Scientific methods and applications to archaeological provenance studies

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Introduction

The study of prehistoric exchange systems is a major topic of archaeological research, since the reconstruction of trade is important not only for understanding economic aspects of ancient societies, but also the social and political systems in which it operated. In addition to changes in theoretical approaches to studying trade, technological advancements in our ability to determine the source of archaeological materials have greatly enhanced the quantity and quality of this data. The analytical methods and instrumentation used in archaeological provenance studies, the research design of projects, and examples of specific studies are presented below.

Analytical methods and instrumentation

For many materials, characterization begins with macroscopic observations and measurements of physical properties such as color, density, hardness, and refractive index. There are few examples, however, where these properties have been sufficient by themselves to reliably distinguish among sources. One example is for the south central Mediterranean where obsidian found at neolithic sites is most likely to be from Pantelleria if dark green, and from Lipari if black/grey. Caution is especially warranted for materials (e.g. flint, ceramics) which at first appear to be identifiable based on color, which may be influenced by depositional circumstances, weathering, natural or intentional heat treatment, etc.
The next step for many materials is microscopic examination, typically in thin section using a petrographic microscope where the mineral grains and inclusions may be identified using natural, polarized, and/or cross-polarized light. Petrographic analysis is destructive since a thin section of at least 1 cm$^2$ is required. However it is not an expensive or difficult procedure and thin-section equipment and petrographic microscopes are available at just about any university with a geology department. There are many examples where petrographic analysis alone has been enough to distinguish lithic and ceramic sources (e.g. “greenstones” in the Alps and southern Italy; flint in northern Italy). In most cases, however, measurements of physical properties and/or petrography cannot distinguish among all possible sources in a given region of study. Since the early 1960s, instrumental methods of chemical analysis have been commonly used in archaeological provenance studies, often focusing on the trace element “fingerprinting” of individual sources. Obsidian was the first material shown to be ideal for such studies [1,2], although success with other lithic materials, ceramics, glass, and even certain metals has been achieved.

Over the past 30 years, instrumental improvements in sample handling, precision and accuracy, along with advances in data reduction, have resulted in a number of analytical methods being successfully employed in archaeological provenance studies on many materials (table I). Methods which measure elemental or isotopic composition have been the most widely used (table II). The most common elemental methods of analysis include neutron activation analysis (NAA), X-ray fluorescence (XRF), and proton-induced X-ray/gamma-ray emission (PIXE/PIGME); optical emission spectroscopy (OES) and atomic absorption spectroscopy (AAS) have been largely superseded by inductively coupled plasma spectroscopy (ICP-S; often referred to as ICP). Quantitative X-ray analysis is also available with an electron microprobe equipped with wavelength-dispersive spec-
### Table II. – Instrumental methods of elemental and isotopic analysis.

<table>
<thead>
<tr>
<th>Method</th>
<th>Materials</th>
<th>Analyte</th>
<th>Bulk chemistry</th>
<th>Trace elements</th>
<th>Isotope ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td>OES</td>
<td>pottery, glass, metal, stone</td>
<td>solution</td>
<td>only a few elements</td>
<td>OK</td>
<td>no</td>
</tr>
<tr>
<td>AAS</td>
<td>pottery, glass, metal, stone</td>
<td>solution</td>
<td>good</td>
<td>very good</td>
<td>no</td>
</tr>
<tr>
<td>NAA</td>
<td>pottery, glass, metal, stone</td>
<td>solid, powder</td>
<td>only a few elements</td>
<td>excellent</td>
<td>no</td>
</tr>
<tr>
<td>XRF</td>
<td>pottery, glass, metal, stone</td>
<td>solid, powder</td>
<td>excellent, surface analysis</td>
<td>excellent</td>
<td>no</td>
</tr>
<tr>
<td>SEM</td>
<td>pottery, glass, metal, stone</td>
<td>solid (spots)</td>
<td>semi-quantitative</td>
<td>none</td>
<td>no</td>
</tr>
<tr>
<td>EPMA</td>
<td>pottery, glass, metal, stone</td>
<td>solid (spots)</td>
<td>excellent, surface analysis</td>
<td>low sensitivity</td>
<td>no</td>
</tr>
<tr>
<td>PIXE/PIGME</td>
<td>pottery, glass, metal, stone</td>
<td>solid (spots)</td>
<td>very good, surface analysis</td>
<td>OK</td>
<td>no</td>
</tr>
<tr>
<td>ICP-AES</td>
<td>pottery, glass, metal, stone</td>
<td>solution</td>
<td>very good</td>
<td>excellent</td>
<td>no</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>pottery, glass, metal, bone, organics</td>
<td>solution; (spots w/laser ablation)</td>
<td>very good</td>
<td>excellent</td>
<td>yes</td>
</tr>
<tr>
<td>SIRA</td>
<td>bone, organics, marble</td>
<td>solid/gas</td>
<td>no</td>
<td>no</td>
<td>C, N, O, S, H, He</td>
</tr>
<tr>
<td>TIMS</td>
<td>glass, metal, stone, bone</td>
<td>solution</td>
<td>no</td>
<td>no</td>
<td>heavy elements (Pb, Sr, Nd)</td>
</tr>
</tbody>
</table>

NAA Neutron Activation Analysis
XRF X-Ray Fluorescence
ICP-MS ICP Mass Spectrometry
ICP-AES ICP Atomic Emission Spectroscopy
AAS Atomic Absorption Spectroscopy
OES Optical Emission Spectroscopy
PIXE/PIGME Proton Induced X-Ray/Gamma Ray Emission
EPMA Electron Probe Micro Analysis
SEM Scanning Electron Microscopy (X-ray analyzer)
TIMS Thermal Ionization Mass Spectrometry
SIRA Stable Isotope Ratio Analysis
trometers (WDS), and most scanning electron microscopes have semi-quantitative analysis capabilities using energy-dispersive spectrometers (SEM-EDS). All of these methods involve the measurement of characteristic wavelengths of electromagnetic radiation (in visible, X-ray, or gamma-ray portions of the electromagnetic spectrum) absorbed or emitted when a sample is “excited” (e.g. by bombardment with neutrons, protons, X-rays, or electrons). A complex spectrum is produced in which peaks at certain wavelengths are characteristic of one or more elements, and the area under a peak (intensity) is proportional to the amount of that element present in the analyzed material. Problems of spectral overlap and matrix interferences, however, are quite common, so the specific elements which can be analyzed vary from technique to technique. While accuracy is addressed through the use of standards of known values, detection limits (precision) vary both between methods and within each method depending on the brand or configuration of the instrument. Detection limits for many elements are in the parts per million range (or less) for most of these techniques; the microprobe and SEM are limited to the analysis of major and minor elements.

Methods based on atomic or molecular mass spectra include thermal ionization mass spectrometry (TIMS), used for precise measurements of the isotope ratios of heavy elements (e.g. lead, strontium); stable isotope ratio analysis (SIRA), for light elements (e.g. carbon, oxygen, nitrogen, sulfur); and ICP mass spectrometry (ICP-MS), for a large range of elements but often at reduced precision relative to TIMS [3,4]. The usefulness of isotopic methods for provenance studies is three-fold: 1) the precision of a mass isotope measurement is typically much greater than for elemental analysis methods because there are far fewer overlaps in mass spectra than in electromagnetic spectra, allowing smaller differences between sources to be identified and measured; 2) elemental composition may be different between a raw material (e.g. metal ore, clay) and a finished product (metal artifact, pottery vessel), whereas the relative abundance of the isotopes of most elements remains unchanged (not important for lithic provenance studies, unless weathering has altered an artifact’s composition); and 3) elemental concentration can also be calculated from mass isotope measurements (as is most commonly done with ICP-MS). TIMS has been extensively used for lead isotope analyses of copper, lead and silver objects in the Mediterranean [5], and for strontium and neodymium isotopes in other materials such as ivory [6], but rarely for lithic provenance studies [7]. Isotope ratio measurements using ICP-MS, however, are less time consuming and costly, and the precision of the newest magnetic sector instruments with multicollectors rivals that of TIMS. The use of a laser ablation device with ICP-MS has already been shown to be particularly important for archaeological materials because only the tiniest scar is left on the artifact where the sample was removed, thus minimizing the destructive nature of sampling artifacts and the time often spent preparing a sample for quantitative chemical analysis. The reduced precision of LA-ICP-MS relative to solution ICP-MS does not appear to be a factor in archaeological provenance studies, especially of homogeneous materials like obsidian [8].

The use of stable isotope analysis of carbon, oxygen, and other light elements for provenance studies is mainly limited to limestone, marble, and other carbonate-containing lithic materials. Cathodoluminescence [9] and electron paramagnetic reso-
nance [10] have also been used in marble provenance studies with some success (see Maniatis, this volume, p. 179). Fission track dating has been widely used for obsidian sourcing, and is very successful when significant differences exist in the age of formation of the different obsidian sources [11,12]. In areas with many obsidian sources and subsources, however, more can be distinguished using elemental methods of analysis. Magnetic parameters [13], Mössbauer spectroscopy [14,15] and backscattered electron petrography [16] have been applied with only limited success to obsidian sourcing.

Unfortunately, in too many cases instrumental methodology has been emphasized at the expense of addressing sourcing issues of archaeological significance. While it is necessary to first demonstrate that a particular analytical technique can be applied to provenance studies, all too often preliminary studies have failed to consider the limitations inherent in the analysis of many archaeological materials. The result has been that many techniques have been tried out, but few have been widely used to determine the source of significant numbers of artifacts. Further details on the scientific principles and instrumentation of the techniques most commonly used in archaeological provenance studies follow [17-21].

Spectroscopy and spectrometry

The atomic properties of elements are the basis for many analytical methods. The number of protons in the nucleus defines each element, while for many elements there are two or more isotopes (which have different numbers of neutrons). The elements with naturally produced unstable isotopes (e.g., carbon, potassium) are useful for dating, while those with stable isotopes (e.g., lead, strontium) may also vary in their isotope ratio and thus are useful for provenance studies. For most elements in the periodic table, though, it is the different numbers and positions of electrons in orbitals and shells around the nucleus that provide the basis for their analytical identification, while in the ground state there are an equal number of electrons to protons, with up to two in the innermost shell, eight in the next, and from eight to eighteen in the third. Each electron position has a specific energy, so that a fixed amount of energy is absorbed or emitted by transitions of electrons from one position to another and each element has a specific pattern of emission or absorption lines. Energy is also characterized as electromagnetic radiation or photons (from radio waves to visible light to X-rays):

\[ \lambda = \frac{c}{\nu}, \]

wavelength \( \lambda \) is inversely proportional to frequency \( \nu \); \( c = 3 \times 10^8 \text{ m/s} \);

\[ E = \frac{hc}{\lambda} = h\nu, \]

energy \( E \) is inversely proportional to wavelength; Planck’s constant \( h = 6.626 \times 10^{-34} \text{ J s} \). Since the intensity of emission or absorption lines (whether measured as energy or radi-
Optical spectroscopy. – Optical emission spectrometry (OES), primarily used in the 1950s to 1970s, used spark volatilization of a solid powdered sample in a graphite cup to excite electrons in the outer orbital, thus causing emission in the visible light spectrum when the electrons return to the ground state. The spectrum of resonance lines produced was then separated with a system of mirrors, diffraction grating, and slits, and recorded on a photographic plate. OES was replaced by the 1980s by atomic absorption spectrometry (AAS), which measures absorption rather than emission for individual elements [22]. In this technique, the sample in solution is atomized in a flame or graphite furnace, irradiated with light of a particular elemental frequency, and the loss of irradiation due to absorption is measured using a photomultiplier tube. The main limitation of AAS is that different lamps are needed for each element measured, so that sample preparation and analysis for many elements is very time consuming.

By the 1990s, inductively coupled plasma spectroscopy (ICP-AES) replaced AAS for multi-element quantitative analysis; besides automation of analysis of different elements, its high-temperature torch dissociates compounds better than AAS and thus eliminates many spectral overlaps. An electrically conductive plasma of about 8000 °C is created by igniting an argon gas flow with Tesla sparks which then flows through a radio frequency induction coil. The sample (typically in solution) is aspirated into the torch and atomized and ionized, producing elementally characteristic ionic spectra which are filtered by a scanning monochromator and measured by a photodetector. ICP instruments have strong temporal and spatial stability resulting in low background noise and thus very low detection limits (ppb range), while automated scanning allows rapid measurement of up to 70 elements. ICP-AES is now the standard instrument used for trace element analysis in archaeological provenance studies, especially of ceramics and materials that easily may be put into solution [23].

X-ray spectroscopy. – X-ray analysis depends on the measurement of high-energy transitions between the deepest orbitals of an atom, rather than the outer orbital transitions measured in optical spectroscopy. The excitation beam causes the ionization of inner (K, L) orbital electrons, which ultimately fall back into their stable energy levels, resulting in the emission of X-rays of characteristic energy and wavelength. Several methods may be used to excite the sample, producing fluorescent X-rays, the most common being X-ray fluorescence (XRF) in which a primary X-ray beam is used to excite the sample [24] (see also Milazzo, this volume, p. 227). For all X-ray techniques, the exciting beam interacts significantly only with sample atoms within 20–200 μm of the surface of a solid or pressed pellet sample. The X-rays produced are measured using either energy dispersive (EDS) or wavelength dispersive (WDS) spectrophotometers. In EDS, energy (E) is measured using a known crystal and angle, while in WDS, wavelength (λ) is measured at different angles from the sample. According to Bragg’s law, wavelength
is directly related to the angle and the $d$ spacing of the crystal:

$$n\lambda = 2d\sin\theta.$$ (3)

In X-ray diffraction (XRD), the $d$-spacing of the sample is determined by measuring theta using a fixed wavelength. Other important features of X-ray techniques includes whether the sample itself is placed within a vacuum chamber, since elements below $z = 22$ (titanium) produce X-rays which are absorbed by air. While older X-ray instruments with vacuum chambers usually could not detect elements below $z = 12$ (magnesium), newer XRF instruments with special filters allow analysis for almost all elements, with sensitivity in the low ppm range. Synchrotrons have also been used recently as extremely intense X-ray sources which allows for microbeam analysis with superior analytical sensitivity (see Pantos et al., this volume, p. 299). Total reflection X-ray fluorescence spectrometry (TXRF) takes advantage of a different excitation geometry setup to analyze a tiny sample (less than 1mg) removed from an object for many trace elements with only minimal matrix effects. The sample chamber is usually filled with air so only elements above $z = 12$ may be detected.

In electron microscopy, an electron beam (typically focused on spots 1 to 40 $\mu$m in diameter) creates the orbital vacancies. Secondary electrons released from surface atoms show topography of 3-dimensional objects, while the backscattered electrons from interactions with the nucleus reflect atomic mass/number. The background continuum of X-radiation produced by deceleration of the primary electron beam, however, limits the sensitivity of this technique to the detection of major and minor elements. For proton-induced X-ray emission (PIXE), it is a proton beam tapped from a particle accelerator which causes the initial vacancies. Sensitivity is in the 1–10ppm range for most elements, with measurement precision of 5–10%. The main advantage of PIXE is its ability to analyze whole objects in air, without sample removal [25] (see also Mandó, oral communication).

**Gamma-ray spectroscopy.** – Similar spectroscopic measurements are also commonly done using two techniques which stimulate gamma-ray emissions. In neutron activation analysis (NAA), the sample is irradiated with a beam of neutrons from a nuclear reactor, while in proton-induced gamma-ray emission (PIGME), the sample is irradiated with protons from a particle accelerator. The irradiation produces “artificial” radioactive elements, which emit gamma-rays at different times based on the length of irradiation and the half-life of each element. In NAA [26,27], crushed solid samples of about 100 mg are typically irradiated for about five seconds, and then the short-lived elements (Ba, Cl, Dy, K, Mn, Na) are measured about 25 minutes later. A second set of crushed solid samples (ca. 250–300 mg) are placed in the neutron flux for about 70 hours, and left to decay for about 8 days before measuring the medium-lived elements (Ba, La, Lu, Nd, Sm, Y and Yb). After another three weeks, the long-lived elements (Ce, Co, Cs, Eu, Fe, Hf, Rb, Sb, Sc, Sr, Ta, Tb, Th, Zn and Zr) are measured. The elements H, B, C, N, P and Pb cannot be detected since they form nuclides with half-lives too short or too long to be
easily measured. Sensitivity for NAA is below 1 ppm for most elements, while precision is perhaps the best of all elemental techniques. The related technique of prompt neutron activation analysis (PNAA) is based on the measurement of the gamma-rays emitted when the nuclei initially absorb neutrons from the nuclear beam.

In PIGME (as for PIXE) the particle beam may be focused, typically to about 1 mm², while different radionuclides are produced compared with NAA, so that different elements are typically measured. PIGME is often done along with PIXE to produce information on the greatest number of elements in the sample.

Isotope spectrometry. – There are three main types of isotope spectrometry applied to archaeological materials. Thermal ionization mass spectrometry (TIMS) has been widely used to precisely measure isotopes of heavy elements such as strontium and lead, while stable isotope ratio analysis (SIRA) is used to precisely measure isotope ratios of light elements such as carbon, oxygen, nitrogen, sulfur and hydrogen. ICP mass spectrometry (ICP-MS), while measuring individual mass units, is more commonly used as an elemental analysis technique, at least when the isotopes in the sample are present in their natural abundance ratio. Newer instruments however also are used for quantitative isotope ratio analysis (see Pernicka, this volume, p. 309).

Thermal ionization mass spectrometry (TIMS) requires a complicated series of sample preparations. Following dissolution, elements of interest must be separated and purified using ion exchange columns before being deposited on a rhenium filament. While excellent precision is achieved, the time and cost of analysis has mostly limited archaeological provenance applications to copper, lead and silver sourcing in the Mediterranean region [28].

In stable isotope mass spectrometers, the sample is converted to a gas (e.g. CO₂, N₂) which is then ionized and the different mass gases (e.g., 44, 45, 46; 28, 29) collected in separate Faraday cups. Samples may be introduced as gases already purified using offline cryogenic distillation units, or through automated systems such as common or individual phosphoric acid baths which produce CO₂ from samples containing carbonates and CHN analyzers which produce CO₂ and N₂ from organic samples. Liquid (HPLC) or gas (GC) chromatographs coupled with stable isotope mass spectrometers allow analysis of isotope ratios of specific components of organic samples.

ICP-MS is similar to ICP-AES, except that after ionization in the plasma, the ions pass into a mass spectrometer for separation and measurement. There are few mass spectral overlaps, and for elemental analysis nearly all can be overcome by analyzing alternative isotopes. An internal spike using indium or rhenium allows for calibration against any instrument drift. In a quadrupole mass spectrometer, the entire mass range may be rapidly scanned, producing results for all but several elements. Solution detection limits are about 1 ppb for light elements, and 50 parts per trillion for heavy elements, with precision 1–3% for most elements. Like ICP-AES, ICP-MS combines small sample size and low per sample cost with the ability to analyze a large number of major and trace elements (including rare-earth elements, platinum group elements, Ag, Au, Th, and U). Magnetic sector ICP-MS instruments with multiple detectors allow simultaneous
measurement of several isotopes and achieve precisions comparable if not superior to TIMS.

ICP-MS can also be used with a laser ablation device (usually Nd-YAG), which can remove from a solid specimen a sample just 200 microns wide, sending it directly to the ICP source. The laser beam is usually allowed to pass over the ablation area once prior to data acquisition to remove surface contaminants, followed by several scans on the same sample. Precision is reduced relative to solution samples, but comparable resolution is achieved by using element ratios rather than absolute concentrations. While the small amount of sample ablated makes this technique minimally destructive, samples must nevertheless fit inside the ablation chamber.

Standards and calibration. – The analysis of standard reference materials is critical for all analytical techniques, both to ensure consistent results on a single instrument, and to allow comparison with results obtained in other laboratories. Ideally, reference materials should be similar in composition to the samples of interest, since matrix effects occur for most analytical techniques. For solution techniques, blanks should be prepared in a similar manner to regular samples. Most laboratories analyze an in-house secondary reference material, as frequently as every 5th to 10th sample, to control for instrumental drift and ensure stability.

Principles and prerequisites of provenance studies

In order for a provenance study of lithic artifacts to be successful, there are several prerequisites: 1) all relevant geological sources must be known; 2) these sources must be characterized for the physical properties or parameters (e.g., color, density, mineralogic, elemental or isotopic composition) which will be measured for the artifacts; 3) one or more properties must be homogeneous within an individual source; 4) measurable, statistically valid differences between sources must exist for one or a combination of these parameters; and 5) they must be measurable using analytical methods appropriate for archaeological artifacts [29].

Many provenance studies have been attempted when not all of the prerequisites have been met. In some cases, not all of the possible sources were known, so not all of the artifacts tested “matched” a known source. In others, intra-source variability and inter-source differences have not been well established because only a small number of geological specimens have been tested; this makes source attributions of artifacts, even when they match one source, unreliable, since some specimens from other sources might also have the same measured values. A sufficient number of well-selected samples from each source is required to make such “overlaps” statistically unlikely. Locating and characterizing all of the geological sources may be difficult for lithic types which occur in multiple, small outcrops; some rocks are more likely than others to form in dispersed patterns yet still have the same physical characteristics.

In general, provenance studies have been most successful when the number of possible geological sources is naturally limited. While many potential sources may be effectively
TABLE III. - Considerations in choosing an analytical method for provenience studies of archaeological materials.

<table>
<thead>
<tr>
<th>Analysis type</th>
<th>Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>bulk or surface?</td>
<td>minimum sample size required</td>
</tr>
<tr>
<td>destructive or non-destructive?</td>
<td>solid or powder form?</td>
</tr>
<tr>
<td>precision and accuracy</td>
<td>pre- and post-analysis handling</td>
</tr>
<tr>
<td>availability and cost</td>
<td></td>
</tr>
</tbody>
</table>

excluded because of geographic distance (especially in certain time periods), we must avoid a tautological situation in which artifacts from “unlikely” sources are never identified as such—often the exception to the rule will be the most significant finding. With fewer natural sources, there is less chance of additional sources remaining unknown, a smaller total number of specimens must be characterized (advantageous for time and cost reasons), and the likelihood of finding some parameter which meets prerequisites 3–5 above will be much greater. The characterization of obsidian in the Mediterranean, the Near East, and elsewhere is the classic success story for just these reasons. Provenance studies of other stone materials (e.g., chert/flint, steatite, greenstone, marble, basalt, granite) also have been successful when the above criteria were satisfied.

The efficacy of many techniques for provenance studies of certain materials has been demonstrated. Even though the use of some techniques may be successful in a scientific sense, they may not be readily applicable to all archaeological studies because of sampling requirements, cost, or availability (table III).

Sample selection and other considerations

Archaeological materials are often compositionally similar to naturally occurring materials—for lithic artifacts the composition is the same as in the raw material—but analytical methods appropriate for geological specimens may not be suitable for archaeological artifacts. First and foremost we must consider the destructive nature of many analytical techniques. In many cases, a sample is physically removed from each artifact, either as a solid or as a powder. This may be done because the artifact is too large to analyze whole; it is impractical or impossible to transport the artifact(s) to the laboratory; or the technique itself requires samples to be powdered or put into solution. AAS and ICP, for example, usually require the sample to be put into solution; XRF and PIXE need a polished flat surface to produce fully quantitative results; and the determination of some elements by NAA will leave the sample too “hot” to be returned.

For heterogeneous materials it is important to take enough sample so that it is reasonably representative of the whole artifact—100 milligrams seems to be a standard amount. Electron microprobe analyses of areas 40 µm in diameter or less have shown that for homogeneous materials like obsidian, it is sufficient to remove 1 mm² samples from an artifact. Similarly, for isotopic measurements of major components, e.g. carbon and oxygen in marble, as little as one milligram may be necessary. While these quantities
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are certainly small, their removal from an artifact may nevertheless have a significant impact on its integrity, especially for small artifacts such as lithic flakes and blades, marble figurines, etc. For elaborate or morphologically distinctive artifacts it may be necessary to remove the sample by drilling from a less visible portion of the artifact, a time-consuming activity at the least. For such artifacts, it is often impossible to remove a solid sample. LA-ICP-MS leaves only a tiny crater where sample has been removed by the laser, but the artifact must be transported to the instrument, and it must fit inside the laser ablation chamber which is typically only two or three inches in diameter.

For solid samples, it is also important to consider whether the technique produces results based on the bulk or surface composition of the sample, and the range of elements (or isotopes) which can be analyzed. For lithics, bulk and surface composition should be the same, but artifact surfaces may become weathered or otherwise altered by the burial environment. Care must be taken therefore when using surface analytical techniques such as XRF, PIXE, and LA-ICP-MS. While NAA gives the bulk composition of the sample, it is rarely used to provide data on the major element composition of lithic materials; XRF and PIXE provide data on major and many trace elements. Among the solution-based techniques, analyses also often focus on trace rather than major element composition.

Precision (the plus or minus, or replicability, of each analysis) and accuracy (nearness to actual values) vary not only for each technique, but also for each element (or isotope) under analysis. Overall analytical precision is limited by a combination of sample preparation techniques and instrumental conditions, while accuracy is typically corrected for through the use of standard reference materials, ideally similar in composition to the sample so as to avoid matrix effects. Elemental (or isotopic) composition cannot be considered characteristic of a particular source if the analytical precision of the measurement approaches the difference in value between two sources.

The actual process of taking compositional data and attributing an artifact to a particular source is not a trivial exercise. Sufficient samples of geological source material must be available to establish the variability within a single source (absolutely a minimum of 15 and preferably 25–30 for homogeneous sources). Elements which have limited ranges of variation within sources, and have little or no overlap with other sources must then be selected; many elements will not be useful in source discrimination. For obsidian, bivariate plots of certain trace elements appear to be sufficient for visual assignment of artifacts to individual island sources, at least in the Mediterranean [30]. In other regions, and/or to assign artifacts to specific subsources, multi-variate statistical analysis is usually necessary (see Baxter, this volume, p. 17). The most powerful method is discriminant function analysis, in which sources are predefined based on the compositional data for geological specimens, and artifacts are assigned based on their posterior probability of belonging to one of these pre-existing groups. As with all statistical techniques, one must verify the suitability of the data for a particular technique (e.g., requirements of normality).

Availability of instrumentation and the cost of analysis unfortunately are two practical aspects in the choice of technique for archaeological provenance studies. Funding, when more than nominal, is nevertheless finite, and per sample costs are likely to be less
when instrumentation at an academic institution—especially one’s own—is employed. A trade-off therefore often results when these factors are considered along with the type of analysis, sample requirements, and particular elements analyzed. Fortunately, costs have been much reduced for many methods due to lower prices for the instrumentation itself combined with automation of the analysis. Lower costs and generally reduced sample size requirements now permit the analysis of larger numbers of artifacts. Such studies overcome the interpretive limitations imposed by small data sets, and allow detailed examination of geographic and temporal differences in lithic exploitation patterns. Comparison of the results from earlier and more recent studies of obsidian artifacts at several sites in the central Mediterranean illustrate the importance of analyzing statistically significant numbers of artifacts prior to drawing conclusions about the relative importance of individual sources.

**Trade and exchange**

Scholarly interest in trade and exchange has been especially high for the past 25 years, especially since technical advances made it possible to determine the source of materials such as pottery, jade, turquoise, amber, marble, copper, lead, and obsidian. Numerous edited volumes have been devoted to this subject [31-41]. In addition to specific case studies, the literature includes a number of essays which discuss the nature of production, trade and exchange, and review the history of their archaeological interpretation [42-45].

Trade is defined in modern economics as the mutual movement of goods between hands, but in the archaeological record it is the movement of the materials themselves, not their ownership or possession, which is easily determined. Anthropologists seek to establish a life history for these goods, from the procurement of their raw materials to their ultimate disposal. Significantly, the goal is not to simply document an economic transaction but also the circumstances and reasons behind it.

Flaked stone artifacts are among the most common in the archaeological record, and are often made from materials that do not occur locally (e.g., obsidian and flint). They are the product of several distinct behaviors, which may have occurred at different times in different places: acquisition of the raw material; preparation of a core; flaking, trimming and shaping; use; maintenance or modification; and disposal. In addition, their presence at a particular site will have been affected by such variables as the rarity of the raw material, the number of production stages necessary, whether production was done by specialists or not, and how long a tool retained its usefulness. Finally, the movement or trade of these stone artifacts may not have been strictly for their utility as tools, but as prestige items used only by select individuals or under special (e.g. ritual) circumstances.

Stone used for axes and other ground rather than flaked tools was also often traded over great distances in prehistoric Europe, with a similar set of factors and variables involved [46]. By the Iron Age (1st millennium BC), though, stone tools were largely replaced by metallic ones, and by Roman times the stone material most widely traded was marble, used mainly for sculpture. Besides the complex sociopolitical systems of classical Greece and Rome which created this demand, large labor forces and advanced
transportation methods were able to support the trade of tons and tons of marble from sources in many areas of southern Europe. Such labor organization did not exist in the Bronze Age, when Stonehenge was constructed, and debate continues over the geographic rather than primary geological sources of the stones used [47].

Ceramics are very common at archaeological sites beginning in the Neolithic period (by the 7th millennium BC in southeastern Europe, and somewhat later in the rest of Europe). The finished product, like flaked, ground, or carved stone, is the result of significant effort by experienced individuals, but which is even more complex in that it involves not only the acquisition of clay, which is likely to have been available locally, but also of temper and in many cases pigments for painting, as well as fuel for the firing. Unlike stone tools, some of the most important properties of ceramics (e.g. form and decoration) are determined entirely by their makers. But while ceramics may have been traded because of variance in these characteristics, in many cases it was the contents of ceramic vessels (e.g., amphoras) which were the primary material being traded over large distances.

Metal artifacts are also the result of considerable effort and transformation from the raw ore. Unlike clay, most metal ores are not readily available, significant effort was often necessary in their acquisition, and an even greater amount of flux and fuel was necessary for the smelting process, along with the furnace and its accessories. While the subsequent melting of already purified metal for casting artifacts is less complex and could be done in any village settlement, smelting would have required greater labor organization. By the Copper and Bronze Ages (4th-2nd millennia BC), both purified metals (lead, silver, gold, copper, tin) and finished, often alloyed (e.g. bronze) artifacts were traded over great distances in Europe and the Mediterranean. Unlike stone tools and ceramics, metal artifacts could be entirely recycled and turned into new objects.

While stone, ceramics, and metals may be the most common materials found at archaeological sites, they were not the only materials traded in prehistoric Europe, nor are they the only ones that can potentially be sourced. Among the other trade items that have been studied are amber, a natural resin [48], and glass, another pyrotechnological product which becomes common only in the Roman period. But as will become evident, trade studies have focused on ceramics and a few types of stone and metals because of certain properties they have which allow artifacts to be scientifically matched with the source of their raw materials. Following brief discussions of European trade in copper and marble will be a full case study of obsidian trade in the Mediterranean.

Copper. – By the Late Bronze Age (ca. 1600–1200 BC), bronze tools and weapons were in high demand in many societies. In the eastern Mediterranean, much of their production and trade must have been to satisfy the needs of the state level societies of Greece, Crete, Anatolia and Egypt. While the tin sources used are still unclear, archaeological and analytical evidence points to Cyprus (from which the word copper is derived) as the most important copper source in this region. Several sites on the island have produced evidence for smelting of copper ores, including slag, tuyeres and crucibles. But the best evidence for trade in Cypriot copper comes from a characteristic style of
pure copper ingots found off the island. Copper oxhide ingots, weighing on average about 30 kg, and resembling the stretched-out hide of an ox but more likely shaped that way to facilitate carrying, are known from sites in Cyprus, Crete, Greece, Turkey, Israel, Egypt, Albania, Bulgaria, Sicily and Sardinia, as well as the famous shipwrecks at Cape Gelidonya and Uluburun in Turkey. Most of the known ingots come from shipwrecks or from coastal sites, suggesting the importance of sea-borne traffic for their distribution. The excavation of the 14th and 13th century BC shipwrecks at Uluburun and Cape Gelidonya has indicated that large cargoes of copper and tin ingots, glass ingots, ivory, ostrich eggs, ebony logs, myrrh and frankincense, and probably resins, olive oil and wine were regularly transported over great distances in the eastern Mediterranean. The personal possessions found on board both wrecks point to the Levant for the identity of the crew. The location of these wrecks, and the main cargo items on board, indicate that they were heading west, while archaeological evidence and ancient texts indicate that shipments also must have headed south to Egypt.

While copper sources also exist in many of these areas, copper is a refined product, ready for alloying and casting, and thus would have been immediately useful and exchangeable for other goods at any Bronze Age settlement regardless of its location. Nevertheless, it is also possible that local copper was used to make oxhide ingots, under the control of Aegean or Levantine prospectors, or simply to imitate a recognized standard type. Modern mass spectrometers are sensitive enough so that in addition to lead objects, copper and silver artifacts containing trace quantities of lead can also be measured. The lead isotope ratios determined for copper artifacts thus can be matched directly to known ore samples because the ratios of the isotopes do not change during the smelting or refining process, although the quantity of the element does [49].

In the last 20 years, an extensive database of lead isotope ratios for copper and other ores throughout Europe and the Mediterranean has been established, and many ingot and artifact collections tested. The results obtained strongly indicate that Cyprus was the source of the vast majority of the copper oxhide ingots tested, including those found in Sardinia, an island with its own significant copper sources. At the same time, the lead isotope ratios for artifacts and other shaped ingots match those of the local ore sources, although there is also evidence that artifacts may have been made of mixed ores or recycled copper and bronze. Since oxhide ingots, although of pure copper, could not have been made in a single smelting but must themselves have been remelted, they too could have mixed lead isotope ratios, resulting in some debate over the reliability of the lead isotope approach since the mixture of ores from two different sources might result in values similar to a third which has not yet been found or documented [50, 51]. While it will always be possible that some artifacts were made from small ore deposits which are now worked out, these should constitute only a fraction of the overall production, and for the most part the analyses of the oxhide ingots have produced very consistent results. Since Mycenaean style ceramics found at many of the same sites as oxhide ingots have also been chemically tested and shown to match Aegean clay sources [52], it is socioeconomically likely that copper ingots and many other materials were traded together with these ceramics and their contents, both by land and sea.
Marble. – Beginning in the Iron Age, marble was widely used for sculpture and architectural decoration because detailed features could be carved and the finished object painted, probably with less effort and expense than for bronze sculpture. Many marble sources in the Mediterranean are still being quarried today, for example the large Carrara quarry system in northern Italy and several on Greek islands, and unfortunately this modern activity has erased much of the direct evidence of ancient quarrying. Sourcing marble is particularly useful since many sculptures are in private or museum collections with no specific information on where they were found. Determining the source of the marble may be important in assessing the sculpture’s authenticity and age, since for example a sculpture in the Greek Archaic style could not have been made of Italian marble unless it was a Roman or later copy. Many excavated sculptures or architectural items were also made in multiple pieces so it is informative about economic and other practices to learn whether certain marble sources may have been specifically preferred for certain parts of sculptures (e.g. the head or bust). Of course, determining the source of the marble that was used documents specific trade connections that existed, and provides some quantification of the relationships that existed between different regions in the Greek, Roman, and later periods.

Since many of the marble sources that were exploited in antiquity are of white marble, it is not easy to distinguish among most of them based on their visual appearance, especially in a sculpture with a smooth and polished surface. Nevertheless, some marble sources have gray streaks, large grains, or other visual characteristics which assist in the sourcing of artifacts. But it is really the application of analytical methods that allow many sources to be positively identified. Some marble is dolomite, rather than calcite, which can be determined by elemental analysis of the magnesium content (calcite is calcium carbonate whereas dolomite is calcium magnesium carbonate) or by X-ray diffraction. For dolomitic marble sculptures found in the central or eastern Mediterranean, it is highly likely that they came from a particular source on the island of Thasos in the northern Aegean. For the more common calcite marble, stable isotope analysis of carbon and oxygen has been the technique most widely used, although this analysis by itself is not enough to distinguish among all of the Mediterranean white marble sources [53]. Instead, a multi-method approach which combines XRD and isotopic analysis with grain size measurements and petrographic features works for most of the main Mediterranean sources [54]. Strontium isotopes are also likely to be very useful, but a large database of values for marble quarries has not yet been established.

The analysis of a large number of classical marble sculptures in museum collections and from archaeological sites has suggested many things about the ancient marble trade, including the chronology of use of different quarry sources and thus the local economic and political circumstances in which intensive marble exploitation occurred. Marble was first quarried on a large scale beginning in the 7th century BC, on Naxos in the Cyclades, with other island sources exploited shortly afterwards. Mount Pentelikon was the major source of marble used for classical Athenian architecture, while the translucent marble of Paros was preferred for important statues. In Italy, Carrara marble was commonly used, but Pentelic marble was chosen for architecture of particular prestige during the
Republican and Imperial periods, and marble from Paros was commonly used for free-standing sculptures. The Romans later opened up many quarries in Asia Minor, and marble from Prokonnesos (Marmara) became increasingly common from the Hadrianic period onward, probably for economic reasons related to ease of transport. During the Imperial period, dolomitic marble from Thasos was also commonly used for fine sculpture, and was probably carved by northern Greek artists working in Greece or who traveled with their materials throughout the Mediterranean. In other parts of Europe, local marble sources were also exploited and used for statues and architecture, but important or prestigious sculptures were often made of marble imported from the Aegean. One of the best examples of this are the Thracian horsemen sculptures from Romania, which express a local religious myth but are commonly made of marble from Prokonnesos or Paros [55].

**Obsidian sourcing in the central Mediterranean: a case study**

Obsidian is widely considered an ideal material for source tracing using elemental methods of analysis, and provenance studies of Mediterranean obsidian have been described as a success story [56]. As such, a review of obsidian research, specifically in the central Mediterranean, illustrates well the principles and prerequisites of provenance studies and their potential contribution to reconstructions of prehistoric trade.

Many trace elements in obsidian are related to the gross compositional makeup of the parent magmatic material because of their individual chemical volatility and solubility. Many “incompatible” elements are insoluble in solid magmatic phases, and have higher concentrations in the liquid magma (e.g., Sr, Ba, Rb, Cs, La, Ce, Y, Ti, Zr, P, Ta, Nb, Be, B and Li). The evolutionary nature of magmas, which continuously incorporate the surrounding crust while forming (crystallizing) new solid rock, results in changing patterns of absorption by different minerals in the solid phases. Both differential crustal contamination and fractional crystallization of the magmatic melt contribute to considerable differences in the concentrations of the incompatible elements in volcanic flows, and these elements are thus particularly useful for obsidian provenance studies. Although water percolating in rock deposits can exchange Sr, Na, K and other elements with volcanic glasses, this effect is much more pronounced in devitrified glass or volcanic ash than in obsidian, and one need not worry about discrepancies between geological specimens and archaeological artifacts deposited under different environmental conditions for the last several thousand years.

While it was only in the early 1960s that chemical characterization studies of obsidian began, the principal Mediterranean sources of obsidian were already known. Prior to the application of instrumental methods of analysis, an ordinary wet chemical analysis of major elements had produced the surprising (and erroneous) result that obsidian artifacts in Malta were of Melian origin [57,58]. The first successful provenance study of Mediterranean obsidians relied on trace element concentrations of barium, zirconium, niobium and yttrium, measured by optical emission spectroscopy [1]. These results demonstrated that it was possible to differentiate many of the sources in the Mediterranean region, but
they did not distinguish between Lipari and Palmarola. Furthermore, all sources were represented by a very limited number of specimens.

More detailed examination of the Mediterranean sources, using neutron activation analysis, was completely successful in attributing artifacts not only to specific islands, but even in distinguishing among multiple flows on Sardinia and Melos [25, 59-61], and in the complex sources of central Europe [62] and central and eastern Anatolia [63]. The existence, however, of multiple Sardinian flows was based on compositional clusters of artifacts rather than of geological samples, so the actual location of several sources remained unknown. For Lipari, several flows have been identified — some of historic age — but only the Gabellotto flow has been studied in any detail [64]. Multiple flows also exist on Pantelleria, but these too have only been preliminarily studied [65]. Fission-track dating also emerged as a useful provenance method since the ages of the different island sources were substantially different [66-68]. Provenance studies based on fission-track dating, however, were unable to distinguish among the multiple Sardinian sources, which were presumably close in age [11, 69]. The interpretive significance of being able to distinguish between multiple flows was not really recognized until provenance studies of large numbers of artifacts began to reveal patterns in the exploitation of specific obsidian sources [70].

During the 1970s and 1980s a number of other archaeometric techniques were tested for their usefulness in provenance studies. Initial attempts at using strontium isotopes [7], Mössbauer spectroscopy [14], electron paramagnetic resonance [71], and magnetic parameters [13] have only rarely been pursued, and were generally unsuccessful in distinguishing among all sources.

It was only in the 1980s that serious attempts were made to locate and properly characterize all of the Sardinian obsidian sources. Besides the well-known source at Conca Cannas (SA), additional Monte Arci sources were located in situ and some of the questions surrounding the SB source previously identified only from archaeological samples were resolved. Unfortunately this research was only briefly published and never continued [72]. Another geologist conducted a thorough survey and analysis of the Sardinian sources but never formally published his thesis [73]. He was able, however, to identify 4 chemical subgroups among numerous localities with small unworkable nodules, in addition to the 4 usable sources previously identified. Also working independently, another researcher identified two SC subgroups, but neither was found in situ [64]. All three of these studies relied on X-ray fluorescence analyses of trace elements, supplemented in two cases by neutron activation. It was also demonstrated that all of the main Mediterranean obsidian sources (Sardinian A, B, C, Lipari, Pantelleria, Palmarola, Melos, Giali) could be chemically differentiated on the basis of major/minor elements alone [64] (fig. 1). The use of major elements to discriminate between three principal Sardinian groups was also confirmed using atomic absorption spectroscopy as part of an obsidian hydration dating project [74].

When this author began his own research on the Sardinian sources, there nevertheless remained a number of problems regarding the sources and usage of Sardinian obsidian. The SC source(s) had not been located in situ, and the number and location of SB sources
was not entirely resolved. A detailed survey of obsidian outcrops in the Monte Arci area began in 1987 and has resulted in the in situ location of all usable sources and their chemical characterization by ICP-MS (fig. 2), XRF and electron microprobe [75-79]. For the purposes of archaeological provenance studies, it is useful to chemically distinguish among four geographically specific sources (SA, SB1, SB2, SC), which also have distinctive characteristics that might have been important in their exploitation by prehistoric peoples (e.g., accessibility and density of source material; color, transparency, and luster; fracture properties). It is not possible to distinguish among these four sources using fission-track dating or SEM-EDS, although both appear to have sufficient precision to distinguish two Monte Arci subgroups [12,80].

Until a decade ago, it was nearly impossible to assess the relative importance of different sources at a single site or within a single chronological period (fig. 3). While obsidian from about 100 western Mediterranean sites had been analyzed, most sites were represented by only a few samples, many from imprecise contexts. Only four sites had more than ten analyses, and only at Skorba in Malta could we look at chronological change in source utilization. This situation has begun to be addressed with larger numbers of artifacts analyzed at several sites in southern France [81]; at Gaione and Arene Candide in northern Italy [82,83]; at many sites in Sardinia and Corsica [76,84-86]; at Acconia [87] and Bova Marina [88] in southern Italy; at Grotta dell’Uzzo in Sicily [89]; at Zembra in Tunisia [84], and several other sites in Tuscany, the Adriatic islands, and elsewhere [90] (fig. 4).

These analyses of significant numbers of artifacts at individual sites allow for hypothesis testing and interpretation that was not possible with limited numbers of analyses [84,70]. For example, it has been hypothesized that in Sardinia during the Early...
Fig. 2. – Multivariate discriminant function analysis of ICP-MS data for Monte Arci (Sardinia) reveals five distinct source groups.

Fig. 3. – Distribution of obsidian in the central Mediterranean. Data for sites from all time periods are shown.
Neolithic (ca. 6000–5000 BC), less-organized selection of source material would result in the presence of obsidian flakes from multiple sources, and in its relatively inefficient use; by the Late Neolithic (ca. 4000–3000 BC), procurement would have been better organized, focusing on the higher quality SA obsidian, and featuring more efficient reduction technology in the production of cores and blades [91]. An apparent shift in source utilization which supports this technological hypothesis of obsidian selection is observed at Arene Candide in Liguria, where less intensive, on-site production of tools from multiple obsidian sources (SA, SB, SC, PI) in the Early Neolithic is followed by nearly exclusive importation of blades of high-quality Lipari obsidian in the Late Neolithic [83].

This pattern, however, is not paralleled in Sardinia and Corsica, where type SC obsidian becomes much more important in the Late Neolithic (fig. 5). At Grotta Filiestru, for example, the use of clear, glassy type SB2 obsidian from the western flanks of Monte Arci decreases over four Neolithic cultural periods, while the use of opaque, less glassy type SC obsidian from the northeastern part of Monte Arci increases; type SA is never more than 20% of the assemblage. In contrast, type SA accounts for an average of 40% of the assemblage at Basi in Corsica, SB2 is never important, and this pattern does not appear to change significantly throughout that site’s occupation, which spans much of the Early and Late Neolithic. At the same time, more than 90% of the Sardinian obsidian found at sites in southern France is of type SA.

These different obsidian use patterns —both geographic and chronological— imply that the cultural factors and exchange mechanisms involved in the chaîne opératoire of
Mediterranean obsidian were complex. Obsidian may not have always been dispersed through simple down-the-line transactions from its respective source zones. It is also possible that maritime contacts between Sardinia and the mainland were not necessarily routed across the shortest open-water crossings (from Sardinia to Corsica to Elba to Tuscany and then northward along the coast to Liguria and southern France). Differences in use-function, especially if considered in the context of more locally available alternative lithic resources, may correlate with obsidian selection and can be investigated through the integration of provenance determination and use-wear analysis [92,93].

Fig. 5. – Change in Monte Arci source usage between the Early (a) and Late (b) Neolithic.
Discussion and conclusion

Many lessons can be learned from this example of obsidian provenance studies in the Mediterranean. First, complete characterization of all relevant geological sources should be conducted prior to the analysis of archaeological artifacts. In the case of western Mediterranean obsidian, analyses of artifacts continued for more than two decades before all of the sources were located in situ. While it is possible to go back and try to assign artifacts based on our current knowledge of the sources, many artifacts have not been analyzed for the particular elements or other characteristics necessary to distinguish among the sources. In other cases the compositional data which would allow reassignment were not published, and the artifacts themselves may have been entirely sacrificed for the analysis, or otherwise are now no longer available for reanalysis.

Second, elemental characterization and fission-track dating are the only methods which have been applied with any success and frequency to Mediterranean obsidian artifacts. A lot of effort has been expended testing a variety of alternative methods to see if they could distinguish among the Mediterranean sources. Other methods, however, have proven to be ineffective, inappropriate for obsidian sourcing because of sample requirements or expense, or just have not been pursued beyond an initial study. While the application of new techniques to archaeological materials should be encouraged, the involvement of both physical scientists and archaeologists at the beginning of the investigation would likely result in a more efficient use of time and resources. A systematic approach to sourcing is highly recommended [94,95].

Third, artifacts from a large number of sites have been analyzed, but until recently the selection criteria were poorly conceived. Far too many obsidian artifacts come from unstratified or imprecisely dated contexts to have any real interpretive value, and with few exceptions too few from a single context have been analyzed to evaluate the relative frequency of the source(s) represented at a single site or in a single cultural phase. Greater effort should be expended on analyzing significant-sized assemblages from properly excavated contexts, and on using the results to address questions of archaeological interest (e.g. exchange mechanisms; transport routes; sociocultural interactions; island colonization; diffusion of technology; raw material selection and use-function). Parallel information could be derived from provenance studies of flint, greenstone and other lithic materials, as well as ceramics.

Fourth, methods must be chosen which are appropriate for archaeological artifacts, and for the particular questions being addressed. The information obtained should be maximized, while any impact on the artifacts should be minimized. Keeping costs down effectively results in the ability to analyze more artifacts and to obtain more reliable use patterns. Consultation or collaboration with geologists or archaeological scientists is recommended to determine which method(s) are most appropriate. Provenance studies, while providing direct information on the exploitation and use of raw materials from specific sources, will continue to contribute towards an understanding of human behaviors at other points in the chaîne opératoire, especially when integrated with typological, technological, and other studies.
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