lower detection limits than other instrumental techniques (e.g., Sr, Sb, Ba, and Zr).

In LA-ICP-MS, the sample is placed inside a sample holder or laser cell where ablation takes place. Ablation areas vary in size depending on the sample matrix, but the analyzed area is usually smaller than 1000 x 1000 μm and less than 30 μm deep. During analysis, the laser beam ablates and vaporizes the area of interest on the sample. The ablated material is transported from the laser cell using a 0.9–1.5 l/min flow of argon and/or an argon/helium/nitrogen-mixed carrier gas through Tygon tubing and introduced into the ICP-MS torch, where argon gas plasma capable of sustaining electron temperatures between 8000 and 10,000 K is used to ionize the injected sample. The resulting ions pass though a two-stage interface (sample and skimmer cones) designed to enable the transition of the ions from atmospheric pressure to the vacuum chamber of the ICP-MS system. Once inside the mass spectrometer (in this case a high-resolution, double-focussing, magnetic sector ICP-MS), the ions are accelerated by high voltage and pass through a series of ion optics, an electrostatic analyzer (ESA), and finally the magnet. By varying the strength of the magnet, the ions are separated according to mass/charge ratio and passed through a slit into the detector, which records only a small atomic mass range at a given time. By varying the magnet and flight-tube settings, the entire mass range can be scanned within a relatively short time.

Although laser-ablation sample preparation and analysis are conducted with relative ease, quantification of data can prove challenging. With liquid samples, the amount of material introduced into the ICP-MS remains relatively constant, and instrument drift is usually corrected through the use of internal standards. However, in LA-ICP-MS, conditions such as the texture of the sample, ablation time, the location of the sample within the laser cell, surface topography, laser

energy, and other factors significantly affect the amount of material that is introduced to the ICP torch and thus the intensity of the signal monitored for the various atomic masses of interest. As a result, researchers have grappled with normalization methods that permit accurate quantification of LA-ICP-MS data (6, 7, 10, 18–22). In the examples below, we present both qualitative (ratios) and quantitative approaches to data interpretation.

Determining Obsidian Provenance

Obsidian is an ideal archaeological material for examining resource procurement patterns and exchange networks because the artifacts can usually be linked to sources with a high degree of reliability. Obsidian has several advantages over a majority of other archaeological materials, especially ceramics, which are found in even greater abundance. First, obsidian sources are restricted to areas where volcanic activity occurred or to locations where secondary deposits were created by other geologic processes. Second, obsidian sources are more often than not chemically homogeneous, and at the same time the individual sources have chemical characteristics that make them different from one another. Measurements of trace element abundances have demonstrated that individual sources can be differentiated from one another, although the characteristic elements are likely to differ for each suite of sources involved in the comparison (23). With sufficient field and laboratory work, the spatial extent of a particular geochemical type of obsidian can be established such that a "source" can be defined. Finally, obsidian artifacts are nearly indestructible in most archaeological contexts. Only by the extremely slow process of hydration which attacks the surfaces of artifacts does the artifact gradually get smaller, but the bulk composition remains unchanged. The latter process takes many tens of thousands of years to totally destroy an artifact. Thus, it is possible to compare the compositional fingerprints of artifacts to those of sources and successfully determine the correct source for each artifact with nearly 100% confidence.

In most obsidian provenance studies, the ability to employ compositional differences to discriminate between sources depends, to a certain extent, on the number of elements measured. Because instrumental neutron activation analysis (INAA) is capable of measuring 25–30 elements in obsidian with excellent precision, numerous combinations of trace and major elements are available for comparing differences between sources. The main requirements for success are that all sources have been located and analyzed, and that the internal variation measured within the sources be smaller than the compositional differences measured between the sources (23).

Sourcing Obsidian Artifacts in the Western Mediterranean

Until recently, there was no systematic survey, documentation, and chemical and physical analyses of western Mediterranean obsidian sources. Recently, Tykot completed an extensive survey and documentation of western Mediterranean obsidian sources on the islands of Sardinia, Palmarola, Lipari, and Pantelleria (24–27) for a more detailed discussion. Samples from these sources were analyzed at MURR by INAA and/or XRF and LA-ICP-MS. As expected, INAA (and XRF and LA-ICP-MS) of geologic samples from these sources demonstrated that obsidian from each island had a unique chemical signature(s). In the case of Sardinia, six compositional groups were identified. Because of the analytical cost and semi-destructive nature of INAA, artifacts were analyzed by LA-ICP-MS rather than INAA. XRF would have provided a viable analytical alternative, but many of the artifacts were smaller than the minimum size required for this analysis on a standard laboratory-based stationary XRF instrument.

Given our extensive analyses of the geologic source samples, the range of chemical variation both within and between western Mediterranean obsidian sources was known in advance. Consequently, it was not necessary to analyze the artifacts for a full suite of elements. Instead a few elements were identified that best separate the various island sources and sub-sources, i.e., iron, cesium, samarium, and barium, and few other elements (Figure 1). The laser was set to ablate along a line, approximately 600 μm in length, over a flat area on the sample. The laser was operated at 80% power using a 100-μm diameter beam operating at 20 Hz. The laser was set to scan across the raster area at a speed of 30 μm/s. Ten measurements were made for each of the isotopes measured. Ratios of the blank-subtracted isotopic-abundance-corrected counts were used to discriminate between the compositional groups for the sources. It is important to note that because this is essentially a "standardless" measurement, that samples of obsidian from the known sources must be analyzed on a daily basis. This is because the operating parameters of the LA-ICP-MS system can change on a daily basis, thus affecting the instrument mass bias. Therefore, data generated for one day's experiment cannot always be readily compared to data generated on a subsequent day. Fortunately, the changes in mass bias do not affect the accuracy of source identification given that samples of known provenance are analyzed with each batch of artifacts.

Although we attributed artifacts to each of the four major western Mediterranean sources, our focus here is on artifacts attributed to Monti Arci, Sardinia. Figure 2 illustrates the use of elemental ratios to discriminate the major island obsidian groups by INAA. By projecting these data as logged ratios of samarium/barium on the X-axis and iron/cesium on the Y-axis, we have maximized the differences between the various Sardinian subgroups in a manner
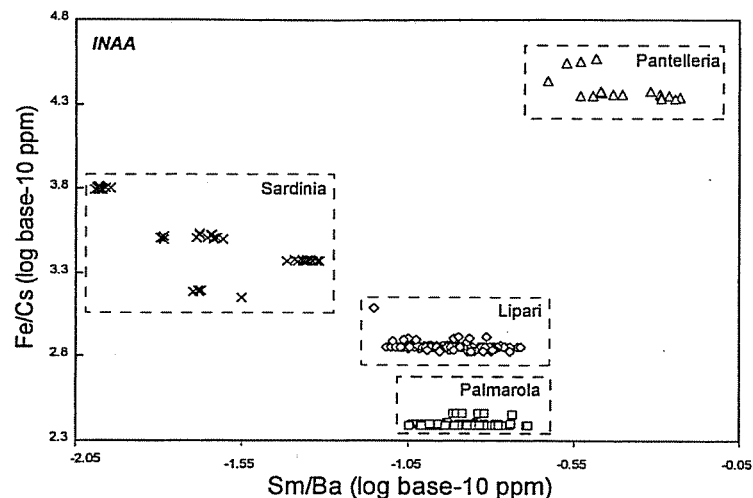
Figure 1. Comparison of INAA elemental ratios for the four major western Mediterranean Island obsidian sources. Only geologic source samples are plotted.
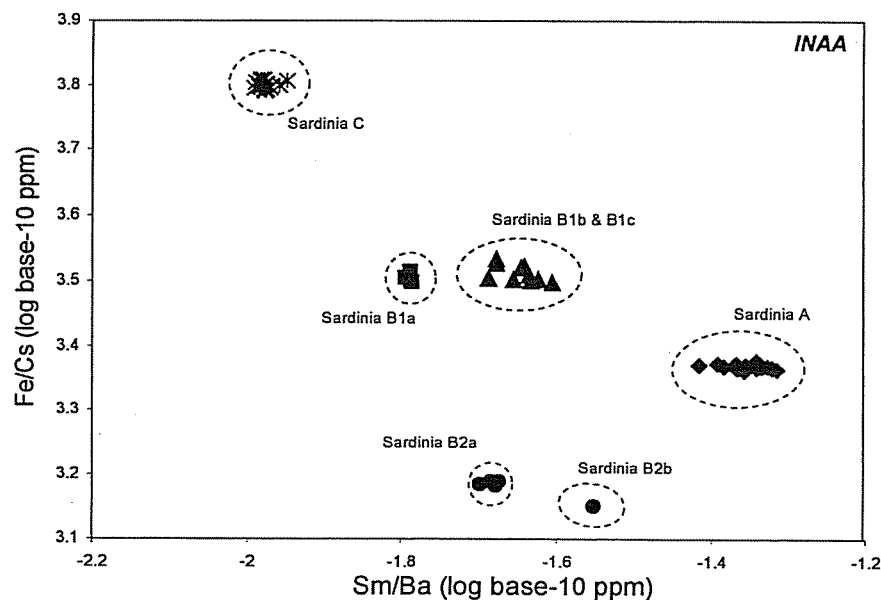

Figure 2. Comparison of INAA elemental ratios for the six Monti Arci (Sardinia) obsidian subgroups. Only geologic source samples are plotted.

that facilitates comparisons with LA-ICP-MS data. As demonstrated in Figure 3, the configuration of the LA-ICP-MS is virtually identical to that observed with the INAA data presented in the previous figure. The analysis of a few geologic source samples permits us to confidently attribute the artifacts to specific sub-source deposits on Monti Arci. As an added advantage, it is possible to analyze between 60 and 100 artifacts per day using this approach.

Discriminating Obsidian Sources When Compositional Variation is Minimal: Sycan Marsh and Silver Lake, Oregon

The Silver Lake/Sycan Marsh obsidian source domes, located in the Fort Rock region of south-central Oregon, were intensively utilized throughout the prehistoric period. Artifact obsidian from this source is found throughout central Oregon, southwest Oregon, northeast California, and southwest Washington, and ranges in age from the Clovis era to the early historic period. Although the two domes that make up the Silver Lake/Sycan Marsh source are usually considered as a single geochemical group, but XRF and LA-ICP-MS studies suggest that their trace element content can be used to distinguish the northern from the southern dome.

The two source domes, located 16 km apart, are separated by a significant physical and ethnographic divide. Obsidian from the northern dome (Silver Lake) is found within the closed Fort Rock Basin that lies at extreme northwestern edge of the Great Basin. Glass from the southern dome (Sycan Marsh) occurs in secondary deposits in the upper reaches of the Klamath Lake Basin. Obsidian from the southern dome would have been available for direct procurement by the Klamath-Modoc groups who occupied the eastern margin of the Klamath Basin. The Northern Paiute groups inhabiting the Fort Rock Basin would have had direct access to geologic material originating from the northern dome. Obsidian from these two culture areas would have been available for use or trade to very different geographic and ethnographic areas. The ability to distinguish artifacts from a specific dome allows examination of the prehistoric use and distribution of the glass with considerably greater archaeological resolution than when considered as a single combined geochemical source.

XRF analyses of Silver Lake and Sycan Marsh obsidian source samples suggested the possibility that the two sources could be differentiated based on small differences in strontium concentrations. However, when the standard error for strontium was taken into account, both groups overlapped at one standard deviation. Because of higher instrumental detection limits for strontium, NAA could not discriminate between the two sources. LA-ICP-MS analyses were conducted to determine if the sensitivity and precision of this analytical technique was sufficient to confirm the existence of the two compositional

groups. For this experiment, the laser was set to ablate along a line, approximately 600 μm in length, over a flat area on the sample. The laser was operated at 80% power using a 100 μm diameter beam operating at 20 Hz. The laser was set to scan across the line at a speed of 30 μm/s. Ten measurements were made for each of the five isotopes measured (^{138}Ba, ^{85}Rb, ^{30}Si, ^{88}Sr, ^{66}Zn). Samples were analyzed in a random order to ensure that instrumental drift would not bias the results of the analysis. A ratio of blank subtracted counts for each isotope to silicon provided a means for examining the differences between the two groups.

Data generated by XRF and LA-ICP-MS are presented in Figure 4. Although the X-axis and Y-axis scales differ for the LA-ICP-MS data (ratios) and the XRF data (ppm), it is clear that the separation suggested by XRF is in fact real when the LA-ICP-MS data are taken into account. Future research will include the analysis of artifacts, thereby enabling archaeologists to examine prehistoric human resource procurement patterns and the spatial distribution of these obsidians.

Bulk Analysis of Ceramic Pastes

For more than three decades INAA has been the primary analytical technique for bulk chemical characterization of archaeological ceramics. Provenance studies of ceramic materials permit archaeologists to examine raw material selection and pottery distribution across wide geographic areas. The rapid proliferation of ICP-MS during the last decade has resulted in compositional studies of ceramics being conducted at numerous institutions throughout the world, rather than a few key facilities. We welcome this shift, but maintain that INAA is still the best analytical method available for bulk characterization of prehistoric ceramic pastes. Nonetheless, we recognize that ICP-MS of solutions, and in some cases LA-ICP-MS of solids, can be used to generate data that are comparable to data generated by INAA.

The increased number of LA-ICP-MS applications to studies of archaeological materials has raised the question *can in situ bulk analysis of ceramics be conducted by laser ablation*? The answer in most cases is no. It is not possible to generate bulk compositional data given that a laser-ablation system is a microprobe that permits specific areas of a sample to be targeted, ablated, and introduced to the ICP-MS. Because ceramic pastes are heterogeneous, it is difficult to sample an area with the laser that is representative of the entire ceramic matrix (in most pottery). Additionally, and perhaps more importantly, it has yet to be demonstrated that LA-ICP-MS has the long-term (months to years) replicability necessary to generate large
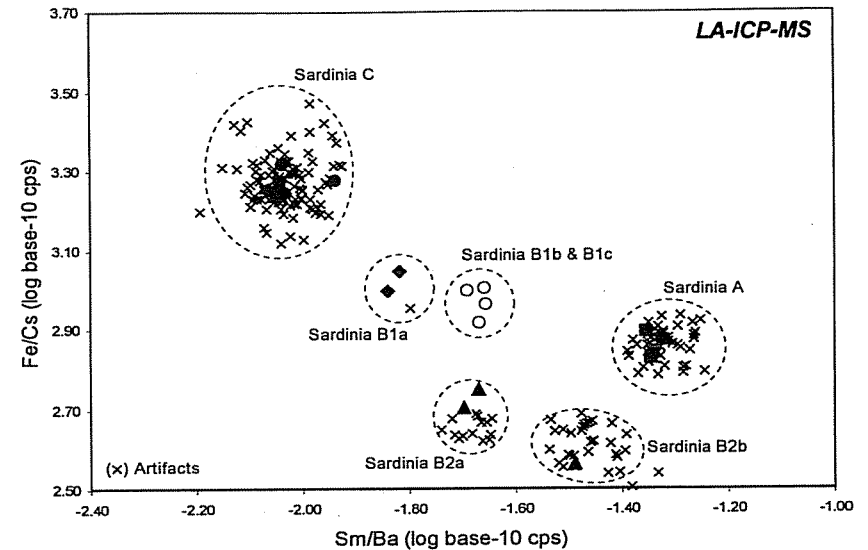
Figure 3. Comparison of LA-ICP-MS elemental ratios for the six Monti Arci (Sardinia) obsidian subgroups. Artifacts are represented by an X. All other symbols represent known source samples that were included in the analyses to verify the accuracy of the assignment of artifacts.
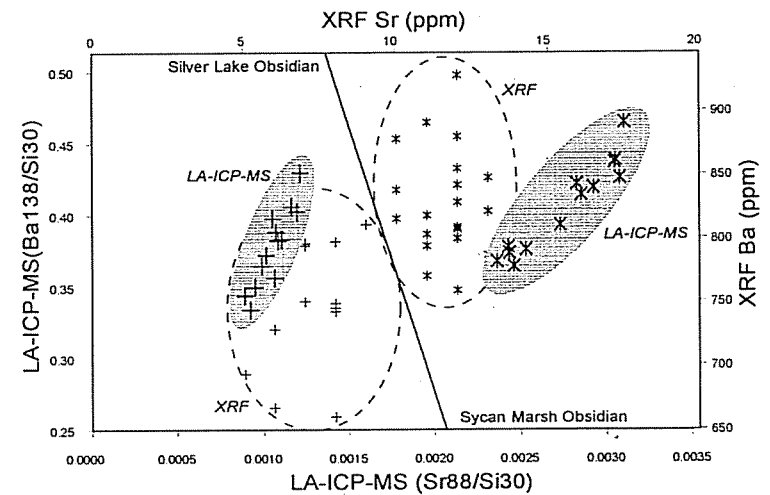

Figure 4. Comparison of LA-ICP-MS and XRF data for Sycan Marsh and Silver Lake obsidian source samples.

compositional databases. Finally, questions remain concerning inter-laboratory comparability of data.

Despite the potential problems with using LA-ICP-MS to generate bulk compositional data for ceramics, there are exceptions where LA-ICP-MS can be effectively employed. The main requirements for ceramic studies of this nature are that the provenance postulate must be fulfilled (28)—that differences between groups must be greater than the differences within groups.

As a case study we analyzed the pastes of Dragon Jars housed in the Guthe or Philippine Expedition Collection at the University of Michigan Museum of Anthropology (UMMA). Dragon Jars are large brown- and/or green-glazed stoneware storage jars that were widely produced and distributed throughout China and mainland southeast Asia. Many were decorated, using a variety of techniques, with representations of dragons, botanical elements, lions, or demons. Chemical studies of these types of vessels have been minimal (29–31), yet data generated by INAA (Figure 5) suggests that chemical differences in pastes are such that alternative analytical techniques such as XRF or LA-ICP-MS might be used to identify different compositional groups.

A subset of samples previously analyzed by INAA were reanalyzed by LA-ICP-MS. A line approximately 600 μm long was placed over a flat area on the sample. The laser was operated at 80% power using a 100 μm diameter beam operating at 10 Hz. The laser was set to scan across the raster area at a speed of 30 μm/s. Each sample was pre-ablated prior to data acquisition to remove possible surface contamination. Data were calibrated using an approach suggested by Gratuze (6, 7). As expected, similar results were obtained by the LA-ICP-MS analyses (Figure 6). We point out, however, that the chemical differences observed for this particular study are not typical of most INAA studies of pottery. Hence, the probabilities of obtaining similar results by LA-ICP-MS were greatly magnified.

Although INAA and LA-ICP-MS Groups 2 and 3 are easily differentiable from one another, examination of the data in bivariate and multivariate space suggest that they are chemically closer to one another than to the other groups. The chemical similarity of these two groups may indicate derivation from separate production centers within the same region, a topic we return to below.

Analysis of Glazes and Paints

One of the potentially more productive avenues of research using LA-ICP-MS involves the characterization of paints and glazes used in the decoration of pottery. Just as bulk analysis of clays by INAA, XRF, ICP-MS, and other analytical methods have demonstrated to be a productive avenue of research for making interpretations regarding past cultural systems, chemical characterization
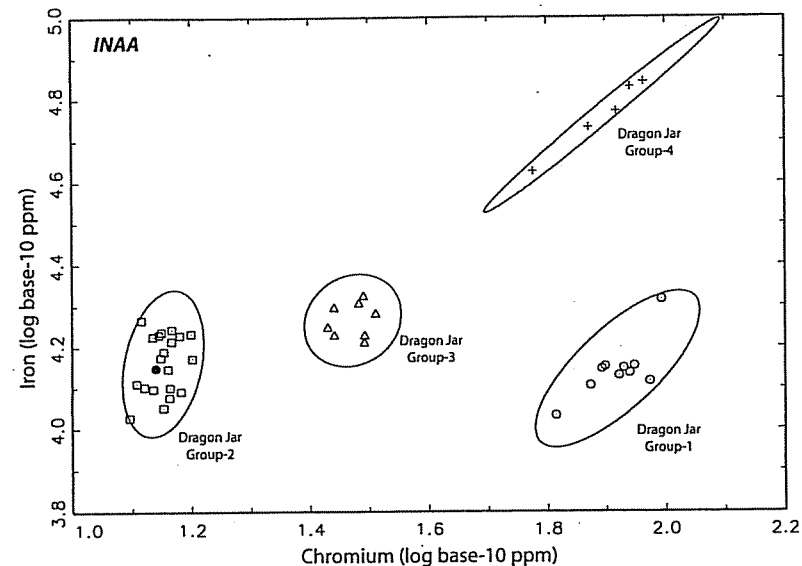
Figure 5. Bivariate plot of chromium and iron base-10 logged concentrations for Dragon Jar paste samples analyzed by INAA. Ellipses represent 90% confidence levels for group membership.
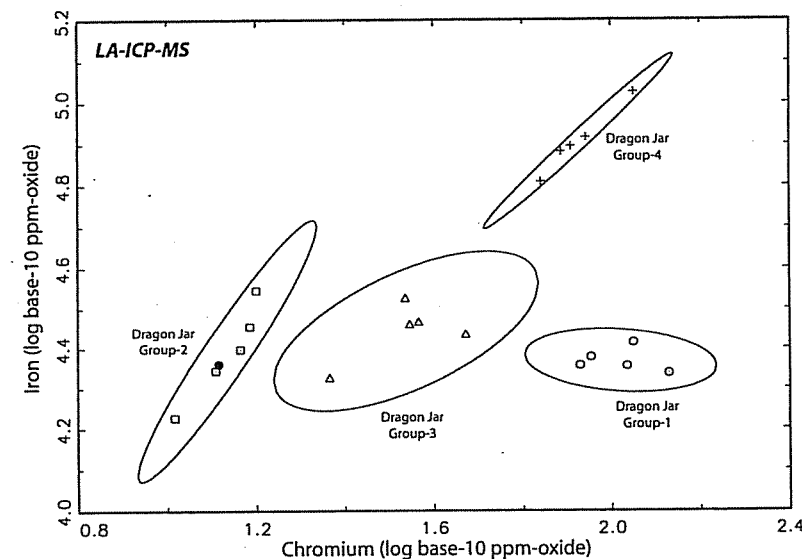

Figure 6. Bivariate plot of chromium and iron base-10 logged concentrations for Dragon Jar paste samples analyzed by LA-ICP-MS. Ellipses represent 90% confidence levels for group membership.

of paints and glazes may prove just as important. Historically, compositional analyses of paints and glazes have been restricted due to limitations imposed by the available analytical techniques. Wet chemistry, physical tests, and other instrumental techniques have been used to characterize paints and glazes with varying degrees of success. However, with INAA, for example, the painted or glazed surface must be separated from the ceramic matrix for analysis. Additionally, analysis of paint by INAA requires a sample size that would result in the destruction of large quantities of paint or glaze. With instrumentation that uses X-rays, it is difficult ensure the underlying clay matrix is not contributing to the analysis. Using LA-ICP-MS, painted and glazed surfaces can be analyzed without having to remove the painted or glazed decoration from the ceramic sherd. By adjusting laser settings the underlying clay matrix can be avoided thus permitting the painted and glazed surfaces to be characterized. Surface contamination can also be removed by using the laser to ablate the decorated surface prior to data acquisition. Additionally, minimal sample preparation time, high sample throughput, and high instrument sensitivity and accuracy make LA-ICP-MS ideal for characterizing this sample matrix.

Characterization of Dragon Jar Glazes

Glazes are an intricate part of the Dragon Jar production process and can contribute independent information on the manufacturing technology of Dragon Jars. In order to investigate the relationships between bulk-paste composition and decoration, (e.g., the glazes), LA-ICP-MS was used to analyze a subset of the 50 samples analyzed by INAA. The number of samples analyzed by LA-ICP-MS is smaller than the number of samples analyzed by INAA given that several of the Dragon Jar specimens (n=13) in the MURR archival collection did not have intact glazes.

As expected, compositional analysis of the Dragon Jar glazes by LA-ICP-MS produced results similar to the INAA study of the pastes (see above) and the study of decorative attributes (see below). Unlike the INAA characterization of the pastes, three groups were identified rather than four. Glaze groups 1 (n=6) and 4 (n=5) correspond directly to INAA paste groups 1 and 4; Glaze Group 2/3 (n=20) is comprised of specimens assigned to the INAA paste groups 2 and 3. The compositional patterning in the glazes is illustrated by a bivariate plot of the cobalt and barium oxides (Figure 7). Seven specimens are unassigned. The pastes from two of the unassigned glazes are assigned to INAA Group 1, but the glaze composition differs from other samples in glaze Group 1. Group 1 Dragon Jar glazes are enriched in Cr, Cs, Li, and Sb; Group 2/3 jar glazes are enriched in Ba, Eu, La, Mg, Sm, Sr, and Th; Group 4 Dragon Jar glazes are enriched in Ag,

Co, Cd, and Pb. The composition of Groups 2 and 3 pastes were found to resemble one another more than either of the other groups. The fact that that glazes found on Group 2 and Group 3 pastes are chemically indistinguishable supports the INAA of the pastes which suggested that Paste Group 2 and 3 may derive from separate production centers within the same region.

Characterization of Mesa Verde Painted Pottery

In a recent project, the black paints on 253 pottery sherds from the Mesa Verde Region of the American Southwest were analyzed to determine the effectiveness of LA-ICP-MS for discriminating between the two major ceramic types, Mancos and Mesa Verde Black-on-white (32). Classification of these ceramics is based primarily on their paint composition. Mancos Black-on-white is typically classified as having a mineral-based paint derived from an iron-manganese ore. The other ceramic type, Mesa Verde Black-on-white is usually described as having an organic-based paint. Temporally, Mancos Black-on-white precedes Mesa Verde Black-on-white, thus these two ceramic types are used as temporal markers and serve to test a variety of hypotheses surrounding technology, production, distribution, and social organization. Accurate classification of these pottery types provides a foundation for testing these hypotheses.

Prior to data acquisition, samples were pre-ablated using the laser to remove possible surface contamination. Power settings for the laser were adjusted to prevent the laser from burning through the paint during analysis, ensuring that the material introduced to the ICP-MS was actually pigment and not the underlying clay matrix. Ablation parameters included a 200 μm diameter beam operating at 20 Hz and a laser scan rate of 30 μm/s. Data were calibrated using an approach suggested by Gratuze (6, 7). The basic structure of the dataset suggests the existence of at least four different compositional groups, or paint recipes—a mineral group, an organic group, a mixed mineral and organic paint group, and an organic paint group characterized by higher concentrations of lead (Figure 8). Paints have different textures, colors, and appearances, and it is difficult if not impossible to accurately categorize all paints using visual criteria, especially when there are multiple chemical groups possible. Fortunately, LA-ICP-MS removes the subjective component from pigment classification. Given that archaeologists use classification of paint types to explore temporal trends, accurate determination of pigment types is important because errors in classification can result in inaccurate archaeological interpretations. In contrast, chemical characterization of pigments will not only permit accurate classification but may also lead to the discovery of previously unknown chemical variation.
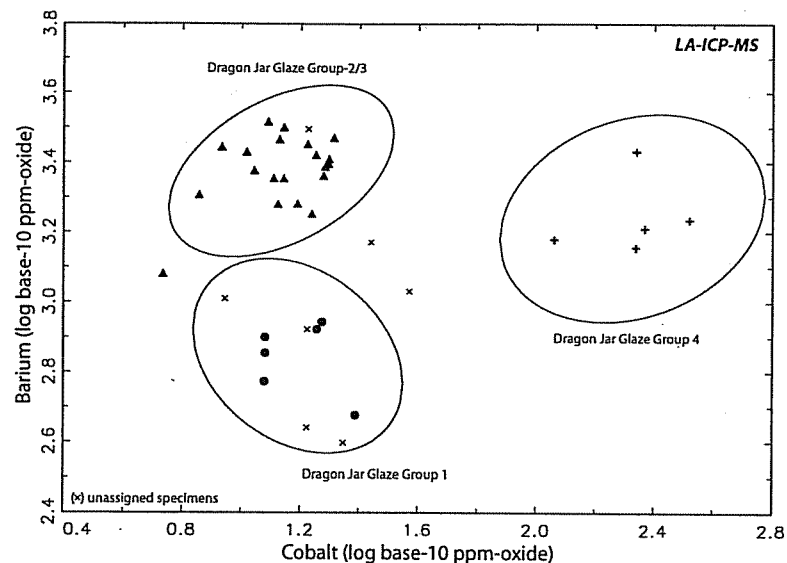
Figure 7. Bivariate plot of cobalt and barium base-10 logged concentrations for Dragon Jar glaze samples analyzed by LA-ICP-MS. Ellipses represent 90% confidence levels for group membership.
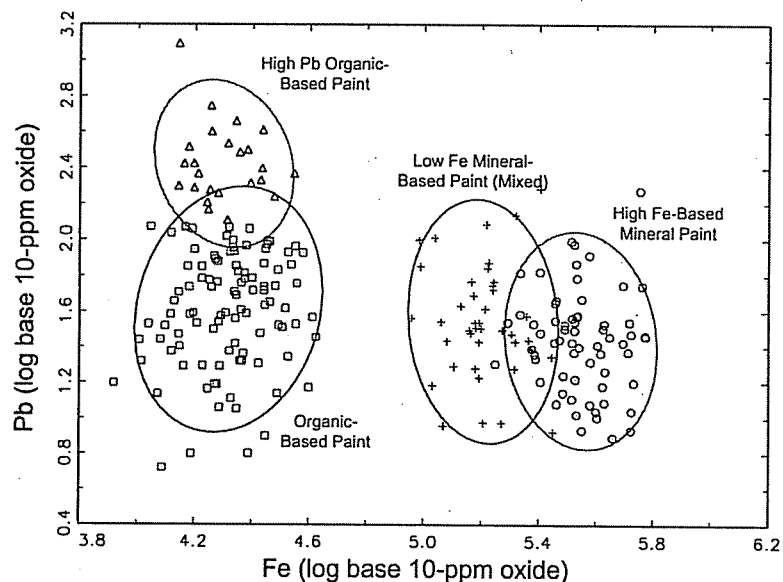

Figure 8. Bivariate plot of iron and lead log base-10 ppm oxide concentrations showing subgroup variation within the mineral and organic-paint groups. Ellipses represent 90% confidence interval for group membership. Unassigned specimens are not shown.

Elemental Contour Maps

One advantage to LA-ICP-MS is that elemental maps of a sherd's surface (and other materials) can be produced by generating data at different areas on a sample and importing these data into a mapping program such as Surfer (Golden Software). Figures 9–11 illustrate differences in paint concentrations on a mineral-painted and two organic-painted sherds. Data for iron, copper, and manganese were generated on an arbitrary grid at 1 mm intervals. The data generated for these experiments were imported into Surfer and manipulated to produce a chemically derived contour map for the surface of each sherd. The highest counts for each element were set to correspond to the color black, the lowest counts to the color white. Darker areas in the figures therefore correspond to higher elemental concentrations. Figure 9 shows the elemental surface map for sample WJJ122, a Mancos B/w sherd. On the left of this figure is a digital photograph of the area analyzed (the black area is paint, the white and gray areas are slip) followed by maps of iron, copper, and manganese. In this case the paint on sample WJJ122 is derived from an iron-based mineral. As a result, the iron and manganese maps show close resemblance to the digital photograph, whereas the copper is somewhat randomly distributed across the surface of the sherd. In contrast, sample WJJ080, an organic-painted sherd classified as Mesa Verde B/w, shows that copper correlates with the painted areas of the sherd whereas the iron and manganese concentrations show little relation to the painted areas (Figure 10). Given that iron and manganese are not expected to occur in significant quantities in organic paint, little agreement between the painted areas and the elemental contour maps is expected. The agreement between copper and the painted area suggests that copper, as well as the other metals (e.g., Zn, Ag, and Pb) found to be elevated in the organic paint, may contribute to the black color in the painted areas as previously discussed. In contrast, sample DMG013, also an organic-painted sherd classified as Mesa Verde B/w, produces a completely different distribution of elements (Figure 11). The distribution of copper in DMG013 does not correlate with the painted area as observed in the copper elemental contour map for WJJ080 (Figure 10). Likewise, the distribution of iron in DMG013 does not correlate with the painted area observed in the iron elemental contour map for WJJ122 (Figure 9). However, there is a suggestion that manganese is slightly enriched in this sample, as the manganese elemental contour map correlates somewhat with the painted area of the sherd.

The elemental contour maps serve to demonstrate that measurable differences between the painted and the slipped areas exist on pottery from the Mesa Verde region. Enrichment of certain metals (Mn, Cu, Ag, Pb) in the organic-painted sherds clearly does not result from diagenesis (post depositional alteration) but instead reflects differences in paint that are related to one or more
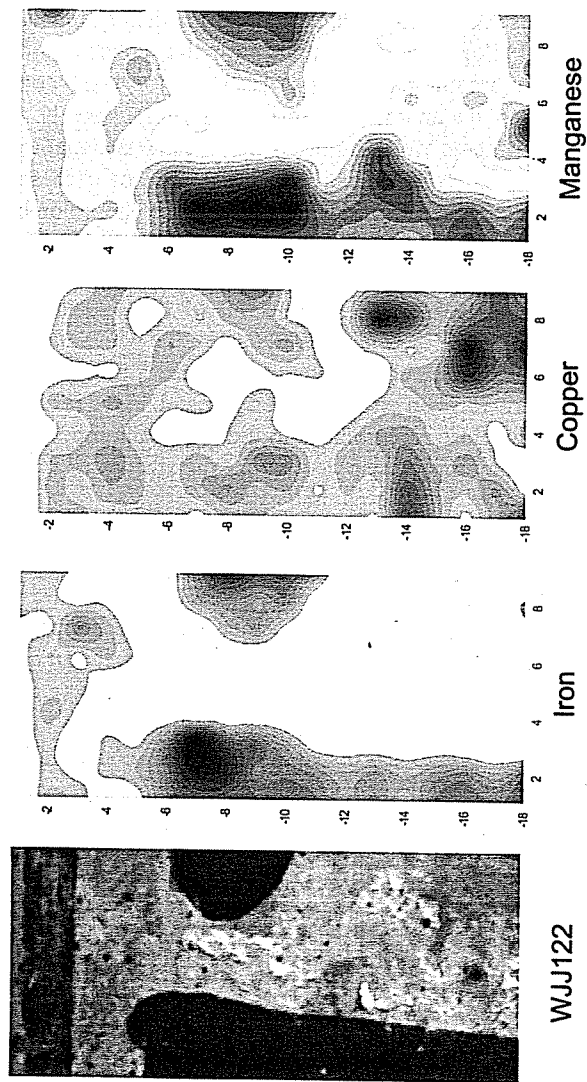
Figure 9. Left: digital photograph of a selected area of sample WJJ122, followed by elemental contour maps of iron, copper, and manganese concentrations on the surface of the sherd. Darker areas on the contour maps indicate higher elemental concentrations for that element. The analyzed area is 10 x 18 mm. Sampling was conducted at 1 mm intervals.
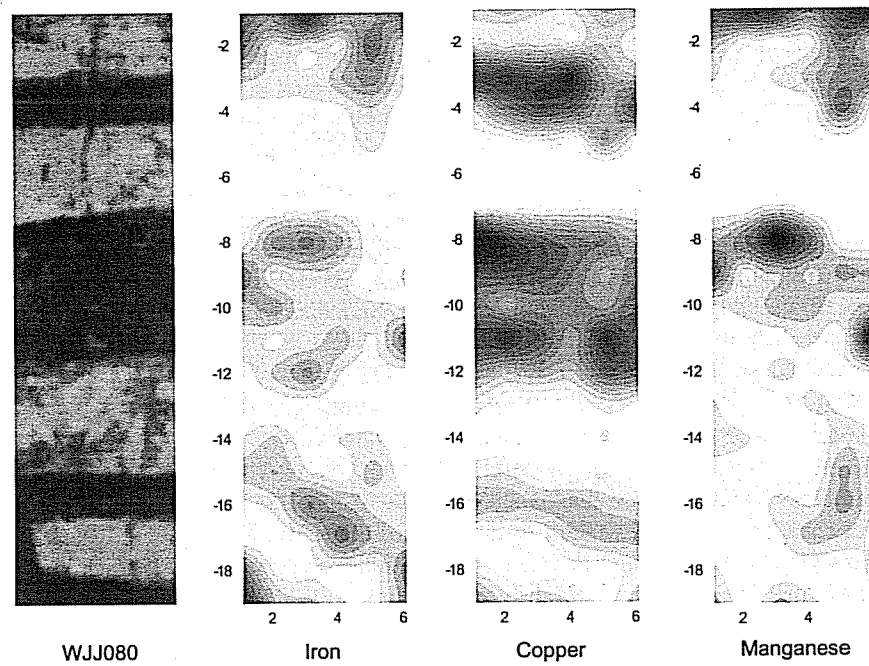
Figure 10. Left: digital photograph of a selected area of sample WJJ080, followed by elemental contour maps of iron, copper, and manganese concentrations on the surface of the sherd. Darker areas on the contour maps indicate higher elemental concentrations for that element. The analyzed area is 6 x 18 mm. Sampling was conducted at 1 mm intervals.

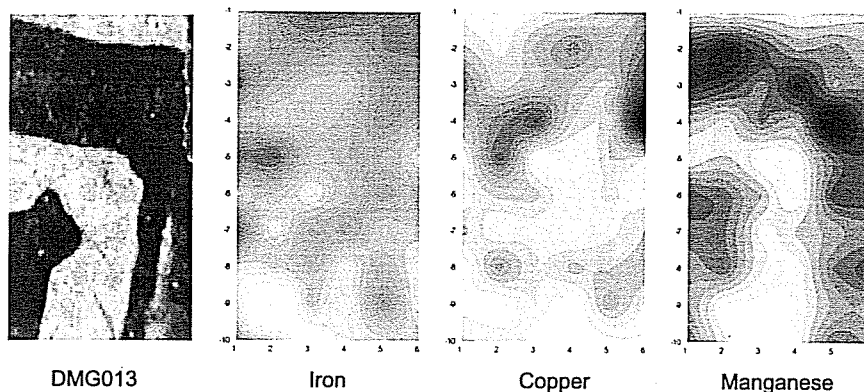DMG013   Iron   Copper   Manganese

*Figure 11. Left: digital photograph of a selected area of sample DMG013,
followed by elemental contour maps of iron, copper, and manganese
concentrations on the surface the sherd. Darker areas on the contour maps
indicate higher elemental concentrations for that element. The analyzed
area is 5 x 9 mm. Sampling was conducted at 1 mm intervals*

of the following: the plant species used to manufacture the pigments, the soil substrate where the plant originated, or the water used to make these plants. If diagenesis were the cause for the enrichment, then the copper contour map for sample WJJ080 and the manganese contour map for sample DMG013 would not correlate as closely to the painted areas of the sherd. Finally, the differences between the two organic-painted sherds further support the argument made above that differences exist in the organic paint.

Human Bone and Teeth

Trace elements in human teeth and bone can be used to reconstruct dietary patterns in prehistoric populations. Several methods have been used to generate chemical data for prehistoric human bone. Among these methods INAA of solid bone and ICP-MS and ICP-ES of solutions have been used most often (*33–35*). With INAA, portions of bone or teeth are cleaned, sealed in vials, and irradiated to provide data for 8–10 elements. Samples analyzed by ICP-MS are digested in acid prior to analysis. In both cases, sample preparation is cumbersome.

An inherent problem with chemical characterization of bones is that diagenesis may confound the results of the analysis. One possible way to avoid diagenesis and contamination is through the use of a microprobe to sample specific areas of the bone. LA-ICP-MS may prove to be ideally suited for this

application given that point-specific analyses can be conducted in which very small areas are targeted, thereby avoiding mineral inclusions and other potentially contaminated areas. Furthermore, by pre-ablating the target, the laser effectively cleans the sample area immediately before data collection begins, reducing the chances of measuring contamination.

In an attempt to evaluate the applicability of LA-ICP-MS to the study of human bone, we analyzed teeth and bone obtained from seventy-six individuals recovered during excavation of the Paloma archaeological site in central Peru. Paloma was occupied from approximately 5850–3750 B.C. and is located along the coastal plain of central Peru (*36, 37*). The only moisture this area receives is in the form of dense fog which is deposited on the landscape between June and December. Consequently, inhabitants of the site would have had limited access to terrestrial food resources and would have greater dependence on marine resources from the nearby ocean for the majority of their nutritional requirements.

Barium is an alkaline-earth metal incorporated into bone through the intestinal tract. In terrestrial environments, barium and strontium are approximately equal in abundance. In marine environments, barium forms an insoluble precipitate as a result of the high sulfate content in salt water. Formation of this compound effectively removes barium from seawater. As a result, Ba/Sr ratios reflect diet and are an indicator of trophic position. In human populations, individuals with diets high in marine-based food resources typically have low Ba/Sr ratios in their bone and teeth. Populations who consume large amounts of terrestrial-based food resources tend to have higher Ba/Sr ratios.

Research by Burton and Price (*38*) demonstrated that Ba/Sr ratios generated by ICP emission spectroscopy (ICP-ES) can be used to infer the diet (marine verses terrestrial) of prehistoric populations. In this experiment we duplicate results obtained by Burton and Price for the Paloma samples. Our results show that the Ba/Sr ratios obtained by LA-ICP-MS are comparable in precision and accuracy to ICP-ES data (Figure 12). Although it is not unexpected that a coastal population would rely heavily upon marine resources, there are applications where this type of research would have value. What we have done here is demonstrate the efficacy of LA-ICP-MS to this line of research by demonstrating that it is possible to generate results similar to those obtained by other analytical techniques.

Final Remarks and Further Developments

In this paper we have presented several applications of LA-ICP-MS to archaeological materials. Although our discussion has centered upon characterization of obsidian, ceramics, pigments, and bone, LA-ICP-MS has
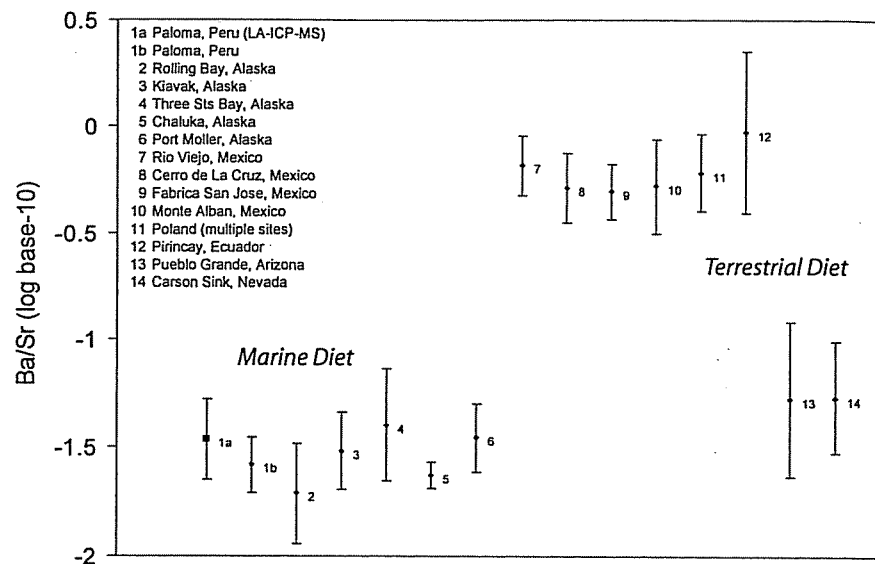
Figure 12. Comparison of barium-strontium element ratios generated by LA-ICP-MS (1a) and ICP-ES (1b) for a sample of individuals from the Paloma, Peru archaeological site, and with other ICP-ES data (2–14). All ICP-ES data were generated by Burton and Price (38).

numerous applications that are not discussed herein. As instrumentation, software, and matrix-matched standards continue to be developed, it is not unreasonable to expect that LA-ICP-MS will evolve into one of the primary analytical techniques employed by researchers for archaeological characterization studies.

Acknowledgments

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Chapter 16

Evaluating the Precision Requirements for Isotope Ratio Determination of Archaeological Materials Using Laser Ablation–Time-of-Flight–Inductively Coupled Plasma–Mass Spectrometry

Increasing Ratio Precision

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High precision isotopic determination of archaeological materials using laser ablation ICP-MS remains an elusive goal. Practical, nearly non-destructive, rapid and cost effective, isotope ratio measures using LA-ICP-MS suffer from transient effects, laser-induced fractionation, and generally lower precision than other methods of sample introduction. However, in contrast to high precision measurement requirements in biological systems, lower levels of analytical precision may still meet threshold levels for isotopic discrimination in archaeological materials, depending on the specificity of the research questions. We here report on our efforts to reduce the spread of replicate isotopic measurements of archaeological materials using pre and post-laser sample treatment, and evaluate the degree to which lower levels of precision affect group attribution in specific cases.