

R.H. Tylkot & S.M.M. Young, Chapter 10  
"Archaeological Applications of Inductively  
Coupled Plasma-Mass Spectrometry"

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# Archaeological Chemistry

## Organic, Inorganic, and Biochemical Analysis

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## Chapter 10

## Archaeological Applications of Inductively Coupled Plasma-Mass Spectrometry

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Inductively coupled plasma-mass spectrometry (ICP-MS) is a relatively new analytical technique increasingly used in the Earth Sciences in the last decade, and in "consumer" fields such as archaeology in the last few years. For archaeologists, ICP-MS has several important advantages over neutron activation and X-ray fluorescence analysis: (1) only a tiny powdered sample is required, so the technique is minimally destructive to valuable artifacts; (2) the large number of elements that can be accurately and precisely analyzed is particularly important for characterization and provenance studies; (3) isotope ratio measurements to three significant figures are possible without extensive sample preparation; and (4) the combination of small sample size and low per-sample cost allows assemblages of artifacts rather than individual objects to be studied. These advantages will be illustrated by the trace element characterization and source tracing of obsidian, the compositional analysis of copper-based artifacts, and the lead isotope ratio analysis of turquoise.

The chemical analysis of archaeological remains is now a widespread and fundamental part of any archaeological research project. The major element composition of metal tools, coins and other objects reflects the alloying technology employed, while the trace element composition of obsidian, copper, gold, marble, and clay has been used to match artifacts with the source of their raw materials. The stable isotope ratios and perhaps elemental content of skeletal remains are reflective of diet, and isotope ratios in metals, marble, ivory and obsidian have also been used to determine their provenance.

A now familiar range of instrumental techniques has been applied to archaeological materials in the last three decades, including neutron activation analysis (NAA), X-ray fluorescence (XRF), atomic absorption spectroscopy (AAS), proton-induced X-ray emission (PIXE), ICP-atomic emission spectroscopy (ICP-AES), and

electron probe microanalysis (with wavelength dispersive X-ray spectrometry) for elemental information, and stable isotope ratio analysis and thermal ionization mass spectrometry for isotopic data. Each of these techniques has its own sample requirements, preparation techniques, and data precision and accuracy which are relevant to particular archaeological materials and questions, and will not be reviewed here since there is an extensive literature on their use (see especially the journals *Archaeometry* and the *Journal of Archaeological Science*).

### Inductively Coupled Plasma-Mass Spectrometry

Inductively coupled plasma-mass spectrometry (ICP-MS) is a relatively new technique in which samples are usually introduced as liquids, atomized and ionized at high temperatures, and the individual atomic species measured by a detector. In this sense, ICP-MS is similar to ICP-AES, except that individual mass units are measured rather than the energy or wavelength of the electromagnetic spectra produced. This technique therefore can be used to determine both elemental concentrations and isotope ratios in sample materials.

Although mass spectrometers were first used with an inductively coupled plasma (ICP) source in the 1980's (1-7), the increasing number of ICP-MS studies presented at analytical conferences confirms this technique as the "most important analytical system [developed] in the last decade of this century" (8). Several volumes on the applications of plasma source mass spectrometry have been published recently (8-12), and include, among others, elemental-compositional studies of metals (13, 14), rocks (15), plant materials (16), groundwaters (17), and automotive catalyst exhaust (18), and isotope ratio studies of metals (19), metabolic and environmental samples (20). A number of studies have even appeared already in the archaeological literature (19, 21-30).

Fisons, Finnegan-Mat and Perkin Elmer are the three major manufacturers of these instruments, of which there are now several hundred at research institutions worldwide. The analyses reported below were obtained using the Fisons PQ 2 Plus in the Department of Earth and Planetary Sciences at Harvard University. The ICP is used not as a source for producing uncharged atomic emission lines, as in the much more common ICP-AES technique (unfortunately, sometimes referred to simply as ICP or ICP-S), but as a source of charged ions for the mass spectrometer. The combination of a high-velocity argon flow, surrounded by a copper load coil, and initiated by an electrical spark, produces a plasma fireball of about 8000 °C at the mouth of the ICP torch. When the sample is injected into the torch through a capillary tube, it is both atomized and ionized into single-charged ions. Molecular and doubly-charged species are very few, reducing the otherwise significant problem of matrix effects. The ions are then passed into a quadrupole mass spectrometer for separation and measurement. Quadrupole mass filters utilize two pairs of oppositely charged rods, each superimposing a radio frequency AC signal on a DC voltage. The combination of RF and DC fields imparts a complex motion to the ion beam. For any set of operating conditions, there is a unique mass which can make its way through the exit slits and to the detector. Other ions will be pumped away by the vacuum system. The entire mass range may be scanned by the detector in about one second. Usually, up to 50 scans are accumulated, producing in a few minutes a simple mass

spectrum, theoretically representing all elements (and their isotopes) in the periodic table except H, He, C, N, O, F, Ne, Cl and Ar. Solution detection limits are much lower than for other analytical methods, typically on the order of 1 ppb for light elements, and 50 parts per trillion for heavy elements. Some ICP mass spectrometers are now equipped with graphite furnaces, lowering detection limits into the low parts per trillion range. Precision is on the order of  $\pm 2-4\%$  for most elements (7, 31), and extensive analyses of U.S.G.S. basalt and andesite reference materials have accuracies better than 3% for 18 of 28 elements tested, with only 1 element differing by more than 7% from published values (6). More detailed information about ICP-MS may be found in a number of recent surveys of the technique (4, 9-11, 31).

Finally, there is also a laser ablation device, which can remove from a solid specimen a tiny sample from a spot much less than 1 mm in diameter, sending it directly to the ICP source (32). Although this method saves all the preparation time involved in dissolving a silicate sample, results are not nearly as precise, and detection limits are "only" in the ppm range, although the precision may be improved for homogeneous materials like glass. The laser has already found an application in the spot analysis of metals, siliceous materials, marble crusts, and bone (22, 30), its detection limits being superior to that of the microprobe (2), and in the rapid microanalysis of uranium compounds (33). While the small amount of sample ablated makes this technique minimally destructive - an important consideration for archaeological materials - samples must nevertheless fit inside the ablation chamber, which is less than 4 cm in diameter.

#### Comparison with Other Techniques

In addition to its ability to provide isotope data, ICP-MS has a fundamental advantage over other instrumental methods. NAA, XRF, AAS, and ICP-AES all rely on the interaction of electromagnetic radiation with the nuclei and electron shells of individual atoms. More specifically, excitation of a sample will produce peaks of characteristic wavelength and energy, with the peak heights proportional to the concentration of each element in the sample. Problems of spectral overlap and matrix interferences plague all of these techniques, and may obscure elements of interest. X-ray techniques generally provide only a surface analysis, and the absorption by air of lower energy wavelengths usually precludes the analysis of elements less than atomic number 12. In ICP-AES, for example, many individual elements have more discrete optical lines in their spectra than the total of 211 possible mass lines for all elements in ICP-MS spectra. ICP-MS gives excellent performance for rare earth elements, platinum group elements, and Ag, Au, Th, and U.

The few potential interferences in ICP-MS may be predicted and in most cases resolved by measuring alternative isotopes of the same element. For example, the argon plasma itself coincides with the major isotope of calcium ( $^{40}\text{Ca}$ ), but one can measure  $^{44}\text{Ca}$  instead.  $^{40}\text{Ar}^{16}\text{O}$  also interferes with  $^{56}\text{Fe}$  (92% natural abundance), requiring the analysis of minor iron isotopes at significantly reduced precision. The only elements without alternative isotopes are fluorine and phosphorus.

ICP-MS (and ICP-AES) response curve calibrations are linear over several orders of magnitude, so that the same sample solution may be used for measuring a range of sample concentrations. In contrast, AAS has very poor linearity, and

interference problems, along with lamp changes, it can be quite tedious if analyzing for more than a few elements (34). When equipped with a graphite furnace, however, AAS does have comparable detection limits to ICP-MS for many elements.

ICP-AES (35, 36) has excellent precision ( $\pm 1\%$ ), and solution detection limits (0.2-25 ppb) several orders of magnitude higher than ICP-MS (certainly sufficient for most archaeological applications), but is limited to the routine determination of 35-40 elements (including rare earth elements, B, Be, S, P, Ti, V), many of which are subject to spectral interferences. ICP-AES has superior precision to ICP-MS for Fe analysis because of the mass spectral overlap described above.

NAA (37) can be non-destructive, otherwise requiring only a powdered sample, and access to a nuclear reactor. For the 30-35 elements that can be routinely measured, it is particularly sensitive for the rare earth elements, and Sc, Co, Cr, Cs, Hf, Ta, Th and U. Matrix effects are not a problem, although there are considerable spectral overlap interferences. Precision is approximately  $\pm 2-5\%$  for rare earth elements, but may be several times that for solid samples, depending on the artifact's shape. The concentrations of 20 elements in a groundwater sample determined by ICP-MS were extremely close to those measured by NAA (17), and were produced much more quickly and less expensively.

XRF (38, 39) is also a solid sample technique, is capable of better analytical precision ( $\pm 0.5\%$ ) than ICP-MS, but the matrix interference corrections required for XRF result in similar accuracy to ICP-MS. XRF is the preferred technique for major element determinations in homogeneous and/or highly refractory materials. Related X-ray techniques like electron probe microanalysis and PIXE are used for spot analyses of thin sections and mounted samples, but at considerably higher elemental detection limits. Laser ablation ICP-MS has superior detection limits (but inferior precision) and can be applied directly to small artifacts without sample removal.

#### Archaeological Applications

ICP-MS has now been used a number of times in archaeological contexts, for determining the major and trace element composition of metals (25, 27-28), marble (21), and obsidian (24). Laser ablation has been applied to coins, glass, ceramics, bone (22), and marble (30), while provenance information has also been obtained from lead isotope ratio analysis of metals (19, 23) and turquoise (40).

ICP-MS appears to offer several important advantages over other analytical techniques: (1) Only a few milligrams of sample are required. Small or precious artifacts (e.g. coins, sculptures) may therefore be analyzed with minimal sample destruction, although larger samples are warranted if the material is heterogeneous, for example ceramics. (2) A very large number of elements can be accurately and precisely analyzed. This is particularly useful for characterization and provenance studies of obsidian, ceramics, jade, and marble; (3) Isotope ratio measurements to three significant figures are possible without extensive sample preparation, allowing preliminary assessment of the provenance of metals, turquoise, and ivory; and (4) The combination of small sample size and low per sample cost allows assemblages of artifacts rather than individual objects to be studied. This is critical for the study of patterns of resource exploitation or technological production in the archaeological record.

We present here a few examples of our own research using ICP-MS, in order to emphasize the advantages and disadvantages of this technique in answering specific archaeological questions about particular types of artifact materials.

#### Sample Preparation

Specific procedures were used to create sample solutions from different materials (41). Copper and iron typically dissolve in nitric acid at room temperature; tin, lead, gold and silver require hydrochloric acid as well as nitric acid. Rock samples require concentrated acid attack: refractory silicates (metal slag, glass, obsidian) and non-siliclastic minerals were dissolved using alkali fusion, or using elevated temperature and pressure digestions. Analytical precision is considerably reduced for rock samples because of the high concentration of flux and silicon in the sample solution, but this problem can be overcome through careful matching of standards to samples, the averaging of replicate samples (ideally at different concentrations), or the use of standard addition.

All sample solutions were diluted so that elements of interest were present in concentrations of about 500 ppb or less, and 100  $\mu\text{L}$  of a 10 ppm  $^{115}\text{In}$  or  $^{186}\text{Rh}$  solution was added to each sample as an internal spike, to correct for drift in the mass count signal.

**Metals.** Samples were removed from archaeological artifacts either by careful drilling to minimize the visual impact of sampling, or by cutting with an emery disk. Surface corrosion was either discarded or removed by soaking in nitric acid for a few minutes. Copper samples weighing 5-10 mg were then dissolved at room temperature in ca. 10 mL concentrated  $\text{HNO}_3$ , and brought up to 100 mL volume; 20 mL of aqua regia (1:3 v/v conc.  $\text{HNO}_3$ /conc.  $\text{HCl}$ ) were also added to dissolve iron, gold, tin and tin-bronze artifacts. Samples containing gold or tin must remain in concentrated acid for 24 hours before dilution. For analysis, a 1 mL aliquot of the sample solution plus 2 mL concentrated  $\text{HNO}_3$  was again diluted to 100 mL.

Calibration curves were produced using commercially available multi-element standards. The average value of several acid blanks was subtracted from that of all sample solutions, and the resulting solution concentration values were multiplied by the dilution factor to reproduce the elemental concentrations in the solid copper sample.

**Obsidian and Slag.** Samples were removed from archaeological artifacts either by flaking or using a high-speed diamond saw, ultrasonically cleaned in distilled and deionized water, and dried at 60 °C. Each sample was then pulverized at liquid nitrogen temperatures for 2.5 minutes using a SPEX 6700 freezer mill. We have then employed two different sample dissolution procedures.

For sealed-vessel digestion, 100 mg of powdered sample were weighed into the inner Teflon beaker of an acid digestion bomb (Parr Instrument Co., Moline, Illinois). 0.2 mL of aqua regia were used to wet each sample; 2.5 mL of hydrofluoric acid were added and the bomb sealed. Bombs were heated at 120 °C for 2 hours, increasing the internal pressure to several tens of atmospheres, causing minerals which are resistant to attack at normal pressures to decompose. After cooling, the digestion

bombs were carefully opened, their contents quantitatively transferred to a 250 mL polypropylene volumetric flask already half-filled with twice-distilled and deionized water, and the sample solution brought up to volume. Samples of less than 100 mg were diluted proportionally so that solution concentrations were similar for all samples. The Teflon containers were cleaned by soaking in a concentrated nitric acid bath for several hours before reuse.

For alkali fusion, 100 mg of powdered sample were mixed with 200 mg of lithium metaborate flux in a high-purity graphite crucible (SPEX Industries). The crucible was heated at 1050 °C for 5 minutes, gently shaken twice, and the hot glass melt poured into a polypropylene sample bottle containing 50 mL of 10% nitric acid. Bottles were vigorously shaken for 5 minutes by hand, and agitated overnight using a shaking table. For analysis, 1 mL aliquots of the sample solution were diluted to 10 mL with twice-distilled and deionized water.

Calibration curves for obsidian were produced using accepted values for the NIST standard obsidian SRM-278, prepared in the same way as the obsidian samples. The average value of several acid blanks was subtracted from that of all sample solutions, and the resulting solution concentration values were multiplied by the dilution factor to reproduce the elemental concentrations in the solid obsidian sample.

**Turquoise.** All additional rock matrix was removed from the mineral ore samples and then samples were removed by flaking. Samples weighing 50-100 mg were dissolved at 60 °C in 5 mL  $\text{HNO}_3$ , 2 mL  $\text{HCl}$ , 0.33 mL IIF, and 10 mL distilled and deionized water in Teflon perfluoroalkoxy (PFA) bottles, and later brought up to a 50 mL volume.

Turquoise samples were analyzed for  $^{209}\text{Pb}$ ,  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$ , and  $^{208}\text{Pb}$ . Care was taken to ensure that all four lead isotopes were in the correct detection range for the instrument. Acid blanks were subtracted from all samples, and isotope ratios of  $^{206}\text{Pb}/^{207}\text{Pb}$ ,  $^{206}\text{Pb}/^{209}\text{Pb}$ , and  $^{206}\text{Pb}/^{207}\text{Pb}$  were calculated and calibrated against NIST lead standards 981 and 982. It must be noted that while thermal ionization mass spectrometry (TIMS), the most common method of isotope ratio analysis, fractionates samples because of differences in volatility, ionization, and space charge effects, ICP-MS fractionates samples only because of mass. For this reason, it is critical to normalize data against frequently run isotopic standards. Accuracy can also be improved by performing separation chemistry on the samples to isolate the element of interest. While three-significant figure precision is insufficient to distinguish among many of the copper and lead ore sources in the Mediterranean, for example, this precision may be sufficient to distinguish among source regions, and perhaps even some sources within those regions.

#### Analytical Results

**Metals.** 14 copper and arsenical bronze artifacts from Gonur in Turkmenistan (29), and one arsenical bronze ingot from near Rooiberg in the Northern Transvaal of southern Africa (42) were analyzed by ICP-MS for major and trace elements. The Gonur material, all from the Bronze Age Margiana civilization, includes axes, spears, bracelets, pins, a small vessel, and a mirror. The Rooiberg ingot is a typical example of the form in which metal was traded in the African Iron Age. Results from NAA

for a sample from the same ingot (Grant, M.; Miller, D.; Young, S. M. M., unpublished report) are also available. Although reasonable agreement for both major and trace elements was obtained (Table I), comparison of these data are not a fair assessment of the relative accuracy of ICP-MS and NAA since metals are potentially heterogeneous. A more extensive comparison of ICP-MS with NAA has produced excellent results for groundwaters (17).

Table I. Comparison of ICP-MS and NAA Data for an Arsenical Bronze Ingot

Element	ICP-MS	NAA
Sn (%)	1.24	1.78
Fe (%)	0.94	2.11
Ni (%)	0.046	0.065
Co (%)	0.009	0.012
Sb (%)	0.027	0.022
Cu (%)	78.5	76.5
Ag (%)	0.0030	0.0035
As (%)	19.1	18.0

Electron probe microanalysis data are also available for the Turkmenistan artifacts (Killick, D. J.; Young, S. M. M.; Hiebert, F., unpublished report), producing general agreement with ICP-MS (Table II). Once again, metal objects do not provide a fair test of these methods since only a small surface area is analyzed by the probe. The detection limits of the probe are also inferior, and subject to spectral interferences.

Nineteen bronze statuettes of Iron Age date from Spain and Italy, now in the collections of the Peabody Museum (PM), Harvard University, and the Department of Classics, Tufts University (TU) were analyzed for their major element composition using the procedure described above. The statuettes were presumably cast by the lost-wax technique in clay molds which were then broken open and discarded (43-45). Knowledge of the alloys used provides information on the types of ores exploited, as well as the technological nature of the production process itself (e.g. was lead added to improve casting properties? Were standardized recipes used, suggesting centralized production? Was fresh metal or scrap bronze used?). Lead isotope ratio analysis by ICP-MS of 11 Sardinian bronze figurines has already suggested the use of local ore deposits, in contrast to the apparent Cypriot origin of the copper oxide ingots found in Sardinia (19). Table III gives the results of the analyses, normalized to 100%. In addition to the elements shown, Cr, Mn, Co, Se, Cd, Sb and Ba were also determined but were never present in more than trace quantities. The 17 Spanish figurines average about 5% Sn and nearly 8% Pb, although there is considerable individual variability

in composition (Sn ranges from 1% to more than 10%, Pb from 0% to 23%). These results are entirely consistent with previous analyses of Iberian bronze figurines (45). The two Italian figurines have 7-8% Sn and 2-4% Pb, also consistent with previous analyses (44, 46, 47). Fe was only significant in one figurine, and none of the figurines had more zinc (maximum 1.4%) than is likely to have been present in the copper ore(s) used.

For these particular studies, the use of ICP-MS permitted a quantitative, minimally destructive analysis for both major and trace elements, while minimizing sample preparation and analysis time and cost.

**Obsidian.** One hundred and eighty-six geological samples from western Mediterranean sources and 33 archaeological artifacts from sites in Italy and France were prepared and analyzed for 38 major and trace elements using the procedures described above. The chemical source-tracing of obsidian in the western Mediterranean has been pursued for more than thirty years (48-53); it is only recently, however, that the multiple flows of the Monte Arci volcanic complex in Sardinia were thoroughly surveyed, chemically characterized, and followed by the analysis of significant numbers of artifacts (24, 54, 55). The analyses confirm the existence of 7 chemically distinct Monte Arci sources, 5 of which are represented among archaeological artifacts. Stepwise multivariate discriminant analysis of the elemental data was performed to determine the statistical probability at which each artifact matched a particular source. A bivariate plot of the first two discriminant functions derived from the concentration data for Ba, Mn, Sc, Rb, Sr, Y, La, Ce, Pr, Nd, Eu, Gd, Tb, Dy and Ho (Figure 1) illustrates the clear source differentiation provided by multi-element analysis. Among archaeological artifacts, geological sources SA, SB2 and SC1 are represented most often, but their relative usage varies considerably from site to site, in some cases in chronological or geographic patterns. These patterns may reflect particular cultural affinities, maritime routes and capabilities, and the exchange of items that are invisible in the archaeological record; chronological changes in distribution may be related to the adoption of a neolithic way of life, and later, to increasing social complexity.

For this particular study, the use of ICP-MS permitted a quantitative analysis of a large selection of elements not technically or monetarily feasible with any other single technique.

**Turquoise.** The lead isotope ratios of turquoise from more than 20 mines in the southwestern United States and Mexico were determined to three significant figures. The preliminary results (Figure 2) show that the Cerrillos mine can be distinguished from the other turquoise sources tested using ICP-MS (26, 40). Based on the limited number of analyses shown here, it appears that inter-source differences are greater than both intra-source heterogeneity and the analytical resolution of ICP-MS. Many more turquoise sources are currently known in the Southwestern US than in Mexico, and it is likely that additional, undocumented sources exist in Mexico which may have also supplied turquoise for archaeological artifacts. Nevertheless, it has been suggested that the residents of Chaco Canyon, where extensive workshops have been found, controlled much of the turquoise market both in the southwest US and in Mexico (56). The carrying capacity of the Chaco area may have been insufficient to

Table II. Comparison of ICP-MS and Electron Probe Microanalysis Data for Copper and Arsenical Bronze Artifacts from Gonur, Turkmenistan

Sample	As (%)		Sb (%)		Fe (%)		Pb (%)		Sn (%)		Ag (%)		Zn (%)	
	ICP	Probe	ICP	Probe	ICP	Probe	ICP	Probe	ICP	Probe	ICP	Probe	ICP	Probe
3	2.26	2.19	0.003	nd	0.54	0.96	0.22	0.12	0.29	0.29	0.10	0.11	0.11	nd
4	1.89	1.57	0.001	nd	0.60	0.61	0.43	0.24	0.09	nd	0.03	nd	0.07	nd
6	2.66	2.56	0.013	nd	0.97	1.47	0.14	0.10	0.19	0.12	0.03	nd	0.08	nd
9	1.61	2.92	0.014	nd	0.38	0.36	0.12	nd	0.03	nd	0.01	nd	0.16	nd
10	1.14	1.10	0.010	nd	0.51	0.76	1.04	0.47	0.08	0.06	0.03	nd	0.36	nd
12	1.31	1.37	0.004	nd	3.12	0.42	0.17	0.14	0.09	nd	0.04	nd	1.08	nd
13	4.89	5.52	0.66	0.32	0.13	nd	0.04	nd	0.05	nd	0.19	0.22	0.22	nd
16	2.85	2.82	0.011	nd	0.51	0.32	0.28	0.22	0.62	0.67	0.05	nd	0.18	nd
18	3.28	4.70	0.008	nd	0.44	0.40	0.06	nd	0.03	nd	0.08	nd	0.38	nd
22	0.40	2.55	0.03	0.08	0.29	0.07	0.12	0.14	0.15	0.16	0.04	0.06	2.67	nd
23	1.56	1.67	0.016	nd	0.50	0.45	0.14	0.09	1.14	0.83	0.05	nd	0.16	nd
24	2.55	2.82	0.06	0.07	0.94	1.34	0.78	0.99	1.54	1.69	0.06	nd	0.20	nd
26	1.79	1.76	0.011	nd	0.67	0.65	0.16	0.14	0.09	0.05	0.03	nd	0.13	nd
27	1.46	1.76	0.25	0.32	0.19	nd	0.23	0.23	0.94	0.95	0.07	0.06	0.15	nd

nd = not detected

Table III. ICP-MS Data for Bronze Figurines from Spain and Italy

Museum Number	Cu (%)	Sn (%)	Pb (%)	Ni (%)	Ag (%)	As (%)	Zn (%)	Fe (%)	Total (%)
PM 33-67-40/113	80.2	6.95	10.6	0.13	0.06	0.14	1.31	0.60	100.0
PM 33-67-40/114	83.2	10.5	4.68	0.03	0.09	0.10	1.36	nd	100.0
PM 33-67-40/118	87.9	3.50	7.47	0.01	0.05	0.02	1.04	nd	100.0
PM 33-67-40/120	94.6	2.62	1.53	0.03	0.06	0.03	1.11	nd	100.0
PM 33-67-40/121	94.5	5.16	0.26	0.00	0.03	0.01	nd	nd	100.0
PM 33-67-40/122	83.2	4.62	11.6	0.06	0.04	0.19	0.33	nd	100.0
PM 33-67-40/123	82.8	5.67	10.6	0.03	0.08	0.07	0.84	nd	100.0
PM 33-67-40/124	70.9	5.54	23.1	0.02	0.06	0.05	0.32	nd	100.0

Figure 1. Bivariate Plot of First Two Discriminant Functions for Obsidian Samples Analyzed by ICP-MS

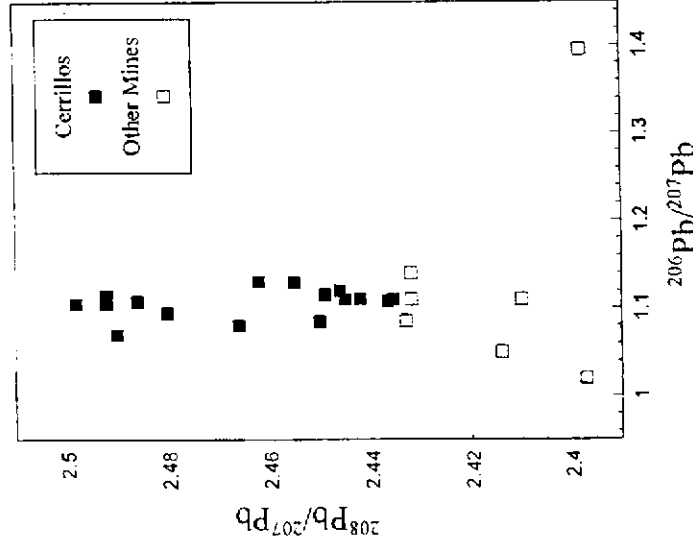
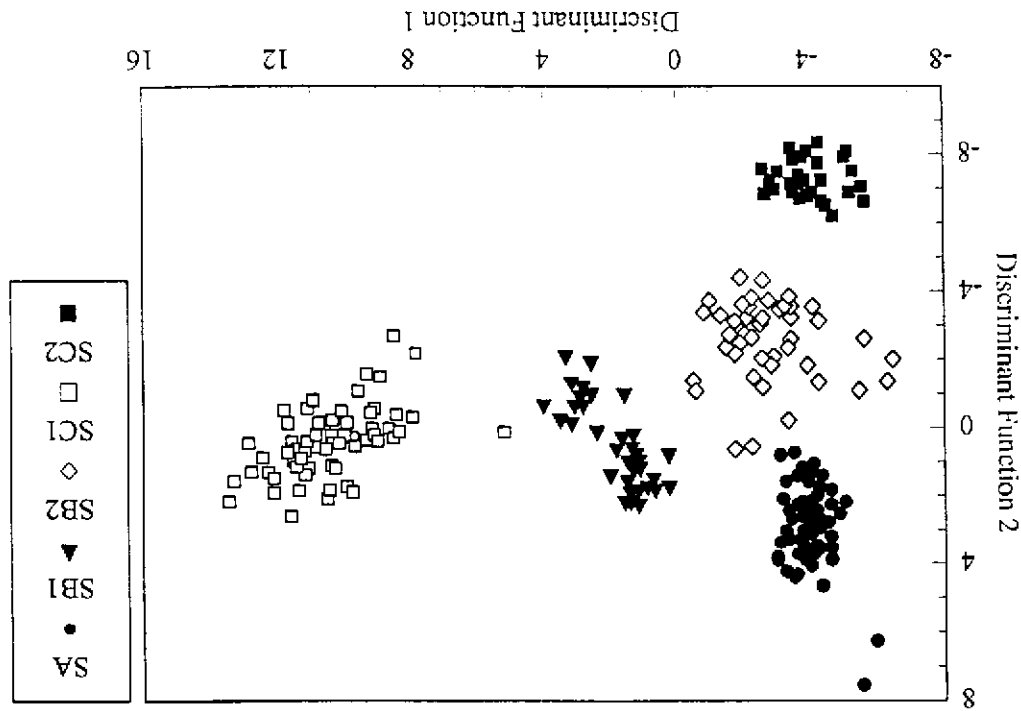


Figure 2. Bivariate Plot of Lead Isotope Ratios for Turquoise Sources in the Southwestern United States and Mexico Analyzed by ICP-MS

support the local population, and turquoise may have been exchanged for agricultural produce. The Cerrillos mine - the closest to Chaco Canyon and far larger than regional consumption would have demanded - could have supplied much of the turquoise worked at Chaco Canyon and traded to other sites. A lead isotope database for all the turquoise sources in this vast region is now being constructed so that these hypotheses may be tested.

**Conclusions**

ICP-MS is rapidly becoming an important technique for the analysis of archaeological materials, with particular advantages over other techniques in terms of the number of elements that can be analyzed, the amount of time required for sample preparation and analysis, the minimal sample size required, the ability to do isotope ratio analysis, and the relatively low cost of analysis. As with other solution analysis techniques, careful selection of dissolution procedures, meticulous sample preparation, and close matrix matching of standards are necessary to insure good results. Archaeologists should continue to use appropriate analytical techniques to answer specific archaeological questions; ICP-MS is now an established method that is available towards this end.

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## Chapter 11

### Studies of Soils from an Aleutian Island Site

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The study of properties of archaeological soils may give valuable information as to the location of middens and previously settled areas. A study is described of a site on Chernabura Island in the Aleutian Islands which was occupied by marine hunter-gatherers for at least 1500 years. Relatively simple analytical procedures for phosphorus and organic content were used to locate possible middens and places and manner of occupation. Phosphorus determination utilizing the molybdovanado-phosphate colorimetric method rather than the molybdenum blue method is described. Methods used for successfully dealing with interference for the determination of total phosphorus, organic phosphorus, and inorganic phosphorus are discussed. Most of the analytical steps for phosphorus and organic carbon determinations were performed by students using simple laboratory equipment. The methods used were simple and rapid.

High soil phosphorus content may indicate past human settlement activity (1). Phosphorus content in soils may indicate past human settlement even after 2500 years. Therefore, there is a need among archaeologists for a simple, rapid, economical, and reasonably accurate means of analyzing phosphorus in soils. Several authors have published modifications of procedures for the analysis of soil phosphorus (2-6), and portable field tests for phosphorus (2, 6, 7). Another consideration is the fractional separation of different forms of phosphorus that relate to aspects of previous human occupation (4). This paper will deal with fractional separations of soil phosphorus in terms of total phosphorus, inorganic phosphorus, and organic phosphorus as recommended by Bethel, et al. (8) as a useful breakdown of soil phosphorus.

The determination of total phosphorus by wet chemical extraction is considered one of the most accurate measures of archaeological soil phosphorus. Wet chemical extraction of total phosphorus from soils and sediments is time consuming and in some cases requires the use of dangerous reagents such as perchloric acid. There is however, a more practical, if slightly less accurate means of preparing the