Identifying the movement of archaeological materials across the landscape at given points in time is a powerful tool for understanding the socio-economic processes of the past. The aim of this chapter is, first, to provide a background for identifying the physical distribution of archaeological materials and, second, to outline some of the more powerful analytical techniques used by archaeologists to identify such movements of materials.

The movement of materials must be demonstrated rather than assumed. Such a demonstration has been made easier for the archaeologist with recent advances in science and technology. The sourcing of archaeological material is not new. Perhaps the most famous early study was by Anna Shepard who, in the 1930s and 1940s, postulated the exchange of pottery over wide areas of the Southwest United States by analyzing mineral inclusions in thin sections to pinpoint the origins of such minerals (Shepard 1965). The modern chemical analyses were much later. Chemical techniques have been used since the mid-19th century on archaeological metal artifacts from Central Europe (Schwab et al. 2006). Neutron activation analysis was applied to coins from the Louvre in 1952, while in 1957 Oriental ceramics were analyzed using nondestructive methods of X-ray fluorescence spectrometry (XRF) and X-ray diffraction (XRD) analysis (Young and Whitmore 1957).

Access to these techniques was restricted and costly.

A major advance in the chemical analysis of archaeological material came from the initiative of Dr. Robert Oppenheimer. On the 8th of March, 1956, he assembled a group of archaeologists and chemists at the Institute of Advanced Studies, Princeton, to discuss the possibility of applying methods of nuclear research to the study of archaeology (Sayre and Dodson 1957). As a result of this meeting, work was undertaken at two laboratories—the Brookhaven National Laboratory in the United States and the Research Laboratory for Archaeology and the History of Art at Oxford in England. Techniques deployed included Neutron Activation Analysis (NAA) and Spectrographic methods. These studies were reasonably successful, being able to separate pottery wares from Asia Minor, Greece, and Italy, as well as different factories of Samian ware. For the next three decades, these studies laid the foundations for chemical analyses in which thousands of varying techniques were carried out on many types of objects, including pottery, stone (obsidian, marble, chert, volcanic rocks), amber, and metals, including coins. Apart from NAA, XRF, XRD and spectrographic methods, techniques currently in use include Proton Induced X-ray Emission and Proton Induced Gamma Ray Emission (PIXE-PIGME) (Bird, Duerden, and Wilson...
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1983), Inductively Coupled Plasma Emission spectrometry (ICP) (Kennett et al. 2004), lead isotope analysis (Webb et al. 2006; Weisler and Woodhead 1995), and electron microscopy (Summerhayes 1997, 2000), to mention a few. Major changes in the instrumentation of these techniques over the last 30 years have meant that more elements can be analyzed with a higher precision. The choice of technique depends on availability to the archaeologist and cost. It is on these techniques that the rest of this chapter focuses.

### Why Undertake These Analyses?

The aim of many physico-chemical analyses is to discern the geological origin of the object under study. Ideally, the sources of material with restricted distribution could be characterized and “fingerprinted” chemically or petrographically. Obsidian, for instance, can be chemically homogeneous within its source flow yet chemically discernable between source areas; its sources can thus be chemically fingerprinted. Obsidian found in archaeological contexts can be analyzed and related back to the geologic source. Earlier work by Colin Renfrew had demonstrated its importance in modeling exchange patterns (Renfrew 1969, 1977; Renfrew, Dixon, and Cann 1966). Identifying the potential source areas of a material requires an intensive search within a known region. For instance, in a recent study on obsidian exchange within the western Pacific over a 20,000-year time span, archaeologists have concentrated on the source areas within West New Britain, Papua New Guinea. Over a number of years, obsidian flows were mapped and samples taken for characterization with the result that a finer discrimination of sources was possible with five source localities chemically defined (Summerhayes et al. 1998). By analyzing obsidian found in archaeological sites (some artifacts more than 3,700 km from their source), it was possible not only to trace obsidian to its source localities but also to define changes in the selection of different sources over time. (For an overview of archaeological approaches to obsidian studies, see Shackley 1998.)

Pottery, however, is more difficult to characterize or fingerprint. Often archaeologists use what is called a “criterion of relative abundance,” which infers that most pottery from a production center is to be found locally. Yet, if pottery was produced for exchange then little would be found locally, thus limiting the application of this concept. The “criterion of relative abundance” is useful, however, in a physico-chemical analysis under study back to its raw materials: nonplastic inclusions (for example, minerals, sands) and clay. Mineral inclusions found within pottery can be related to local geology and both river and beach sands. Clays, in contrast, vary greatly in respect of the underlying geology, and a study of the elemental composition of pottery may give a clue to their origin. The chemical analysis of clay is complex. Bishop and associates (1982) note that clay minerals not only depend on their parent material but are also affected by weathering or hydrothermal activity, climate, and geomorphology. They state that “even if a region is considered to be homogeneous in its gross geologic characteristics, significant mineralogical and chemical differences may be discerned between clay deposits” (Bishop, Rands, and Holley 1982).

The relationship of other material to its origin depends on the materials under study—chert, volcanic stone, amber, glass, metals, and so on; each has different parameters to take into account when an attempt is made to identify origins. In any provenance study of archaeological objects, a cautionary statement from Garman Harbottle, a nuclear physicist, best be heeded:

> archaeologists love the term sourcing, with its upbeat, positive thrust—that you analyze or examine an artifact and, by comparison with the material of known origin, “source” it. In point of fact, with very few exceptions, you cannot unequivocally source anything. What you can do is characterize the object, or better, groups of similar objects found in a site or archaeological zone by mineralogical, thermoluminescent, density, hardness, chemical and other tests, and also characterize the equivalent source materials, if they are available, and look for the similarities to generate attributions. A careful job of chemical characterization, plus a little numerical taxonomy and some auxiliary archaeological and/or stylistic information, will often do something as useful: It will produce groupings of artifacts that make archaeological sense. This, rather than absolute proof of origin, will often necessarily be the goal. (Harbottle 1982)

### Popular Techniques Available

The following review looks at five techniques. The first three (PIXE-PIGME, the electron microscope, XRF) work on the basis that each atom emits a characteristic X-ray wavelength and energy. All one
the emitted secondary X rays. This allows the identification of elements present and their quantity in weight. The fourth technique uses nuclear technology (NAA), and the last technique is ICP-MS.

**PIXE-PIGME**

Proton Induced X-ray Emission and Proton Induced Gamma Ray Emission have been used extensively for obsidian analysis and, to a lesser extent, on pottery and other substances, such as bone, metal, and glass. It is the preferred technique in the Pacific obsidian sourcing program, in which obsidian from archaeological contexts in the Pacific region are sourced (see Summerhayes et al. 1998). The sample is hit with a high energy beam and measured first for X rays emitted by protons and then for gamma rays generated. (For a detailed description of the technique and its uses, see Bird, Duerden, and Wilson 1983.)

**Accessibility.** This technique has been used only on archaeological samples from less than 25 centers worldwide. PIXE-PIGME is dependent on the generation of a high energy ion beam. Accelerators to produce such beams are not found at every university. At the Australian Nuclear Science and Technology Organisation (ANSTO), a higher energy ion beam of 2.5 MeV for PIXE-PIGME was generated by a 3 MeV de Graff accelerator. This accelerator has now been replaced with a Tandetron STAR accelerator. These accelerators are not common; accessibility to PIXE-PIGME as such is thus a problem. Furthermore, a license is needed to generate the proton beam. An archaeologist would not be expected to train to operate such a machine.

**Sample Preparation.** Samples such as pottery are crushed into a powder and pressed into a pellet for analysis. At ANSTO, obsidian samples are attached onto a specially prepared aluminum sample holder, holding up to 60 samples. The area of obsidian to be analyzed is exposed by a hole in the holder. The obsidian selected for analysis should have some of its surface flat for attachment to the sample holder. One of the major advantages of analyzing obsidian using PIXE-PIGME is that it is nondestructive in the real sense. Many techniques (see below) are said by their practitioners to be nondestructive. Yet, nondestructive means something different to the archaeologist than it does to the chemist. For the chemist, it means that a sample residue is left after the analysis. Thus, samples that are crushed or melted, such as pottery, are regarded by the chemist to be nondestructive. Fortunately, the only sample preparation for obsidian undergoing PIXE-PIGME is cleaning.

**Data Provided.** A major advantage of PIXE-PIGME is that it can provide data on over 60 elements (major, minor, and trace), with many samples being capable of analysis per day. At ANSTO, up to 20 samples per day can be analyzed within a normal working day (see Summerhayes et al. 1998 for machine conditions). If the machine is run around the clock, this figure is closer to 60 samples per day.

Emitted X rays are detected and counted by a Si (Li) detector; a higher energy Ge (Li) detector is used for counting gamma rays. Elements to be analyzed for obsidian analyses include F, Na, and Al using PIGME, and Si, K, Ca, Ti, Mn, Fe, Cu, Zn, Ca, Rb, Sr, Y, Zr, Nb, and Pb using PIXE. PIXE-PIGME can, however, analyze for most of the range of major, minor, and trace elements within detection limits.

Thus, in a week, it is possible to have 300 samples analyzed using PIXE-PIGME and, in the case of obsidian, the flakes returned without modification. The same number can be achieved for pottery as well. Ochre has also been similarly analyzed.

**Electron Microscope and Microprobe**

This technique basically measures X rays that are generated from the surface of a sample by a low energy (10–20 keV) electron beam directed onto a sample—both the Electron Microprobe and the Scanning Electron Microscope (SEM) proving popular in characterizing archaeological material. They are easily accessible, relatively inexpensive to use, and easy for archaeologists to learn to operate. They can analyze micro-sections of metals, glazes, and slips on pottery and can allow the imagery of macro- and micro-materials. In addition, the probe is important in analyzing coarse-ware pottery. A major problem in the use of pottery chemical characterization concerns the effect of manually added mineral inclusions on elemental concentrations. Mineral inclusions either occur naturally in the clays or are artificially added to counteract shrinkage during the pot’s drying process. Their manual addition to the clay will affect the chemical profile of a pot and, if not compensated for, will result in erroneous data used for modeling production, exchange, and consumption. For instance, pots made from the same clay source could have different chemical elemental concentrations owing to the addition of either varying amounts of similar minerals or different mineral inclusions. This, in turn, could result in the pottery being attributed to different loci of production with misleading exchange and consumption.
the electron microprobe is of importance. By positioning the specimen under the electron beam, the microprobe can discriminate between non-plastic inclusions and the clay matrix.

Accessibility. This technique is very accessible. Nearly every university or major research organization has a scanning electron microscope or a specialist electron microprobe. Most research centers and departments housing this equipment will allow archaeologists to use it after adequate training.

Sample Preparation. For a full qualitative analysis, all samples must be perfectly flat. This means a lengthy preparation for rocks, pottery, and metals. For pottery, this involves impregnation with an epoxy resin, and the sample's placement into a resin pellet. For rocks, a thick section on a glass slide would suffice. For obsidian, chips are cut from the obsidian piece and placed into a specialist sample holder. No matter what the material is, the samples are highly polished as surface irregularities will affect the results. Extreme caution must also be taken when preparing pottery to remove oxygen within the sample. Oxygen will cause problems when the sample goes into the vacuum for analysis. Unlike with rocks and minerals, it can take 20 minutes for the probe to pump down the vacuum prior to analysis.

Lastly, samples are cleaned with ethanol and freon in an ultrasonic cleaner and coated with carbon under vacuum. A conductive coating is needed to “provide a path for the probe current to flow to earth” (Reed 1977: 178). Carbon is selected because of its low atomic number, “which ensures that the coating does not significantly absorb the energy X-rays” (Reed 1977: 179).

Data Provided. Both a wavelength dispersive spectrometer (WDS—whereby crystals separate out the X rays by wavelength) and energy dispersive spectrometer (EDS—a black box detector measuring wavelength energy) are used with the electron microprobe; an EDS is mostly used only with a SEM (EDXA). Both WDS and EDS separate and measure the intensity of the X ray, and both are used with geological standards. WDS, however, provides a better separation and resolution of many of the elements. The electron microprobe and SEM will provide most major and minor elements, and the former can even analyze trace elements. However, the SEM’s resolution below 1% is not good. For pottery analysis, the following elements (as oxides) are often used: Mg, Al, Si, K, Ca, Ti, and Fe. In previous research, these elements were found more useful than the trace elements in discriminating not only prehistoric pottery groupings but also pots made from a single production center.

In summary, these microscopes are perfect for pottery, obsidian rock, and metal analyses. They are relatively easy to use (even an archaeologist could be trained), and easy to access. The probe is, however, much more costly by a factor of four over the SEM.

X-Ray Fluorescence Spectroscopy (XRF)

XRF has been one of the most popular techniques for the past 40 years (Best et al. 1992; Weisler 1998; Weisler and Kirch 1996; see Weisler 1997 for a detailed background to its use in identifying trade in the Pacific). Every geology department has one, plus it is easy to learn and easy to maintain. It basically involves the sample being hit with a primary X ray—the resulting characteristic elements are measured either by a WDS or an EDS (see above). Like PIXE-PIGME and the Electron microscope, it is fast, efficient, and effective. For archaeological materials, it has been used mostly for rocks, pottery, obsidian and glasses, and metals.

Accessibility. This is probably the most accessible of all techniques. As noted above, it is found in most geology departments and is the favorite machine of instruction to undergraduates.

Sample Preparation. The sample preparation depends on the machine detectors. When one is using a WDS, two archaeological samples are required for a complete coverage of major, minor, and select trace elements. The first, for major and minor elements, is crushed into a powder. The second, for trace elements, is melted and fused into a pellet. When one is using an EDS, the sample does not have to be either powdered or melted—but a word of caution: the sample must be polished for good results. It is possible to analyze a complete artifact if the sample chamber will allow it, but the results would be semiquantitative in nature.

Data Provided. The distribution of elemental data is commensurate with the electron microprobe. It is obvious that XRF is a fast and easy to access technique. It works well with rocks (stone tools), glass, and metals. It is adequate for fine pottery, but for coarse ware it suffers from the same problem with temper outlined above.

Neutron Activation Analysis (NAA)

Neutron activation analysis is a technique that involves the production of radioactivity that decays on an observable time scale. Basically, a sample is hit with neutrons. The neutrons interact with the neutrons of the sample resulting in elements to form radioactive isotopes. The decay
measured, informs us of the element and its concentration. This is the preferred technique by most archaeologists for sourcing.

**Accessibility.** NAA is not an easily accessible technique as it needs a nuclear reactor. There are a number of laboratories that specialize in archaeological work, the best known being at the University of Missouri–Columbia. Samples can be sent there for analysis on a commercial basis.

**Sample Preparation.** Sample preparation is minimal. A crushed sample or, if small enough, an entire object can be analyzed directly. NAA can also analyze liquid and gaseous samples.

**Data Provided.** NAA provides a variety of elements, with little material needed (10 mg). It has the best detection limits of sensitive elements (down to parts per billion), making it the premier technique available. It is perfect for rock (stone tools), obsidian, and glass. As well as for pottery, since it can measure the rare earths found within the clay matrix, which are undetectable using other techniques.

This is the premier technique for sourcing. (See Neff 1992 for detailed examples of the application of NAA to pottery.)

**Inductively Coupled Plasma-Mass Spectrometer (ICP-MS)**

ICP-MS is a technique on the increase. Although it was developed in the late 1980s, the number of applications on archaeological data has risen steeply over the last few years. There are many reasons for this; one, of course, is its purchase in science-based university departments and research centers for geological research, and its subsequent "big sell" for archaeological studies. ICP-MS has been promoted as faster, more sensitive, and having superior detection limits on many elements (see Kennett et al. 2004). The technique basically involves an argon plasma to atomize and ionize the elements in a sample. A mass spectrometer is used to measure the elements in a sample.

**Accessibility.** ICP-MS is becoming very accessible, with most universities investing in one. Unlike XRF or the probe, which are common in geology departments, this technique would be more at home in a chemistry department. This is not a technique that an archaeologist would be able to use by him- or herself without extensive training.

**Sample Preparation.** Sample preparation is lengthy. There are two types of ICP-MS: one using laser ablation, the other using microwave digestion. The preparation for both differs, with microwave digestion being more labor intensive with acids, evaporated and mixed again, decanted and purified with water, and decanted again. This is a lengthy and complicated procedure. The other preparation involving laser ablation of the sample is faster and less messy. (See Kennedy et al. 2004 for an example of ICP-MS with microwave digestion.)

**Data Provided.** ICP-MS is argued to measure the whole range of elements—major, minor, and trace down to parts per billion. For example, in a recent analysis on Lapita pottery, 37 elements were measured: Be, Mg, Al, K, Sc, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Rb, Sr, Y, In, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu, Pb, Bi, Th, and U.

This is a new technique that needs more street credibility before it becomes popular. The crushing of the sample, or even using laser ablation, would be ill-advised for coarse-ware pottery, but for materials with a homogeneous matrix, such as obsidian, it would be ideal.

**Conclusions**

The choice of technique used by archaeologists has unfortunately often rested on what is close at hand. Instead the choice should be dependent on the questions asked by the archaeologist, the material being analyzed, the elements needed to discriminate between sources, and the availability of the technique. There are many techniques available, too numerous to list them here. Some are old and well known, such as X-ray diffraction analysis (XRD), which is commonly used for mineral analysis (in particular clay minerals); others are rarely used, such as mineral magnetics, which has been used for ochre characterization (Mooney, Geiss, and Smith, 2003) still others are becoming popular such as Raman Spectroscopy (both dispersive and interferometric Fourier transform) on mineral analyses, which has a wide variety of uses. (See Edwards and Chalmers's [2005] edited volume; and Smith and Clark's [2004] review article.) With a bit of common sense, and wisdom from geologists and archaeologists experienced with these techniques, the task of choosing between techniques will be a much easier one.

**References**


