Using Nondestructive Portable X-ray Fluorescence Spectrometers on Stone, Ceramics, Metals, and Other Materials in Museums: Advantages and Limitations

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Abstract

Elemental analysis is a fundamental method of analysis on archaeological materials to address their overall composition or identify the source of their geological components, yet having access to instrumentation, its often destructive nature, and the time and cost of analyses have limited the number and/or size of archaeological artifacts tested. The development of portable X-ray fluorescence (pXRF) instruments over the past decade, however, has allowed nondestructive analyses to be conducted in museums around the world, on virtually any size artifact, producing data for up to several hundred samples per day. Major issues have been raised, however, about the sensitivity, precision, and accuracy of these devices, and the limitation of performing surface analysis on potentially heterogeneous objects. The advantages and limitations of pXRF are discussed here regarding archaeological studies of obsidian, ceramics, metals, bone, and painted materials.

Introduction

Many methods of elemental analysis have been successfully used on archaeological materials to address their overall composition or specific elements to identify the source of their geological components. These include optical emission spectroscopy (OES), atomic absorption spectroscopy (AAS), neutron activation analysis (INAA), electron microprobe (EPMA), scanning electron microscope (SEM), X-ray fluorescence spectrometry (XRF; both energy- and wavelength-dispersive), inductively coupled plasma–optical emission spectroscopy (ICP-OES), and laser ablation ICP mass spectrometry.[1–3]

For many studies, having access to such instrumentation, their often destructive nature, and the overall time and cost of analysis have limited the number and/or size of archaeological artifacts tested. Over the last several years, however, portable XRF (pXRF) instruments have become widely popular, allowing nondestructive analyses to be conducted in museums around the world, on virtually any size artifact, producing data for up to several hundred samples per day. Museums have increasingly not allowed artifacts of any kind to be taken for analysis elsewhere, even within the same country, while the transport of large artifact assemblages is unwieldy. Major issues have been raised, however, about the sensitivity, precision, and accuracy of these devices, and how to compare pXRF data from different models as well as with other analytical methods.[4–9] As with other analytical instruments, this involves the analytical settings chosen, the use of standard reference materials, and the calibration software utilized. One specific limitation of XRF is performing surface analysis on potentially heterogeneous materials like ceramics and, especially with some pXRF models, not having the ability to focus on spots smaller than a few millimeters in diameter.

Presented here are the advantages and limitations of pXRF, based on my usage for many years on thousands of obsidian, ceramic, metal, and other artifacts.[10–22] Overall, the use of pXRF has greatly expanded our archaeological

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data sets, in many cases where elemental analysis simply was not previously possible.

X-ray Fluorescence and pXRF

X-ray fluorescence spectrometers measure the energy level and intensity of secondary (fluorescent radiation) X-rays produced by primary X-rays striking the sample and creating vacancies in an inner shell of the atoms, which are then filled by lower-energy electrons from an outer shell.[1–3,23] The energy difference between specific shells is fixed but varies between elements, so that secondary X-rays have characteristic transition energy and thus may be attributed to specific elements. The strongest X-ray intensity is a result of an L-shell electron replacing a K-shell vacancy, and is called K_α, while an M-shell electron replacing a K-shell vacancy is called K_β. The replacement of L-shell vacancies by M-shell electrons is called L_α and by N-shell electrons, L_β. Since there are also energy differences among the orbitals within each shell, the X-ray spectra include $K_{\alpha 1}$ and $K_{\alpha 2}$ lines, but they essentially overlap for elements $Z < 35$. There are more L-lines than K-lines for elements $Z > 20$, and with greater differences between $L_{\alpha 1}$, $L_{\alpha 2}$, $L_{\beta 1}$, $L_{\beta 2}$, and L_γ.

For producing quantitative results, the intensity of the primary X-rays must be high enough to produce sufficient secondary X-rays for statistical measurement, and therefore is different between major and trace elements in the sample. The energy of the primary X-rays must be higher than that of the elements being measured. Always to consider is the background signal from primary radiation that reaches the detector. Filters designed for different materials may be used to reduce this background signal and increase detection limits and precision. For both portable XRF and ED-XRF spectrometers, energy level and intensity is measured by a detector, while the raw data may then be calibrated using standards and appropriate software. The standards must be of similar material to the objects being analyzed, as the ability of the secondary X-rays to reach the detector is affected by the composition of the matrix.

One fundamental difference between regular and pXRF instruments is the location of the sample; while the pXRF does not require sampling of larger objects, the sample is not within a vacuum chamber that is necessary for the detection of X-rays from lower Z elements which otherwise are absorbed in air. This is partly resolved when a vacuum is created within the pXRF (using a portable generator connected by a small tube) and the sample is flat so that there is no air space in between the sample and the instrument window. The precision of measurements on elements such as Mg, Al, Si, and P, however, is not nearly as good as for higher Z elements, and elements below Na are not detectable at all. The other major difference with pXRF is its detection limits, as much as an order of magnitude less than for ED-XRF, and therefore fewer trace elements which may be used in archaeological sourcing studies.

Issues About the Use of pXRF

Following its introduction to archaeological applications, issues have been raised about the reliability and comparability of different instruments, and the limitations of XRF in general on potentially heterogeneous materials.[4–9] While calibration software has been developed for many materials, including obsidian and other rocks, ceramics, and metals, there remain concerns about the nondestructive analysis of ceramic and metal artifact surfaces in particular. In addition to the depth of X-ray penetration increasing with higher elements, pottery may be a combination of clay and temper, as well as having slip or paint on the surface, and copper-based metals may have pooling of lead and other elements, as well as patination and/or contamination on the surface. This will be discussed below with the particular studies carried out. At this point, the use of pXRF on archaeological materials has become widespread, and its regular users have a better understanding of both its potentials and limitations.[24–26]

Bruker Models III-V+ and III-SD

Two different models of the pXRF have been used for the projects discussed in this paper;[27] from 2007 to Spring 2012 it was the Bruker III-V+, and since then the III-SD. The main differences are that the III-SD model uses a silicon drift detector (SDD) which is much more sensitive and has better resolution than the Si-PIN detector on the III-V+ model. This results in less analytical time necessary per sample and better element identification from the calibration software. The beam size is 5×7 mm, so that a substantial horizontal area is being measured. For trace element analysis of lithics and ceramics, a filter of 12 mil Al + 1 mil Ti + 6 mil Cu was used to enhance results for these elements, and settings of 40 kV and 10 or 11 μA, and 180 or 120 s; for major element analysis of copper-based metals, the filter was just 12 mil Al and 1 mil Ti, with settings of 40 kV, 1.5 or 4 μA, and 60 or 30 s.

Precision and Accuracy

Separate from issues of heterogeneity in archaeological samples is the precision of the pXRF. To determine this, 25 separate analyses were conducted on the same spot, on five different prehistoric pottery sherds from Italy. For Fe, present in the 2–3% concentration range, the highest standard deviation for the five samples was just 0.038%, with that sd being a tiny percentage of the concentration (100*sd/mean = 1.6%); for Rb, Sr, and Zr, present in the 80–400 ppm range, the % sd was 2–5%; for Y and Nb, present in <25 ppm, the % sd was 5–15% (e.g., a range for Nb of 7–11 ppm for the 25 analyses of one of the sherds). This study shows that the precision of the measurements are much better than the actual variation in ceramics as shown by multiple analyses of different spots on a single sherd, and

are only a tiny fraction of the differences observed between ceramic source groups. The issues of precision and accuracy have been addressed in other studies[9,25,28] while there remains more work needed on calibration, especially when necessary to compare results with other studies.

Case Studies

Obsidian

Given the homogeneity of obsidian, and insignificant weathering or other changes between raw material and artifact, it is perhaps the most appropriate and easiest material to analyze by pXRF, with a number of studies around the world published.[29–39] More than 6000 obsidian artifacts from sites in the western Mediterranean (Figure 1) have been analyzed to determine their geological source and reconstruct trade, doubling the total number of obsidian artifacts tested since the first study in 1964,[40,41] and complementary studies done by others in the Aegean and Near East.[42–4] My research began with a detailed survey and

collection of geological source samples on the Italian islands of Lipari, Palmarola, Pantelleria, and Sardinia, with analyses by pXRF (and previously by INAA, LA-ICP-MS, and regular XRF) demonstrating in Figure 2 that each may be distinguished from each other as well as from Melos in the Aegean and the Carpathian sources in the Balkans by just a few trace elements (Rb, Sr, Y, Zr, Nb).[17,20,45]

Significantly, the pXRF is even capable of distinguishing subsources for each island (Figures 3 and 4), with studies showing geographic and chronological differences in their relative usage.[13,17,20,46–48] It is the attribution of obsidian artifacts to specific geological subsources that enables better understanding and interpretation of material selection, trade routes, and the socioeconomic systems in which they were embedded.[49,50]

Malta. The use of the pXRF was essential in the study of obsidian from neolithic sites in Malta, since for a number of years no artifacts could be taken out of the country and there were no suitable analytical facilities within this small island nation. The results were highly significant and

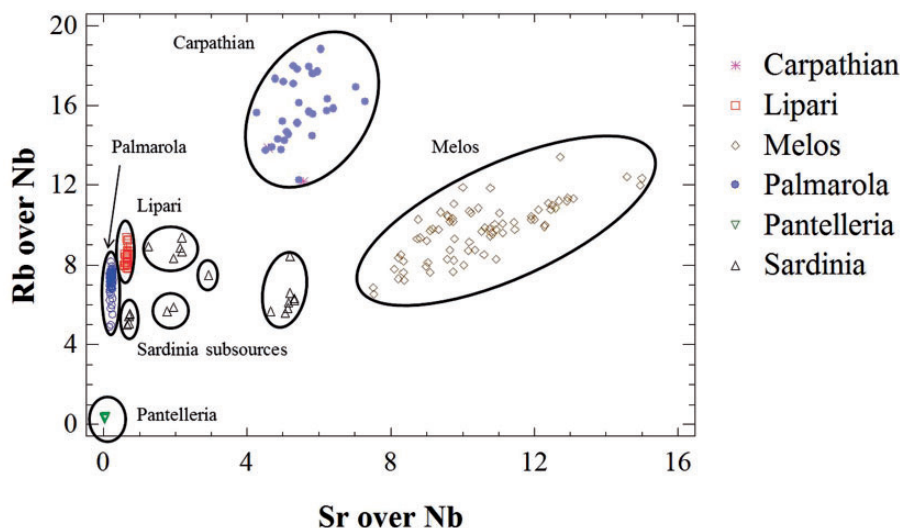**Figure 1.** Mediterranean obsidian sources and archaeological site assemblages tested by pXRF.

Figure 2. Mediterranean obsidian source groups. Subsources for each may be determined with other elemental data.
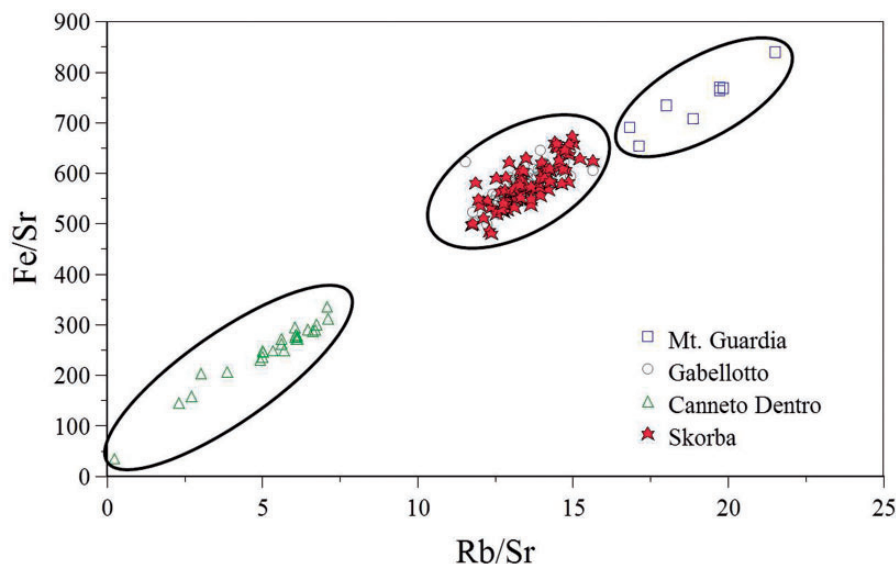

Figure 3. Graph of Lipari subsources and archaeological samples from Skorba, Malta.

demonstrate specific selection practices, with the residential site of Skorba on Malta having obsidian mostly from Lipari (79%; 21% Pantelleria) and the Brochtorff Circle burial chamber complex on Gozo nearly the opposite (28% Lipari, 72% Pantelleria). All of the Lipari obsidian artifacts on Malta were assigned specifically to the Gabellotto Gorge subsource, while on Sicily, through which the Lipari obsidian would have passed to reach Malta, a small percentage of Canneto Dentro obsidian was utilized.[20] Both on Malta and in Sicily, multiple subsources of the Pantelleria obsidian were used (Lago di Venere; Balata dei Turchi).

Calabria. Unsurprisingly, obsidian found in Calabria is nearly all from Lipari, but with only a few pieces from Canneto

Dentro; to date not a single piece of Canneto Dentro has been found further north in Italy. Tentative interpretations of this pattern support the hypothesis that cores were produced by Lipari residents and then transported/traded to mainland Italy for further distribution, rather than being acquired by seafarers with occasional visits to this island. Lipari obsidian continues to have been distributed in notable quantity as far north as southern France, northern Italy, and to the islands and mainland of Croatia.[19]

Croatia. For the many sites now tested along the Dalmatian coast, only a few pieces of obsidian are attributed to the Carpathian sources, with almost all of the rest from Lipari–Gabellotto. Notable, however, are several pieces on the
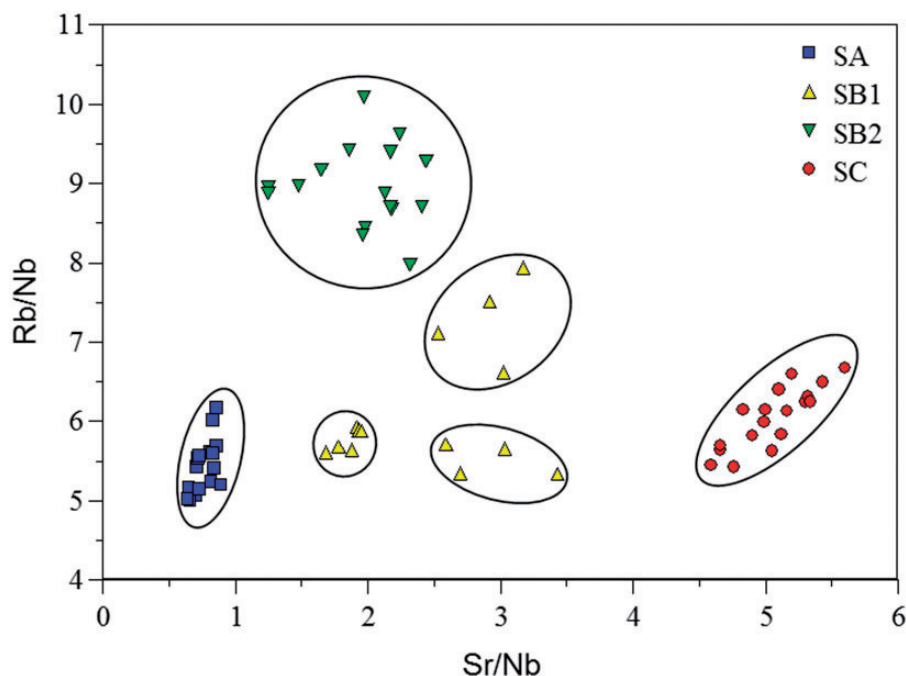
Figure 4. Monte Arci (Sardinia) obsidian subsources. There are three chemical groups for SB1, which were rarely used for artifacts.

island of Palagruža, dating to the Late Neolithic/Chalcolithic time period, coming from Melos. Obsidian from Palmarola also made its way across the Apennines to the Tavoliere, and to the Croatian island of Sušac.[45]

Sardinia and Corsica. Portable XRF analyses of obsidian artifacts from many sites in Sardinia and Corsica have been conducted to chronologically and geographically expand on earlier studies which indicated changes over time in the usage of the Monte Arci subsources.[21,46,47] These analyses have shown that at the Early Neolithic site of Santa Caterina, major amounts of all three Monte Arci subsources (SA, SB, and SC) were utilized, while at the Late Neolithic sites of Contraguda, San Bartolomeo, and Sant'Elia, SB is no longer used, and by the Bronze Age at sites including Duos Nuraghes, SC dominates the obsidian assemblages. It is argued that by the Late Neolithic, territorial control around Monte Arci led to major production centers, such as at Sennixeddu near the SC source.[13,17]

Ceramics

Unlike obsidian, pottery may be heterogeneous due to how the clay is prepared, whether temper is added, and if the surface has slip, paint, or glaze. This may cause an obstacle in doing nondestructive pXRF analysis on ceramics. Separately, there are far more potential clay sources that may have been used, with potential access to many points along rivers, and rarely a database to compare results on sherds with. Instead, pottery "sources" are defined

archaeologically with finds of production sites (e.g., kilns, wasters) and large assemblages of everyday wares. Using the pXRF allows analyses of more than enough sherds to establish a local group, even if coming from multiple outcrops in the area and of different clay types. Conducting such studies on multiple sites in a region provide information on possible locations that outliers from one site come from.

A number of ceramic studies using pXRF analyses have been published, several directly focused on the methodology and comparison with other analytical instruments,[51–55] and others on particular research questions in Cyprus, Egypt, the Near East, Mesoamerica, and the United States.[56–62] Research by myself and a number of graduate students (3 PhD, 10 MA) have included pXRF analyses of more than 4000 ceramic artifacts from Croatia, Ethiopia, Italy, Kuwait, Malta, Mesoamerica, Peru, and the southeast US, with some examples provided below.[10,11,16,22,63–75] Most of these studies were on ceramics without painted or glazed surfaces, with multiple analyses performed on inside and outside surfaces, and on broken edges. The pXRF analyses focused on the same trace elements as for obsidian, and used the same analytical settings. The results of each spot analysis were examined and when (rarely) trace element concentrations were found to be inconsistent, due to paint or slip on one surface, were removed from calculation of averages.

Southeastern United States. More than 500 ceramic artifacts from northwest Florida were tested to study production

and trade during the Late Archaic, Late Prehistoric, and Protohistoric periods.[22,63–65,72,73] Assemblages were selected from eight sites along the Apalachicola River in the Florida panhandle, mostly everyday ware although many with decorations, as well as clay balls known as Poverty Point Objects (PPO) from the Choctawhatchee Bay area, Tick Island in northeastern Florida, and the site of Poverty Point in Louisiana (Figure 5). Principal components analysis using Rb, Sr, Y, Zr, and Nb for the PPO-style objects from the Late Archaic sites in Choctawhatchee Bay, at Clark Creek and Tick Island, shows that several fall well outside the Apalachicola River group, and match with those from Poverty Point (Figure 6). These results support the hypothesis of small-scale, long-distance ceramic exchange between northern Florida and Louisiana.

Variability in principal component analysis (PCA) values for three later period Apalachicola River sites tested (Curlee, Depot Creek, Otis Hare) suggests the use of multiple clay sources near each site, but still having trace element differences in the sources typically used for each site. Some clay sources probably were located in between archaeological sites so there was movement over short distances and/or access to the same source by pottery producing sites (Figure 7). Ideally, clay sources near the
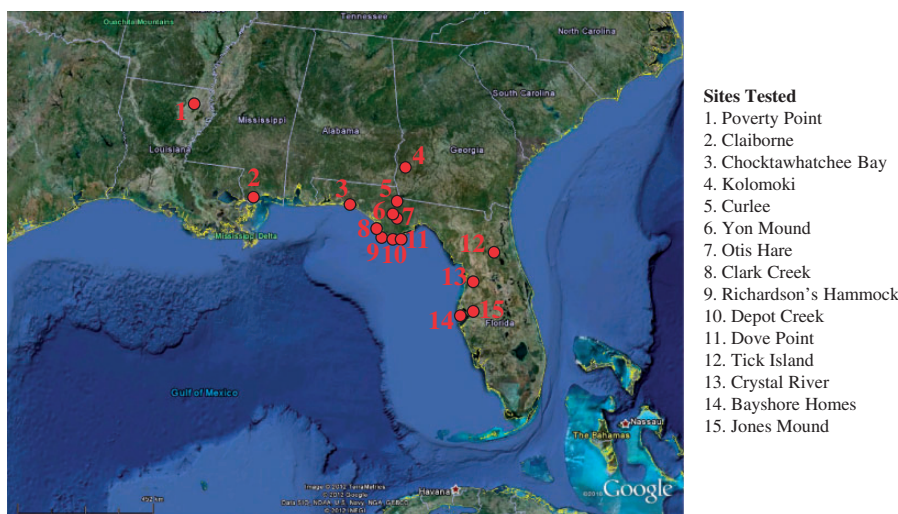

Sites Tested
1. Poverty Point
2. Claiborne
3. Chocktawhatchee Bay
4. Kolomoki
5. Curlee
6. Yon Mound
7. Otis Hare
8. Clark Creek
9. Richardson's Hammock
10. Depot Creek
11. Dove Point
12. Tick Island
13. Crystal River
14. Bayshore Homes
15. Jones Mound

Figure 5. Map of archaeological sites in the south-east US with ceramic analyses by pXRF.
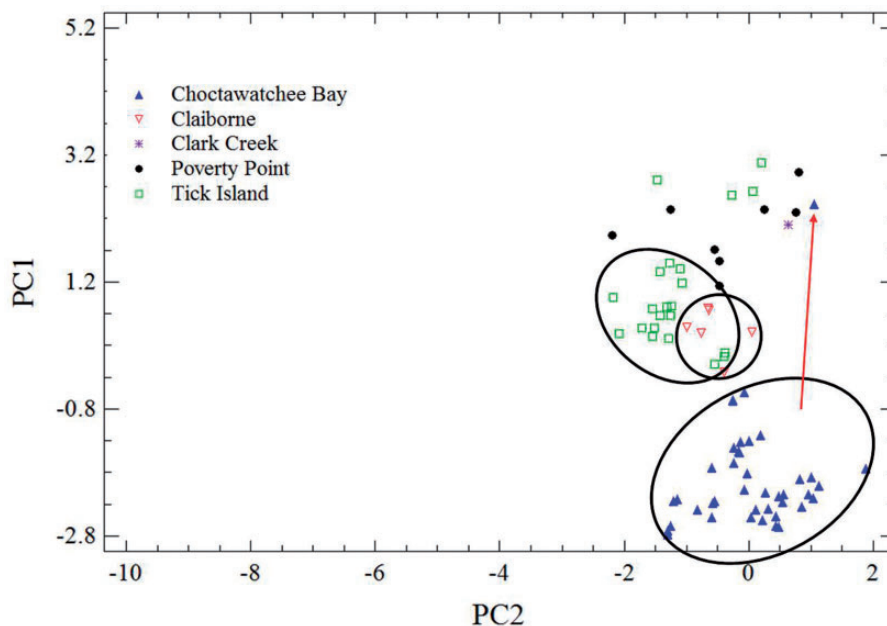

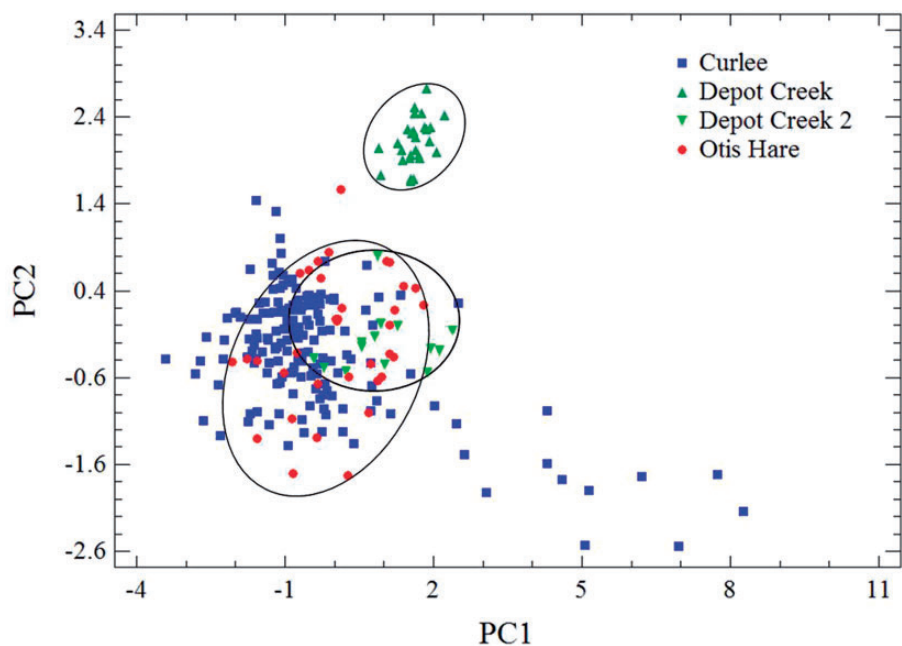**Figure 6.** Principal components graph of trace elements Rb, Sr, Y, Zr, Nb for Poverty Point Objects.

Figure 7. Principal components graph of trace elements Rb, Sr, Y, Zr, Nb for three Apalachicola River sites.
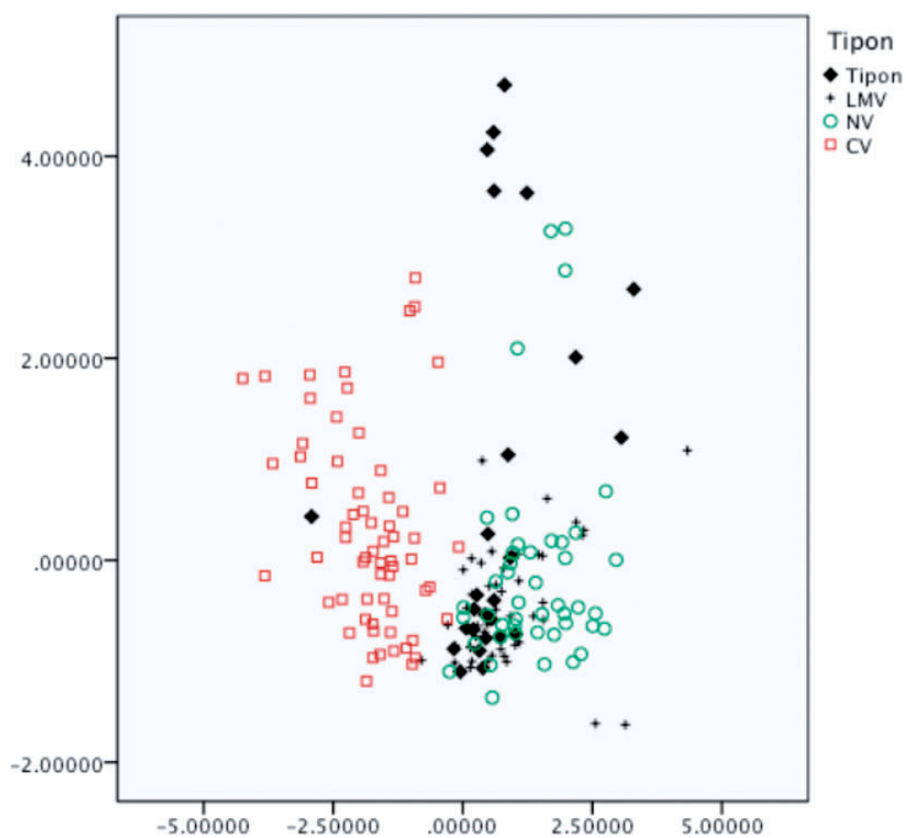

Figure 8. Discriminant function analysis of trace elements Rb, Sr, Y, Zr, Nb produces some separate groups for ceramic production in Mesoamerica. Adapted from Ref. 68. © McCormick 2013.

sites of interest should be identified, and samples tested, for much clearer interpretation of the archaeological ceramic analytical data. Analysis of large numbers of selected ceramic artifacts could also be done to assess whether there are patterns based on specific pottery types or decoration.

Southeast Mesoamerica. Pottery sherds from Classic period sites in the Lower Montagua (LMV), Naco (NV), and Cacaulapa (CV) Valleys of southeast Mesoamerica were tested in order to construct profiles of local pottery production areas.[68,76] Multiple spots were analyzed, with painted areas avoided, while many surfaces did have slip. Discriminant function analysis was performed, with Rb, Sr, Y, Zr, and Nb important trace elements in distinguishing these groups (Figure 8). The results show that most samples from the Cacaulapa and Lower Montagua Valleys fall into separate groups, while for the Naco Valley there are two separate source groups, with one overlapping with LMV. The geological complexity of this area provides a likely explanation, with the LMV and western NV having volcanic-based soils and the eastern NV having sedimentary soils. Archaeologically significant is that likely imports from Copán have different values, while Tipon type pottery was locally produced in the LMV/NV and NV groups, and Usulután type pottery was locally produced in both LMV and CV. These include both utilitarian and fine wares.

Croatia. More than 200 pottery samples from Neolithic sites in Croatia were tested, in part to complement the obsidian studies also done there to address contact and trade both at regional and long-distance levels. The sherds came from five sites near the Dalmatian coast (Danilo, Pokrovnik, Cista Mala, Smilcic, Krivace), along with some from the Slavonia area in northeastern Croatia (Figure 9). Principal component analysis was used on the trace elements, and distinguishes the Slavonia
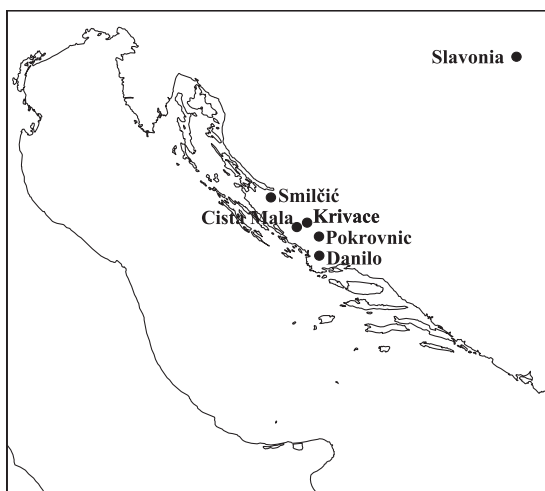
group, while there is lots of overlap between the other sites despite significant distances between these sites (Figure 10). While samples from the Krivace site tightly cluster, those from Danilo, Pokrovnic, and Smilcic vary. One unusual artifact from Danilo, a phallus, is on the very edge of the Danilo group (and near the center of Pokrovnic) and likely comes from some distance. Overall, the variability in trace element values for most of these sites suggests the use of clay from many areas, with either the clay or fired pottery transported over great distances. Ceramic studies in this region clearly need further analyses, including thin sections and trace element analysis by INAA or ICP-MS, to test this hypothesis.

Metals

The main use of elemental analysis on metal artifacts is for determining bulk element composition. Nondestructive analysis by pXRF has allowed many studies to be conducted on valuable museum-quality metal objects, and providing as precise and accurate results as other instruments.[77–83]

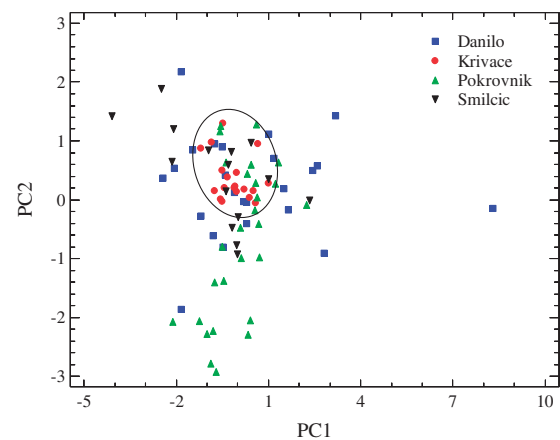**Figure 10.** Principal components graph of trace elements for Croatia ceramics.

Figure 9. Archaeological sites in Croatia with ceramics analyzed by pXRF.

Figure 11. Nondestructive analysis of "gold" mask from Colombia, in Orlando Museum of Art display case.

The results for large numbers of copper-based as well as gold, silver, and lead objects may be used for assessing changes in production technology, access to tin and other metals, consistency in alloying different materials (e.g., tools, weapons, jewelry), and practices of recycling. Even for small numbers of objects, analyses provide proper identification and description for both museum exhibits and publications. Conducting nondestructive surface analysis, however, raises two potential problems: degradation and/or contamination of metal surfaces, and conservation practices that may have altered the surface composition. Analysis of multiple spots can quickly reveal signif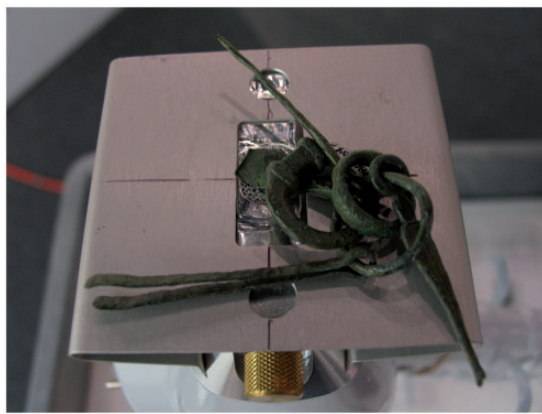icant variability in composition which is not characteristic of a cast object, and perhaps a small area may be cleaned for reanalysis. Such cleaning is necessary for those artifacts previously treated with conservation chemicals that contain zinc or other metal elements, and should be handled with appropriate caution.

For museums in the United States, most of the Greek, Roman, South American, and other metal artifacts on display were acquired through purchase or donation, rather than from excavations, and thus there often are questions about authenticity. I have analyzed extensive collections at the Orlando Museum of Art (South American, 125 objects) (Figure 11) and the Tampa Museum of Art (mostly Greek and Roman, 80 objects) (Figure 12), as well as Etruscan mirrors (33) at several museums in the US (Figure 13).

Orlando and Tampa Museums of Art. For the Orlando Museum, all of the objects labeled as "gold" are in fact tumbaga alloys, with high percentages of silver and copper as well. Concentrations vary considerably based on depth, since depletion gilding using acid treatment and oxidation of the surface was used to make the immediate surface mostly gold. Other objects were simply labeled as "copper" or "metal", with analyses revealing many that are arsenical copper and just a few that are bronze (with just 2–3% Sn). One artifact, a knife, has far too much Zn to be authentic. In the Tampa Museum, all of the objects were labelled as "bronze" or "silver". One Roman late first century AD object was brass ($Cu + Zn$), while another object with Zn had been thought to be Etruscan but brass was not produced at that time. Four of the "silver" coins in fact are mostly nickel, therefore also fake.

Figure 12. Analysis of separate pieces of Roman bronze chatelaine in the Tampa Museum. Lead concentration varies significantly, while some have small amounts of silver.

Figure 13. Multi-spot testing of an Etruscan mirror in the Baltimore Museum of Art.

Etruscan mirrors in the collections of the Smithsonian, Johns Hopkins University, Walters Art Museum, Baltimore Museum of Art, Emory University, and the Tampa Museum of Art are fairly well-preserved objects, with at least some if not most of the detailed images still showing. While most have been treated with a preservative, only a few of the tested spots showed some zinc. All were true bronzes, with at least 7% Sn, but ranging up to nearly 30%. It appears that the use of very high tin content was characteristic of the later Etruscan time period (third to second centuries BC), and most of those mirrors also included lead, which would have reduced the viscosity and allowed better casting detail.

Roman site in Morocco. More than 80 copper-based artifacts from the Roman site of Thamusida, Morocco, were analyzed. Some of these were military equipment, and the rare preservation of such items as buckles, scabbard and horse harness fittings, and military diplomas required nondestructive analyses.[14,15] Dating to the early second to the third century AD, there were a great variety of copper-based alloys, with Sn and Zn in nearly all, many with Pb, and a surprising number with As and/or Ag (Figure 14). The compositions do not appear to be related to the social or functional purpose of the objects, but rather to the availability of raw and scrap materials. There were also many artifacts mostly of lead, along with Cu, Sn, Zn, and Ag, again with no pattern for their use.

Other Materials

The portability and nondestructive nature of pXRF has also led to analyses on many other materials and in many locations.

Norway Paintings. While in a museum in Norway analyzing some Viking bronzes, I was asked if I could use the pXRF to determine what kind of paint was used on different figures in two large paintings from the 17th century (Figure 15). While XRF cannot directly detect carbon-based paints such as charcoal and cannot distinguish some colors due to different oxidation states, it can identify the metals used in many paints, as well as other compounds (e.g., murex which has high Br).[84,85] In this small project, it was quickly determined that most painted areas that appeared to be gold really were, those in green had Cu peaks, and those in red had Fe peaks. But a surprise was that the red dress and accessories on one figure in the center of each painting was also due to mercury (Hg). Some Hg also was detected in areas not red at all, suggesting that cinnabar-based paint was used in an earlier version of the painting and was now

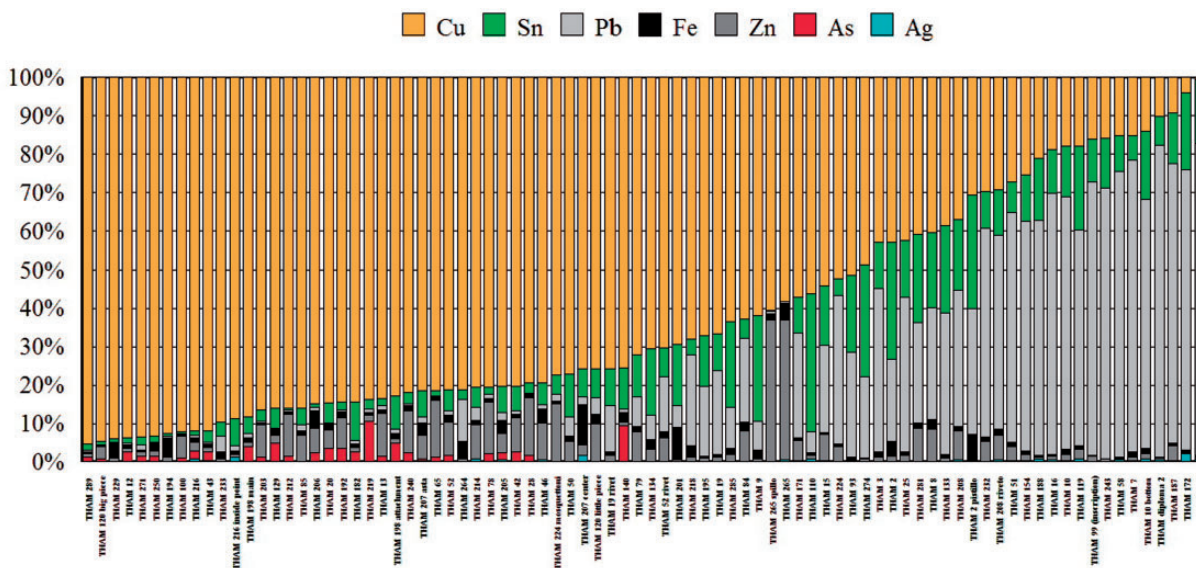**Figure 15.** Analysis of particular paint colors on painting in a Norway museum.

Figure 14. Bar chart showing extensive variation in composition of Roman metal artifacts from Morocco.

covered over. The analytical results are not quantitative regarding the paint visible on the surface, given that the paint thickness and depth of penetration of the X-rays cannot be controlled, such nondestructive methods of analysis on museum paintings may be very informative and add information for the description of those in display.

Genovese Cave. Use of the pXRF on actual archaeological sites is also advantageous. It was brought by small boat to the Genovese Cave on the island of Levanzo, west of Sicily, to analyze Neolithic and potentially much earlier paintings and determine their composition (Figure 16). Unsurprisingly, the black figures had higher iron

Figure 16. Analysis of prehistoric paintings in the Genovese cave.

concentrations, sometimes also manganese, and others with no difference than the adjacent unpainted rock surface, suggesting the use of charcoal. Red figures were always of iron (ochre), while white paint was high in calcium. Further study is under review for this cave, along with the hope of sampling some of the charcoal-based paint for radiocarbon dating.

Florida Bone Samples. Measuring elemental concentrations in bone or teeth is well-established for studying dietary practices (Ca, Sr, Ba) and potential consumption of poisons (Pb, As), and can complement isotopic analyses.[86] The ratios Sr/Ca and Ba/Ca decrease with trophic level, so are especially indicative of the consumption of aquatic resources, while differences in values between teeth formed at a young age and adult bone may be interpreted as due to marital or other mobility, or status change. While studies using AAS or ICP-S were done on interior samples that were then ashed, nondestructive analysis by pXRF of a well-cleaned surface also may be successful. Bones from 67 individuals from four sites in Florida were analyzed (Figure 17). Those from the inland site of Belle Glade had the highest ratios; Miami One on the Atlantic coast had lower values; and the sites of Horr's Island and Weeden Island on the Gulf coast had the lowest (Figure 18). The tight clustering of the Horr's Island and Weeden Island individuals supports the premise that the results are reliable

Weeden Island
Manasota period
550 BC – 800 AD
Estuarine

Belle Glade
Glades I-II period
500 BC – 1100 AD
Inland/lacustrine

Horr's Island
Archaic period
3100 BC – 250 AD
Coastal

Miami One
Glades I-III
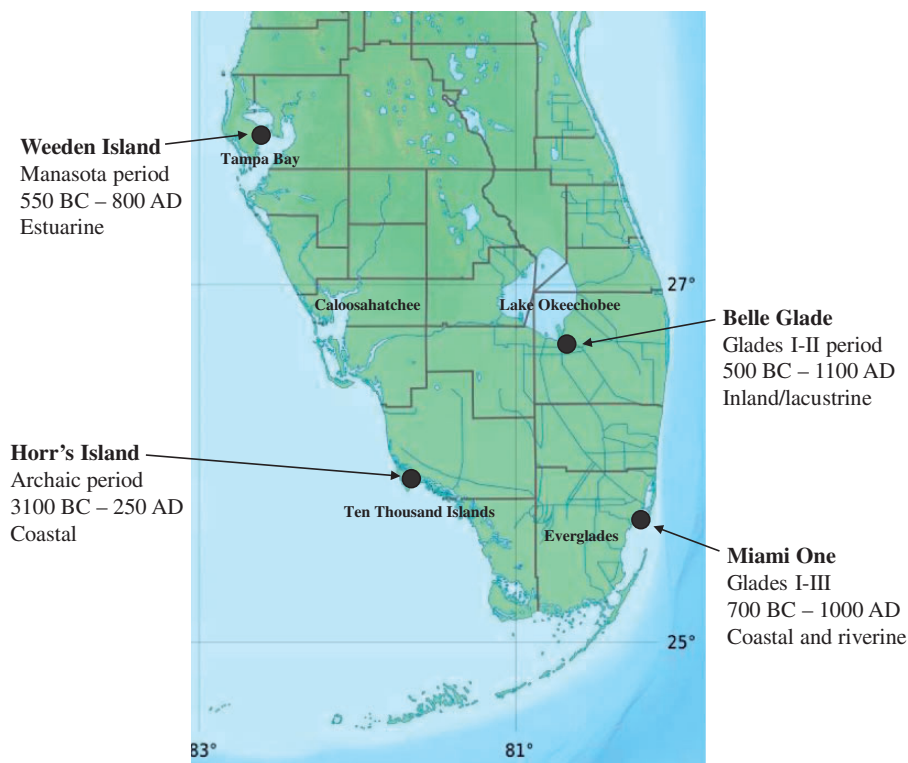700 BC – 1000 AD
Coastal and riverine

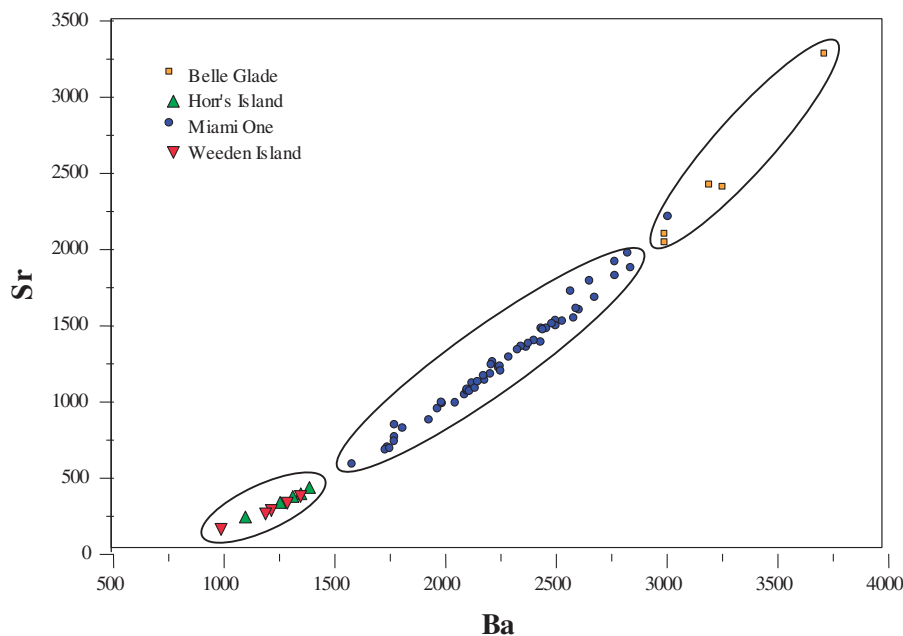**Figure 17.** Florida sites with skeletal remains tested by pXRF.

Figure 18. Element ratios from pXRF analyses indicating differences in aquatic food consumption.

and not significantly altered by contamination and/or decay. The results also are consistent with greater and more regular accessibility of marine foods on the shallower Gulf side, as shown by stable carbon and nitrogen isotope analyses of bone collagen and apatite.[87]

Conclusion

At this point, pXRF is being used by archaeologists around the world, on many different materials. It has been clearly shown to be excellent for obsidian sourcing studies, given the homogeneity of the material and the modest number of geological sources to distinguish between. For ceramics, care must be taken in dealing with potential heterogeneity, and given the many potential clay sources used, results for just five trace elements is limiting. Especially when no thin sections are made and studied to identify the overall clay type, knowledge (and ideally samples) of different clay sources is necessary, while analysis of major elements is also recommended. Follow-up analyses by INAA or ICP on at least a subset of samples is needed since some compositional groups based on pXRF data may actually represent multiple subgroups identifiable with results for more trace elements. For elemental results on metals, painted material, and bones, the issues are not about the instrument, but doing nondestructive surface analyses; as said in TV ads for a clothing business, "an educated consumer is the best customer". Using a pXRF is not just point-and-shoot; as with many other scientific methods of analysis, practitioners, collection managers, and data consumers need to be educated as to the advantages and disadvantages of pXRF for archaeological materials.

References

1. E. Ciliberto, G. Spoto, editors. Modern Analytical Methods in Art and Archaeology. New York, NY: John Wiley and Sons, 2000.
2. A.M. Pollard, C. Batt, B. Stern, S.M.M. Young. Analytical Chemistry in Archaeology. Cambridge, UK: Cambridge University Press, 2007.
3. A.M. Pollard, C. Heron, editors. Archaeological Chemistry. Cambridge, UK: The Royal Society of Chemistry, 2008.
4. M.S. Shackley. "Is There Reliability and Validity in Portable X-ray Fluorescence Spectrometry (PXRF)". The SAA Archaeological Record. 2010. 10(5): 17–20, 44.
5. E. Frahm, R.C.P. Doonan. "The Technological Versus Methodological Revolution of Portable XRF in Archaeology". J. Archaeol. Sci. 2013. 40: 1425–1434.
6. R.J. Speakman, M.S. Shackley. "Silo Science and Portable XRF in Archaeology: a Response to Frahm". J. Archaeol. Sci. 2013. 40: 1435–1443.

7. E. Frahm. "Is Obsidian Sourcing about Geochemistry or Archaeology? A Reply to Speakman and Shackley". J. Archaeol. Sci. 2013. 40: 1444–1448.

8. E. Frahm. "Validity of "Off-the-Shelf" Handheld Portable XRF for Sourcing Near Eastern Obsidian Chip Debris". J. Archaeol. Sci. 2013. 40: 1080–1092.

9. E. Frahm. "Characterizing Obsidian Sources with Portable XRF: Accuracy, Reproducibility, and Field Relationships in a Case Study from Armenia". J. Archaeol. Sci. 2014. 49: 105–125.

10. C. Alexander, K.A. Brown, I.M. Muntoni, R.H. Tykot. "Archaeometry of Neolithic Tavoliere Ceramics: Preliminary Results of a New Project". In: A. Gravina, editor. Atti – 34 Convegno Nazionale sulla Preistoria, Protostoria, Storia della Daunia. San Severo, 2013. pp. 131–140.

11. H. Ashkanani, R.H. Tykot. "Interregional Interaction and Dilmun Power in the Bronze Age: A Provenance Study of Ceramics from Bronze Age Sites in Kuwait, and Bahrain Using Non-destructive pXRF Analysis". In: R.A. Armitage, J.H. Burton, editors. Archaeological Chemistry VIII. ACS Symposium Series. 2013. 1147: 245–267.

12. M.F. Bonomo, J.P. Lowry, R.H. Tykot, J.A. Gifford. "An Exploratory Non-destructive Provenance Analysis of Two Middle Archaic Greenstone Pendants from Little Salt Spring, Florida, USA". Geoarchaeology. 2014. 29: 121–137.

13. K.P. Freund, R.H. Tykot. "Lithic Technology and Obsidian Exchange Networks in Bronze Age Nuragic Sardinia (Italy)". Archaeol. Anthropol. Sci. 2011. 3: 151–164.

14. E. Gliozzo, R. Arletti, L. Cartechini, S. Imberti, W.A. Kockelmann, I. Rinaldi, R.H. Tykot. "Non-invasive Chemical and Phase Analysis of Roman Bronze Artefacts from Thamusida (Morocco)". Appl. Radiat. Isot. 2010. 68: 2246–51.

15. E. Gliozzo, W.A. Kockelmann, L. Bartoli, R.H. Tykot. "Roman Bronze Artefacts from Thamusida (Morocco): Chemical and Phase Analyses". Nucl. Instrum. Methods Phys. Res. B. 2011. 269: 277–283.

16. C. Stremtan, H. Ashkanani, R.H. Tykot, M. Puscas. "Constructing a Database for pXRF, XRD, ICP-MS and Petrographic Analyses of Bronze Age Ceramics and Raw Materials from Failaka Island (Kuwait)". In: R.B. Scott, D. Braekmans, M. Carremans, P. Degryse (eds) Proceedings of the 39th International Symposium for Archaeometry. Leuven, Belgium: Centre for Archaeological Sciences, KU Leuven, 2014, pp. 274–279.

17. R.H. Tykot. 2010. "Sourcing of Sardinian Obsidian Collections in the Museo Preistorico-Etnografico 'Luigi Pigorini' Using Non-destructive Portable XRF". In: C. Lugliè, editor. L'ossidiana del Monte Arci nel Mediterraneo. Nuovi apporti sulla diffusione, sui sistemi di produzione e sulla loro crono-logia. Atti del 5° Convegno internazionale (Pau, Italia, 27–29 Giugno 2008). NUR, Ales. pp. 85–97.

18. R.H. Tykot. "Non-destructive Trace Element Analysis of Human Bones to Examine Diet and Mobility". In: D. Braekmans, J. Honings, P. Degryse (eds) 39th International Symposium on Archaeometry, 28 May–1 June 2012, Leuven, Belgium. Programme and Abstracts. Leuven, Belgium: Centre for Archaeological Sciences, 2012, p. 308.

19. R.H. Tykot. "Advantages and Disadvantages of using pXRF in Europe on Ceramics, Metals, Paintings, Stone, and Bone". 20th Annual Meeting of the European Association of Archaeologists. Abstracts of the Oral and Poster Presentations, 2014. p. 206.

20. R.H. Tykot, K.P. Freund, A. Vianello. "Source Analysis of Prehistoric Obsidian Artifacts in Sicily (Italy) Using pXRF". In: R.A. Armitage, J.H. Burton, editors. Archaeological Chemistry VIII. ACS Symposium Series. 2013. 1147:195–210.

21. R.H. Tykot, L. Lai, C. Tozzi. "Intra-site Obsidian Subsource Patterns at Contraguda, Sardinia (Italy)". In: I. Turbanti-Memmi (ed.) Proceedings of the 37th International Symposium on Archaeometry, Siena, Italy, May 13–16, 2008, Siena, Italy. New York, NY: Springer, 2011, pp. 321–328.

22. R.H. Tykot, N.M. White, J.P. DuVernay, J.S. Freeman, C.T. Hays, M. Koppe, C.N. Hunt, R.A. Weinstein, D.S. Woodward. "Advantages and Disadvantages of pXRF for Archaeological Ceramic Analysis: Prehistoric Pottery Distribution and Trade in NW Florida". In: R.A. Armitage, J.H. Burton, editors. Archaeological Chemistry VIII. ACS Symposium Series. 2013. 1147: 233–244.

23. MU Archaeometry Laboratory. "Overview of X-ray Fluorescence". http://archaeometry.missouri.edu/xrf_over-view.html [accessed Jul 15 2015].

24. I. Liritzis, N. Zacharias. "Portable XRF of Archaeological Artifacts: Current Research, Potentials and Limitations". In: M.S. Shackley (ed.) X-ray Fluorescence Spectrometry (XRF) in Geoarchaeology. New York, NY: Springer, 2013, pp. 109–142.

25. N. Goodale, D.G. Bailey, G.T. Jones, C. Prescott, E. Scholz, N. Stagliano, C. Lewis. "pXRF: A Study of Inter-instrument Performance". J. Archaeol. Sci. 2012. 39: 875–883.

26. A.N. Shugar, J.L. Mass, editors. Handheld XRF for Art and Archaeology. Leuven, Belgium: Leuven University Press, 2012.

27. Bruker. "Tracer Series pXRF Spectrometer". https://www.bruker.com/products/x-ray-diffraction-and-elemental-analysis/handheld-xrf/tracer-iii/overview.html [accessed Jul 15 2015].

28. K. Newlander, N. Goodale, G.T. Jones, D.G. Bailey. "Empirical Study of the Effect of Count Time on the Precision and Accuracy of pXRF Data". J. Archaeol. Sci. Reports. 2015. 3: 534–548.

29. N. Craig, R.J. Speakman, R.S. Popelka-Filcoff, M.D. Glascock, J. David Robertson, M.S. Shackley, M.S. Aldenderfer. "Comparison of XRF and PXRF for Analysis of Archaeological Obsidian from Southern Peru". J. Archaeol. Sci. 2007. 34: 2012–2024.

30. L.G. Cecil, M.D. Moriarty, R.J. Speakman, M.D. Glascock. "Feasibility of Field-portable XRF to Identify Obsidian Sources in Central Peten, Guatemala". In: M.D. Glascock, R.J. Speakman, R.S. Popelka-Filcoff (eds) Archaeological Chemistry. Analytical Techniques and Archaeological Interpretation. Washington, DC: American Chemical Society, 2007, pp. 506–521.

31. S.C. Phillips, R.J. Speakman. "Initial Source Evaluation of Archaeological Obsidian from the Kuril Islands of the Russian Far East Using Portable XRF". J. Archaeol. Sci. 2009. 36: 1256–1263.

32. A.J. Nazaroff, K.M. Prufer, B.L. Drake. "Assessing the Applicability of Portable X-ray Fluorescence Spectrometry for Obsidian Provenance Research in the Maya Lowlands". J. Archaeol. Sci. 2010. 37: 885–895.

33. P.W. Jia, T. Doelman, C. Chen, H. Zhao, S. Lin, R. Torrence, M.D. Glascock. "Moving Sources: A Preliminary Study of Volcanic Glass Artifact Distributions in Northeast China Using PXRF". J. Archaeol. Sci. 2010. 37: 1670–1677.

34. D.V. Burley, P.J. Sheppard, M. Simonin. "Tongan and Samoan Volcanic Glass: pXRF Analysis and Implications for Constructs of Ancestral Polynesian Society". J. Archaeol. Sci. 2011. 38: 2625–2632.

35. J.K. Millhauser, E. Rodriguez-Alegria, M. Glascock. "Testing the Accuracy of Portable X-ray Fluorescence to Study Aztec and Colonial Obsidian Supply at Xaltocan, Mexico". J. Archaeol. Sci. 2011. 38: 3141–3152.

36. N. Forster, P. Grave, P. "Non-destructive PXRF Analysis of Museum-curated Obsidian from the Near East". J. Archaeol. Sci. 2012. 39: 728–736.

37. P.R. Williams, L. Dussubieux, D.J. Nash. "Provenance of Peruvian Wari Obsidian: Comparing INAA, LA-ICP-MS, and Portable XRF". In: I. Liritzis, C.M. Stevenson (eds) Obsidian and Ancient Manufactured Glasses. Albuquerque, NM: University of New Mexico Press, 2012, pp. 75–85.

38. E. Dyrdahl, R.J. Speakman. "Investigating Obsidian Procurement at Integration Period (ca. AD 700–1500) Tola Sites in Highland Northern Ecuador via Portable X-ray Fluorescence (pXRF)". In: R.A. Armitage, J.H. Burton (eds) Archaeological Chemistry VIII. Washington, DC: American Chemical Society, 2013, pp. 211–232.

39. K. Rademaker, M. Glascock, B. Kaiser, D. Gibson, D. Lux, M. Yates. "Multi-technique Geochemical Characterization of the Alxa Obsidian Source, Peruvian Andes". Geology. 2013. 41: 779–782.

40. J.R. Cann, C. Renfrew. "The Characterization of Obsidian and its Application to the Mediterranean Region". Proceedings of the Prehistoric Society. 1964. 30: 111–133.

41. A.M. De Francesco, G.M. Crisci, M. Bocci. "Non-destructive Analytic Method Using XRF for Determination of Provenance of Archaeological Obsidians from the Mediterranean Area: A Comparison with Traditional XRF Methods". Archaeometry. 2008. 50: 337–350.

42. M. Milič. "PXRF Characterisation of Obsidian from Central Anatolia, the Aegean and Central Europe". J. Archaeol. Sci. 2014. 41: 285–296.

43. E. Frahm, R. Doonan, V. Kilikoglou. "Handheld Portable X-ray Fluorescence of Aegean Obsidians". Archaeometry. 2014. 56: 228–260.

44. E. Frahm, B.A. Schmidt, B. Gasparyan, B. Yeritsyan, S. Karapetian, K. Meliksetian. "Ten Seconds in the Field: Rapid Armenian Obsidian Sourcing with Portable XRF to Inform Excavations and Surveys". J. Archaeol. Sci. 2014. 41: 333–348.

45. R.H. Tykot. "Obsidian Use and Trade in the Adriatic". In: P. Visentini, E. Podrug (eds) The Adriatic, a Sea Without Borders: Communication Routes of Populations in 6000 BC. Udine, Italy: Civici Musei di Udine, Museo Friulano di Storia Naturale, 2014, pp. 171–181, 224–225.

46. R.H. Tykot. "Obsidian Procurement and Distribution in the Central and Western Mediterranean". Journal of Mediterranean Archaeology. 1996. 9: 39–82.

47. R.H. Tykot. "Chemical Fingerprinting and Source-tracing of Obsidian: The Central Mediterranean Trade in Black Gold". Acc. Chem. Res. 2002. 35: 618–627.

48. R.H. Tykot, M.R. Iovino, M.C. Martinelli, L. Beyer. "Ossidiana da Lipari: le fonti, la distribuzione, la tipologia e le tracce d'usura". In: Atti del XXXIX Riunione Scientifica dell'Istituto Italiano di Preistoria e Protostoria: Materie prime e scambi nella preistoria italiana, Firenze, 25–27 November 2004. Firenze, 2006. pp. 592–597.

49. R.H. Tykot, A.J. Ammerman. "New Directions in Central Mediterranean Obsidian Studies". Antiquity. 1997. 71(274): 1000–1006.

50. R.H. Tykot. "Obsidian Finds on the Fringes of the Central Mediterranean: Exotic or Eccentric Exchange?". In: A. Vianello (ed.) Exotica in the Prehistoric Mediterranean Oxford, UK: Oxbow Books, 2011, pp. 33–44.

51. R.J. Speakman, N.C. Little, D. Creel, M.R. Miller, J.G. Iñañez. "Sourcing Ceramics with Portable XRF Spectrometers? A Comparison with INAA Using Mimbres Pottery from the American Southwest". J. Archaeol. Sci. 2011. 38: 3483–3496.

52. N. Forster, P. Grave, N. Vickery, L. Kealhofer. "Non-destructive Analysis Using PXRF: Methodology and Application to Archaeological Ceramics". X-Ray Spectrom. 2011. 40: 389–398.

53. L. Bonizzoni, A. Galli, M. Gondola, M. Martini. "Comparison Between XRF, TXRF, and PXRF Analyses for Provenance Classification of Archaeological Brick". X-Ray Spectrom. 2013. 42: 262–267.

54. J. Johnson. "Accurate Measurements of Low Z Elements in Sediments and Archaeological Ceramics Using Portable X-ray Fluorescence (PXRF)". Journal of Archaeological Method and Theory. 2014. 21: 563–588.

55. A. Hunt, R.J. Speakman. "Portable XRF Analysis of Archaeological Sediments and Ceramics". J. Archaeol. Sci. 2015. 53: 626–638.

56. M. Morgenstein, C.A. Redmount. "Using Portable Energy Dispersive X-ray Fluorescence (EDXRF) Analysis for On-site Study of Ceramic Sherds at El Hibeh, Egypt". J. Archaeol. Sci. 2005. 32: 1613–1623.

57. L. Emery, M. Morgenstein. "Portable EDXRF Analysis of a Mud Brick Necropolis Enclosure: Evidence of Work Organization, El Hibeh, Middle Egypt". J. Archaeol. Sci. 2007. 34: 111–122.

58. J. Matsunaga. "Using Portable Energy Dispersive X-ray Fluoresence (EDXRF) Spectrometry in the Study of Ceramic Technology at Vinca-Belo Brdo, Serbia". Society of Archaeological Sciences Bulletin. 2009. 32: 8–12.

59. Y. Goren, H. Mommsen, J. Klinger. "Non-destructive Provenance Study of Cuneiform Tablets Using Portable X-ray Fluorescence (pXRF)". J. Archaeol. Sci. 2011. 38: 684–696.

60. D. Frankel, J.M. Webb. "Pottery Production and Distribution in Prehistoric Bronze Age Cyprus. An Application of pXRF Analysis". J. Archaeol. Sci. 2012. 39: 1380–1387.

61. F. Forouzan, J.B. Glover, F. Williams, D. Deocampo. "Portable XRF Analysis of Zoomorphic Figurines, "Tokens", and Sling Bullets from Chogha Gavaneh, Iran". J. Archaeol. Sci. 2012. 39: 3534–3541.

62. J.J. Aimers, D.J. Farthing, A.N. Shugar. "Handheld X-ray Analysis of Maya Ceramics: a Pilot Study Presenting Issues Related to Quantification and Calibration". In: A.N. Shugar, J.L. Mass (eds) Studies in Archaeological Sciences. Handheld

XRF for Art and Archaeology. Leuven, Belgium: Leuven University Press, 2012, pp. 423–449.

63. M. Koppe. Étude de céramiques de la vallée de l'Apalachicola en Floride par spectrométrie portable de fluorescence X. [M.A. Thesis]. Bordeaux, France: Université Michel de Montaigne Bordeaux 3, 2010.

64. J.P. DuVernay. The Archaeology of Yon Mound and Village, Middle Apalachicola River Valley, Northwest Florida. [Ph.D. Dissertation]. Tampa, FL: University of South Florida, 2011.

65. D. Woodward. Paleo-Indian to Spanish Occupation around Choctawhatchee Bay, Northwest Florida, as Documented in a Private Artifact Collection. [M.A. Thesis]. Tampa, FL: University of South Florida, 2012.

66. M. Teoh. Craft Specialization and Production Scale: Understanding Figulina Ware in Neolithic Dalmatia. [M.A. Thesis]. Eugene, OR: University of Oregon, 2012.

67. J. Pena. Elemental Analysis of Late Horizon Pottery from the Huancabamba Valley, Cajamarca - Peru. [M.A. Thesis]. Tampa, FL: University of South Florida, 2013.

68. D. McCormick. Exploring Potential Applications of Portable X-ray Fluorescence on Earthen Materials from Southeast Mesoamerica. [M.A. Thesis]. Tampa, FL: University of South Florida, 2013.

69. R.V. Nostrom. Portable X-ray Fluorescence Analysis of Pottery at the Bayshore Homes site in Pinellas County, Florida. [M.A. Thesis]. Tampa, FL: University of South Florida, Tampa, 2014.

70. J.B. McLeod. Digital Modeling and Non-Destructive Technological Examination of Aboriginal Burial Practices at Picnic Mound 8Hi3, Hillsborough County, Florida. [M.A. Thesis]. Tampa, FL: University of South Florida, 2014.

71. H. Ashkanani. Interregional Interaction and Dilmun Power in the Bronze Age: A Characterization Study of Ceramics from Bronze Age Sites in Kuwait. [Ph.D. Dissertation]. Tampa, FL: University of South Florida, 2014.

72. P. Woodruff. Etruscan Trade Networks: Understanding the Significance of Imported Materials at Remote Etruscan Settlements through Trace Element Analysis Using a Non-Destructive X-Ray Fluorescence Spectrometer. [M.A. Thesis]. Tampa, FL: University of South Florida, 2014.

73. E. Prendergast. The Archaeology of the McKinnie Site and Collection, Apalachicola Valley, Northwest Florida (8Ja1869). [M.A. Thesis]. Tampa, FL: University of South Florida, 2015.

74. E. Mckendry. Interpreting Bronze Age Exchange in Sicily through Trace Element Characterization of Ceramics Utilizing Portable X-Ray Fluorescence (pXRF). [M.A. Thesis]. Tampa, FL: University of South Florida, 2015.

75. F. Pirone. Regional Interaction Spheres and Mobility: An Archaeometric Characterization Study of Ceramics from the Maltese Neolithic to Middle Bronze Age. [Ph.D. Dissertation]. Tampa, FL: University of South Florida, 2016.

76. D.R. McCormick, E.C. Wells. "Pottery, People, and pXRF: Toward the Development of Composition Profiles for Southeast Mesoamerican Ceramics". In: S.L. Lopez Varela (ed.) Social Dynamics of Ceramic Analysis: New Techniques and Interpretations. Oxford, UK: Archaeopress, 2014, pp. 22–35.

77. A.G. Karydas. "Application of a Portable XRF Spectrometer for the Non-invasive Analysis of Museum Metal Artefacts". Annali di Chimica. 2007. 97: 419–432.

78. M.W. Rowe, S.J. Cole, M. Yousuf. "pXRF Analysis of Arsenic When Lead is Present: A Cautionary Tale". In: R.A. Armitage, J.H. Burton (eds) Archaeological Chemistry VIII. Washington, DC: American Chemical Society, 2013, pp. 269–276.

79. A.N. Shugar. "Portable X-ray Fluorescence and Archaeology: Limitations of the Instrument and Suggested Methods to Achieve Desired Results". In: R.A. Armitage, J.H. Burton (eds) Archaeological Chemistry VIII. Washington, DC: American Chemical Society, 2013, pp. 173–195.

80. S. Dylan. "Handheld X-ray Fluorescence Analysis of Renaissance Bronzes: Practical Approaches to Quantification and Acquisition". In: A.N. Shugar, J.L. Mass (eds) Studies in Archaeological Sciences. Handheld XRF for Art and Archaeology. Leuven, Belgium: Leuven University Press, 2012, pp. 37–74.

81. V. Orfanou, T. Rehren. "A (not so) Dangerous Method: pXRF vs. EPMA-WDS Analysis of Copper-based Artefacts". Archaeol. Anthropol. Sci. 2015. 7: 387–397.

82. A. Charalambous, V. Kassianidou, G. Papasavvas. "A Compositional Study of Cypriot Bronzes Dating to the Early Iron Age Using Portable X-ray Fluorescence Spectrometry (pXRF)". J. Archaeol. Sci. 2014. 46: 205–216.

83. L. Dussubieux, H. Walker. "Identifying American Native and European Smelted Coppers with pXRF: a Case Study of Artifacts from the Upper Great Lakes Region". J. Archaeol. Sci. 2015. 59: 169–178.

84. C. McGlinchey. "Handheld XRF for the Examination of Paintings: Proper Use and Limitations". In: A.N. Shugar, J.L. Mass (eds) Studies in Archaeological Sciences Handheld XRF for Art and Archaeology. Leuven, Belgium: Leuven University Press, 2012, pp. 131–158.

85. I. Liritzis, E. Polychroniadou. "Optical and Analytical Techniques Applied to the Amfissa Cathedral Mural Paintings Made by the Greek Artist Spyros Papaloukas (1892–1957)". Revue d' Archaeometrie (Archaeosciences). 2007. 31: 97–112.

86. R.H. Tykot. "The Contribution of Isotopic and Elemental Analysis to Understanding the Importance of Maize and Aquatic Foods in the Southeastern United States". Southeastern Archaeological Conference Bulletin. 2013. 56: 72.

87. R.H. Tykot, J.A. Kelly, J.T. Milanich. "Stable Isotope Analysis and Subsistence Adaptations Along the Gulf Coast of Florida from the Archaic Through Safety Harbor Periods". Geoarchaeological and Bioarchaeological Studies. 2005. 3: 517–520.