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Sourcing ceramics with portable XRF spectrometers? A comparison with INAA using Mimbres pottery from the American Southwest

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ABSTRACT

Seventy-five intact Mimbres and Jornada pottery sherds from the American Southwest were analyzed by portable XRF and instrumental neutron activation analysis (INAA). Examination of the data demonstrates that INAA and portable XRF results for elements common to both analyses can be used to construct similar compositional groups. When individual compositional groups are compared to one another, it is apparent that unambiguous separation of compositional groups is challenging by portable XRF given (1) the limited number of key discriminating elements that can be measured relative to INAA, and (2) the relative analytical precision and accuracy of portable XRF for measurements of intact heterogeneous ceramics. We conclude that sourcing intact ceramics by portable XRF is challenging and that bulk analytical measurements, such as INAA, remain a better approach for sourcing archaeological pottery.

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1. Introduction

Since the first archaeological applications of X-ray fluorescence (XRF) spectrometry in the 1960s, XRF has emerged as one of the most commonly used analytical tools for determining (both qualitatively and quantitatively) the chemical compositions of a variety of archaeological and historical materials—primarily obsidian (e.g., Shackley, 1998) and metals (e.g., Guerra, 1998), but also ceramics (e.g., Buxeda et al., 2003; Hall, 2004; Iñañez et al., 2007), flint (e.g., Hughes et al., 2010), metallurgical slags (e.g., Charlton et al., 2010), and soils (e.g., Marwick, 2005). Until recently, most archaeological applications of XRF have been confined to dedicated laboratories where XRF research has been overseen by scientists knowledgeable about physics and chemistry. During the past ten years, this model has changed significantly as archaeologists, museum conservators, and curators with limited-to-no background in chemistry, physics, and/or provenance-based studies of archaeological materials, have begun to acquire and use with increasing frequency commercially available portable XRF spectrometers. Dubbed portable XRF (PXRF, pXRF), field-portable XRF (FPXRF), or handheld XRF, such instrumentation has been commercially available since the early-to-mid 1960s (Piorek, 1997), and was being used to analyze archaeological materials as early as the 1970s (e.g., Cesareo et al., 1973). By the mid-1990s, following technological developments in computing and instrumentation (e.g., tubes, detectors, and associated electronics), portable XRF instruments were beginning to see increased use in geology (e.g., Potts et al., 1995, 1997a) and archaeology (e.g., Emery and Morgenstein, 2007; Morgenstein and Redmount, 2005; Pantazis et al., 2002; Potts et al., 1997b; Williams-Thorpe et al., 1999, 2003). And, since about 2005, there has been a tremendous increase in the number of portable instruments sold to the art and archaeological communities. We conservatively estimate there are approximately 200 such instruments worldwide currently being used at universities and museums in support of archaeological research and art conservation science. Despite the commercial availability of portable XRF analyzers for almost 50 years, the most common applications have been, and remain today, the metals recycling and mining industries.

Although portable XRF instruments have proven to be valuable research tools, the wide-spread adoption of portable XRF is not without issues. It is abundantly clear to many of us in the field of archaeological chemistry that a large number of handheld XRF users lack fundamental knowledge of X-ray spectroscopy, chemistry, physics, materials science, and/or statistics (see Shackley, 2010a, 2010b for additional discussion). Likewise, many such users have little or no background in provenance studies of archaeological

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materials, and fail to grasp the most basic principles that underlie the provenance postulate (e.g., Neff, 2000; Weigand et al., 1977). This "black box" approach is inherently problematic to archaeological science. We underscore that it is not the analytical technique that is flawed, but rather the general lack of experience and knowledge of the users of this technology. Certainly this is not the case for all researchers who use portable XRF, but rather a broad generalization. We note that that there are no fundamental differences in the physics or capabilities between portable XRF and more conventional energy dispersive XRF (EDXRF) instruments—both instruments types (lab and portable) have X-ray tubes and detectors that allow elemental information about a given sample to be generated. The major differences are that portable XRF instruments are portable; typically lack the ability to measure lower atomic weight elements under "true" vacuum; objects are typically measured outside of a chamber using a point and shoot approach. Additionally, portable instruments generally lack the higher powered software necessary for the deconvolution of spectra and quantification of data that is available in most laboratory-based instruments. Finally lab-based XRF instruments can produce slightly higher energy X-rays that may allow measurement of an additional element or two, but these differences are relatively minor. Hence for quantitative analyses, portable XRF instruments are ruled by the same constraints as any other laboratory-based XRF spectrometer. These include among others, clean flat surfaces, homogeneous samples, and calibration algorithms that ideally are based on matrix-matched standards and reference materials.

Although many portable XRF instruments come with factory-installed quantification routines that convert X-ray intensities to abundance data, these calibrations typically are not comparable to the types of artifacts being analyzed and oftentimes produce spurious results. From a qualitative perspective, analysts can use the XRF spectra to identify the presence and/or absence of various elements, such as the presence of heavy metals (e.g., As, Hg, and Pb) used to protect ethnographic objects from insect infestations. However, quantification by XRF ideally requires that users be capable of creating their own calibrations and be able to evaluate these calibrations and resulting data in terms of accuracy, precision, and sensitivity. Whereas some portable XRF vendors might argue their preinstalled calibration routines are satisfactory and therefore this step is not necessary, the fact remains that reliable and accurate factory calibrations for ceramics and obsidian[1] do not exist. We argue, that in many (if not most) cases, factory-installed calibrations are not adequate for quantification of elements in non-metallic archaeological materials. Portable XRF users who initiate projects based on the analyses of ceramics, obsidian, and other archaeological materials, using untested factory calibrations (i.e., calibrations not validated by the user through the analysis of known reference materials similar in composition to the objects being analyzed), do so at risk of generating data that are problematic and/or unusable. With respect to factory calibrations, the one exception (based on our experience) is that most factory calibration routines for metal alloys tend to produce accurate results—at least for the major elements (e.g., Heginbotham et al., 2010). However, most archaeological metals are corroded and/or heavily patinated on the surface. Because XRF involves a shallow penetration of X-rays into the sample, elements that are enriched (or depleted) on the surface are predominantly being measured, which may be significantly different from the bulk composition of the metal.

Companies that sell portable XRF spectrometers routinely make claims that it is possible for individuals to analyze—with minimal training—a wide variety of archaeological, ethnographic, and art objects, such as ceramics, native copper, paints and pigments, and man-made glass. These claims are absolutely true! Anyone can be trained, with little effort, in the mechanics of using such a device to produce a spectrum. The disconnect lies in that the *analysis* (in this case the mechanics of producing a spectrum) is not necessarily the same as *sourcing* (in the sense of the term as we have come to expect). Simply generating numbers and creating compositional groups is not a sourcing study regardless of the analytical technique. Likewise, qualitative approaches that involve stacking spectra on top of one another and pointing out differences in the spectra is not sourcing either. Researchers who generate (or incorporate) portable XRF data into their programs should question how the data compare to data generated by other analytical techniques? Are they reproducible? How do they compare to other published reference materials and standards? Can the data be used by other researchers in the future, or are the numbers only "internally consistent" and therefore only valid for the purposes of the current study. The same holds true for any analytical technique. Although we have singled out portable XRF in the above discussion, these criteria apply to all types of analyses. We underscore that we are not biased against the use of portable XRF, and in fact, the senior author of this paper has long been a proponent of this technology for both qualitative and quantitative analyses of cultural heritage and geological materials (e.g., Aldenderfer et al., 2008; Brostoff et al., 2009; Craig et al., 2007, 2010; Cecil et al., 2007; Farris et al., in press; Glascock et al., 2007a,b; Goebel et al., 2008; Grissom et al., 2010; Heginbotham et al., 2010; Little et al., in press; Phillips and Speakman, 2009; Reuther et al., 2011; Slobodina et al., 2009; Speakman et al., 2007; Wolff et al., in press).

For decades, laboratory-based XRF analyses of ceramics have occurred with some degree of regularity, but XRF of ceramics never has quite achieved the popularity of other analytical methods. The reason for this, in part, is the reduced sensitivity for trace elements relative to other analytical techniques such as instrumental neutron activation analysis (INAA) or inductively coupled plasma-mass spectrometry (ICP-MS), and generally speaking fewer "potentially discriminating" elements are analyzed (e.g., rare earth elements). It is no surprise then that laboratory-based XRF analyses have not witnessed the same degree of popularity as INAA of ceramics despite the ubiquitous nature of laboratory-based XRF instruments at most major universities, whereas only a handful of reactors exist with research programs dedicated to characterization of archaeological ceramics. What is surprising is the apparent interest by archaeologists in using portable XRF to *source* ceramics (as witnessed by presentations at recent national and international archaeology and archaeometry meetings). Typically, and under optimal conditions, a laboratory-based XRF analysis of ceramics can provide usable data for approximately 20–25 elements versus the 10–20 elements that can reasonably be expected from a portable XRF analyzer. Traditionally, for quantitative analyses by laboratory-based XRF, several grams of homogenized ceramic powder typically is pressed into pellets, fused into disks, or both in order to measure majors and trace elements separately (e.g., Hein et al., 2002). The same approach is equally valid for portable XRF instruments, but does not seem to have been widely adopted by users of portable instruments. Although portable XRF is theoretically non-destructive, to correctly analyze ceramics the surface must be clean of slip, paint, glaze, dirt, etc. At a minimum this means that (1) the ceramic surface should be abraded with something akin to a silicon carbide burring tool to prepare the ceramic surface for analysis or (2) that the samples be prepared as pressed pellets or fused disks. A cut or broken edge also is a possibility assuming that

[1] We have recently learned that one portable XRF manufacturer (Bruker) has obtained a set of ca. 30 well characterized obsidian reference samples for calibrating instruments for obsidian analysis.

Fig. 1. Examples of Mimbres Black-on-white pottery. Photographs courtesy of the Smithsonian National Museum of Natural History.

the sherd thickness is greater than the diameter of the XRF beam (ca. 4–10 mm, depending on the instrument) and that the area being analyzed is relatively flat[2] and more or less homogeneous. Hence, true non-destructive sourcing of whole pots in museum collections is likely not a reality, although portable XRF may be the only practical method of acquiring any chemical compositional data in cases where museums will not permit "destructive" sampling for INAA or other analytical methods.

In a recent report, Tagle and Gross (2010) described the use of μXRF for the non-destructive analysis of Mesoamerican and other ceramics. The specific μXRF used in Tagle's study had a spot size of ca. 3 mm diameter, which is not considerably different from the 3–5 mm diameter spot size of some commercial portable XRF instruments—including the instrument used herein. However, the idea of using a "true" μXRF spectrometer (e.g., an instrument with a beam size of ca. 30–100 μm diameter, or smaller) to source ceramics is troubling. At the 30–100 μm level of analysis what exactly is being measured—the clay, non-plastics, or a combination of both? As part of this research, we conducted a limited μXRF study (see below) to illustrate the effects of homogeneity and heterogeneity at the μm level.

Despite the challenges and limitations of using portable XRF to source ceramics, the possibility for sourcing pottery remains, provided that there is adequate sample preparation, i.e., removal of soil, slip, pigments, etc. from the sherd. In a recent paper, Goren and colleagues (Goren et al., 2011) concluded that portable XRF instruments could be used to nondestructively source clay tablets in cases where internal groupings had previously been established (e.g., by INAA). The authors correctly stressed that portable XRF was not a substitute for other chemical analyses or petrography, but that portable XRF could be useful for sourcing clay tablets when intrusive sampling is not possible. In this paper, we explore the possibility of using portable XRF to source Mimbres and Jornada pottery from the American Southwest. Unlike the Goren et al. study which was conducted on what can be considered fine paste ceramics, we focused on pottery containing varying amounts of temper.

2. Samples

2.1. μXRF samples

μXRF analyses were conducted on three samples: (1) an archaeological pottery specimen, MRM049, which has a moderate amount of coarsely crushed igneous rock; (2) a fine paste ceramic, New Ohio Red Clay; and (3) a sample of obsidian from Wiki Peak, Alaska—a theoretically homogeneous material.

2.2. Portable XRF samples

Since publication of Gilman et al.'s (1994) seminal INAA study of Mimbres pottery (Fig. 1), dozens of research projects involving the analyses of Mimbres and Jornada pottery have been conducted at

[2] With calibration schemes that involve ratioing counts to the Compton peak or Bremsstrahlung continuum sample "flatness" is less of a problem in EDXRF. Flatness is a major concern when fundamental parameters (FP) calibrations are being used given that the calculations are based on the theoretical relationships between X-ray intensities and element concentrations in an *ideal* sample.

Table 1
Descriptive information for pottery samples analyzed by portable XRF and INAA.

Anid	Group	Ceramic Type	Site Name	Site #
ANI022	Mimbres-21	Mimbres B/w Style III		AZ BB1635
ANI024	Mimbres-21	Mimbres B/w Style III		AZ U15127
ANI026	Mimbres-21	Mimbres B/w Style III		AZ U15127
ANI029	Mimbres-21	Mimbres B/w Style III		AZ BB1641
ANI030	Mimbres-21	Mimbres B/w Style III		AZ BB1641
MRM003	Mimbres-11	Mimbres B/w Style III	Hueco Tanks	41EP00002
MRM006	Mimbres-11	Mimbres B/w Style II	Hueco Tanks	41EP00002
MRM026	Mimbres-02a	Mimbres B/w Style III	North Hills I	41EP00355
MRM028	Mimbres-04a	Mimbres B/w Style III	North Hills I	41EP00355
MRM033	Mimbres-02a	Mimbres B/w Style III	North Hills I	41EP00355
MRM035	Mimbres-02a	Mimbres B/w Style III	North Hills I	41EP00355
MRM042	Mimbres-01	Mimbres B/w Style III	North Hills I	41EP00355
MRM043	Mimbres-02a	Mimbres B/w Style III	North Hills I	41EP00355
MRM049	Mimbres-02a	Mimbres B/w Style III	North Hills I	41EP00355
MRM050	Mimbres-02a	Mimbres B/w Style III	North Hills I	41EP00355
MRM052	Mimbres-02a	Mimbres B/w Style III	North Hills I	41EP00355
MRM053	Mimbres-02a	Mimbres B/w	North Hills I	41EP00355
MRM054	Mimbres-02a	Mimbres B/w Style III	North Hills I	41EP00355
MRM057	Mimbres-04a	Mimbres B/w Style III	North Hills I	41EP00355
MRM062	Mimbres-11	Mimbres B/w Style III	North Hills I	41EP00355
MRM063	Mimbres-01	Mimbres B/w Style III	North Hills I	41EP00355
MRM077	Mimbres-01	Mimbres B/w Style III	Divad	LA 096687
MRM081	Mimbres-11	Mimbres B/w Style III	Divad	LA 096687
MRM086	Mimbres-01	Mimbres B/w Style III	Divad	LA 096687
MRM087	Mimbres-02a	Mimbres B/w Style III	Divad	LA 096687
MRM090	Mimbres-11	Mimbres B/w Style III	Divad	LA 096687
MRM094	Mimbres-11	Mimbres B/w Style III	Divad	LA 096687
MRM104	Mimbres-04a	Mimbres B/w Style II	Turq Ridge	FB6307
MRM115	Mimbres-01	Mimbres B/w Style III	Sandcliffe	Sandcliffe
MRM116	Mimbres-11	Mimbres B/w Style III	Sandcliffe	Sandcliffe
MRM126	Mimbres-01	Mimbres B/w Style III	Temporal	LA 001085
MRM128	Mimbres-11	Mimbres B/w Style III	Temporal	LA 001085
MRM130	Mimbres-01	Mimbres B/w Style III	Temporal	LA 001085
MRM131	Mimbres-01	Mimbres B/w Style III	Temporal	LA 001085
MRM146	Mimbres-04a	Mimbres B/w Style II	Roth	LA 073942
MRM150	Mimbres-03	Mimbres B/w Style II	Roth	LA 073942
MRM166	Mimbres-11	Mimbres B/w Style III	Los Tules	LA 016315
MRM191	Mimbres-08	Mimbres B/w Style II	Los Tules	LA 016315
MRM276	El Paso Core	El Paso Polychrome	Hueco Tanks	41EP00002
MRM282	El Paso Core	El Paso Bichrome	North Hills I	41EP00355
MRM286	El Paso Core	El Paso Brownware	Diablo 1	41HZ0491
MRM289	El Paso Core	El Paso Brownware	Diablo 3	41HZ0493
MRM290	El Paso Core	El Paso Brownware	Conejo	LA 091044
MRM295	El Paso Core	El Paso Brownware	Hill 100	LA 097088
MRM305	El Paso Core	El Paso Brownware	Roth	LA 073942
MRM307	El Paso Core	El Paso Brownware	Roth	LA 073942
MRM311	El Paso Core	El Paso Brownware	Los Tules	LA 016315
MRM312	El Paso Core	El Paso Brownware	Los Tules	LA 016315
OT102	Mimbres-08	Mimbres B/w Style III		LA 018342
OT157	Mimbres-08	Mimbres B/w Style III	Ronnie Pueblo	83-NM-400
OT174	Mimbres-11	Mimbres B/w, Style II	Old Town	LA 001113
OT187	Mimbres-21	Mimbres B/w, Style II	Old Town	LA 001113
OT189	Mimbres-21	Mimbres B/w, Style II	Old Town	LA 001113
OT195	Mimbres-03	Untyped, Unslipped B/w	Old Town	LA 001113
OT196	Mimbres-03	Untyped, Unslipped B/w	Old Town	LA 001113
OT197	Mimbres-03	Untyped, Unslipped B/w	Old Town	LA 001113
OT198	Mimbres-03	Untyped, Unslipped B/w	Old Town	LA 001113
OT199	Mimbres-03	Untyped, Unslipped B/w	Old Town	LA 001113
OT200	Mimbres-03	Untyped, Unslipped B/w	Old Town	LA 001113
OT205	Mimbres-21	Mimbres B/w, Style II	Old Town	LA 001113
OT230	Mimbres-03	Untyped, Unslipped B/w	Old Town	LA 001113
OT231	Mimbres-03	Untyped, Unslipped B/w	Old Town	LA 001113
OT233	Mimbres-03	Untyped, Unslipped B/w	Old Town	LA 001113
OT234	Mimbres-03	Untyped, Unslipped B/w	Old Town	LA 001113
OT235	Mimbres-21	Mimbres B/w, Style II	Old Town	LA 001113
OT243	Mimbres-03	Untyped, Unslipped B/w	Old Town	LA 001113
OT504	Mimbres-08	Mimbres B/w Style III	Avilas Canyon Village	LA 045000
OT506	Mimbres-08	Mimbres B/w Style III	Avilas Canyon Village	LA 045000
OT511	Mimbres-04a	Mimbres B/w Style III	Avilas Canyon Village	LA 045000
OT512	Mimbres-04a	Mimbres B/w Style III	Avilas Canyon Village	LA 045000
OT513	Mimbres-04a	Mimbres B/w Style III	Avilas Canyon Village	LA 045000
WCRM003	Mimbres-04a	Mimbres B/w Style III	Badger Ruin	LA 111395
WCRM004	Mimbres-04a	Mimbres B/w Style III	Badger Ruin	LA 111395
WCRM007	Mimbres-11	Mimbres B/w Style III	Jackson Fraction	LA 111413
WCRM010	Mimbres-08	Mimbres B/w Style III	Jackson Fraction	LA 111413

Texas A&M and the University of Missouri Research Reactor Center (MURR). These projects have ranged in scale from small cultural resource management projects involving the analyses of relatively few samples to large-scale research projects initiated by Mimbres scholars. Most of the early work involving Mimbres pottery was conducted at Texas A&M in the early-to-mid 1990s by nuclear chemist Dennis James in collaboration with archaeologist Harry Shafer, Robbie Brewington, Holly Meier, and Eleanor Dahlin. Under the Texas A&M program, more than 1100 Mimbres, Jornada, and related pottery and clays were analyzed. Since the mid-1990's, archaeologists Myles Miller, Darrell Creel, and numerous other researchers (e.g., Pat Gilman, Nancy Kenmotsu, Lori Reed, Bernard Schriever, Chris Turnbow, and others) have initiated dozens of INAA-based research projects through the MURR laboratory that were complementary to the Texas A&M program and Gilman's earlier research through the Smithsonian-NIST INAA program. As a result of these combined efforts, more than 4000 Mimbres, Jornada, and related pottery specimens and clay samples from more than 250 sites throughout southern New Mexico, eastern Arizona, west Texas, and Chihuahua have been analyzed to date. Although these subsequent studies confirmed the patterns reported by Gilman et al. (1994) and have produced evidence for local ceramic production at a number of sites in the Mimbres Valley and elsewhere, there has been no published synthesis of the data. An ongoing major analytical effort, by Speakman, Creel, and Miller, focused on all extant INAA data has resulted in the identification of at least 45 Mimbres, Jornada, and related compositional groups. Interpretation and publication of these data is ongoing.

For this study we selected 75 Mimbres and Jornada pottery samples representing eight of what we believe to be the most clearly defined and chemically distinct of the 45 compositional groups. Each sample selected for portable XRF analysis had previously been analyzed by INAA at MURR allowing us to directly compare the results.

The eight compositional groups represented in the portable XRF sample include Mimbres-1, Mimbres-2a, Mimbres-3, Mimbres-4a, Mimbres-8, Mimbres-11, Mimbres-21, and El Paso Core. Descriptive information and group assignments (based on INAA) for each sample are presented in Table 1. With the exception of the samples assigned to the El Paso Core group which represents Jornada brownwares produced in the vicinity of El Paso, Texas, most pottery is typologically classified as Mimbres Black-on-white Style III and dates to ca. AD 1000–1150.

Despite the large numbers of Mimbres pottery analyzed by INAA, the assignment of the compositional groups to a specific site or groups of sites is problematic for several reasons. The first is that the criterion of abundance (Bishop et al., 1982) simply does not apply to Mimbres pottery. In most cases Mimbres pottery (including plain wares) was so widely moved around the landscape that at best only 20–30% of pottery analyzed from a given site might be considered locally produced. Consequently, we cannot confidently attribute compositional groups to a specific site or sites based on numbers alone. In addition, relatively few clays (<150) have been analyzed, and fewer than five compositional groups can be confidently linked to specific sites based on clay chemistry. Finally, the larger dataset of pottery represents numerous projects,

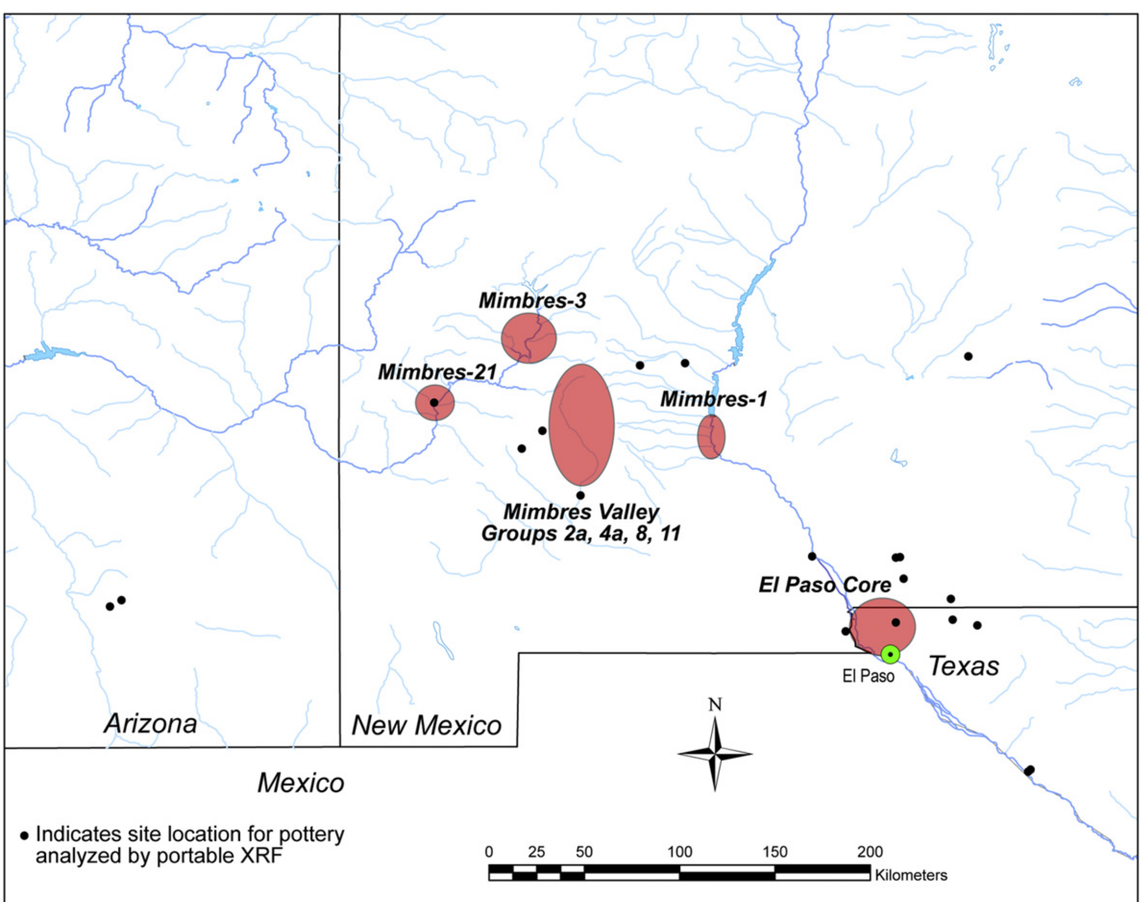

Fig. 2. Map of eastern Arizona, southwest New Mexico, and west Texas showing the site locations of pottery analyzed in this study and the productions areas for the 8 compositional groups discussed in the text.

each with different research questions. As a result, the sample is highly biased with approximately 15 sites representing ca. 50% of the sample. Having said this, we underscore that the point of this specific experiment is not to source the ceramics (we've already done that). Instead, our primary purpose here is to evaluate the potential of portable XRF for constructing compositional groups that can be used for provenance-based studies of ceramics.

The eight compositional groups selected for this study represent pottery production in five discrete geographic areas (Fig. 2). As indicated above, pottery assigned to the El Paso Core group represents pottery production in El Paso, Texas. The Mimbres-1 group represents pottery production in the Rio Grande Valley of southern New Mexico, probably the Rio Vista site and possibly the area immediately north of Rio Vista. Mimbres-3 pottery was

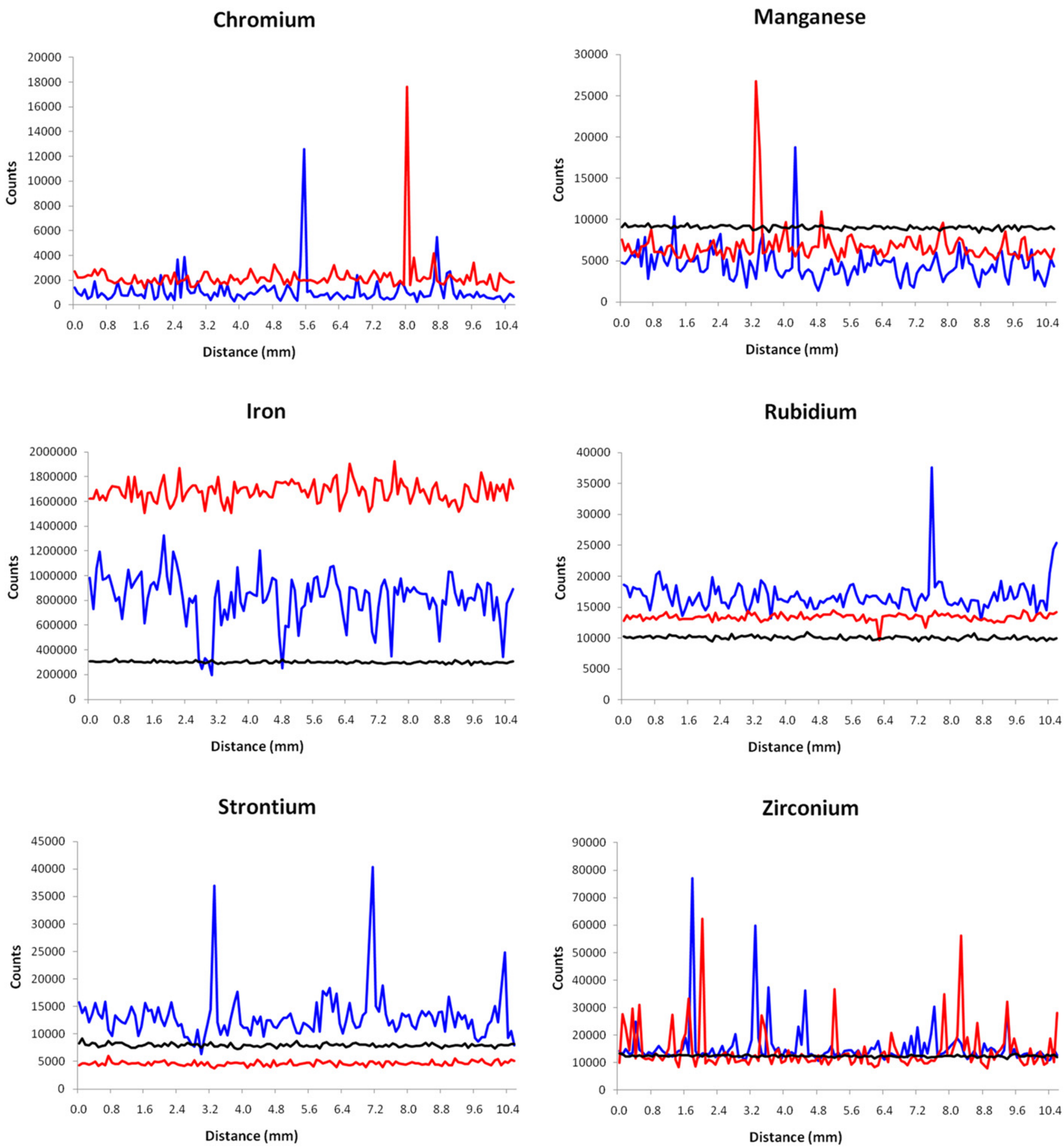

Fig. 3. μXRF line scans for selected elements showing chemical variability in Ohio Red Clay (Red line), archaeological pottery (MRM049; Blue line), and obsidian (Wiki Peak, AK; Black Line). A total of 130 individual measurements are represented by each line. Measurements occurred at 80 μm intervals, at 50 kV and 600 μA for a live-time count of 60 s each in a helium atmosphere. Note: Cr and Mg are below detection limits in the obsidian sample. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

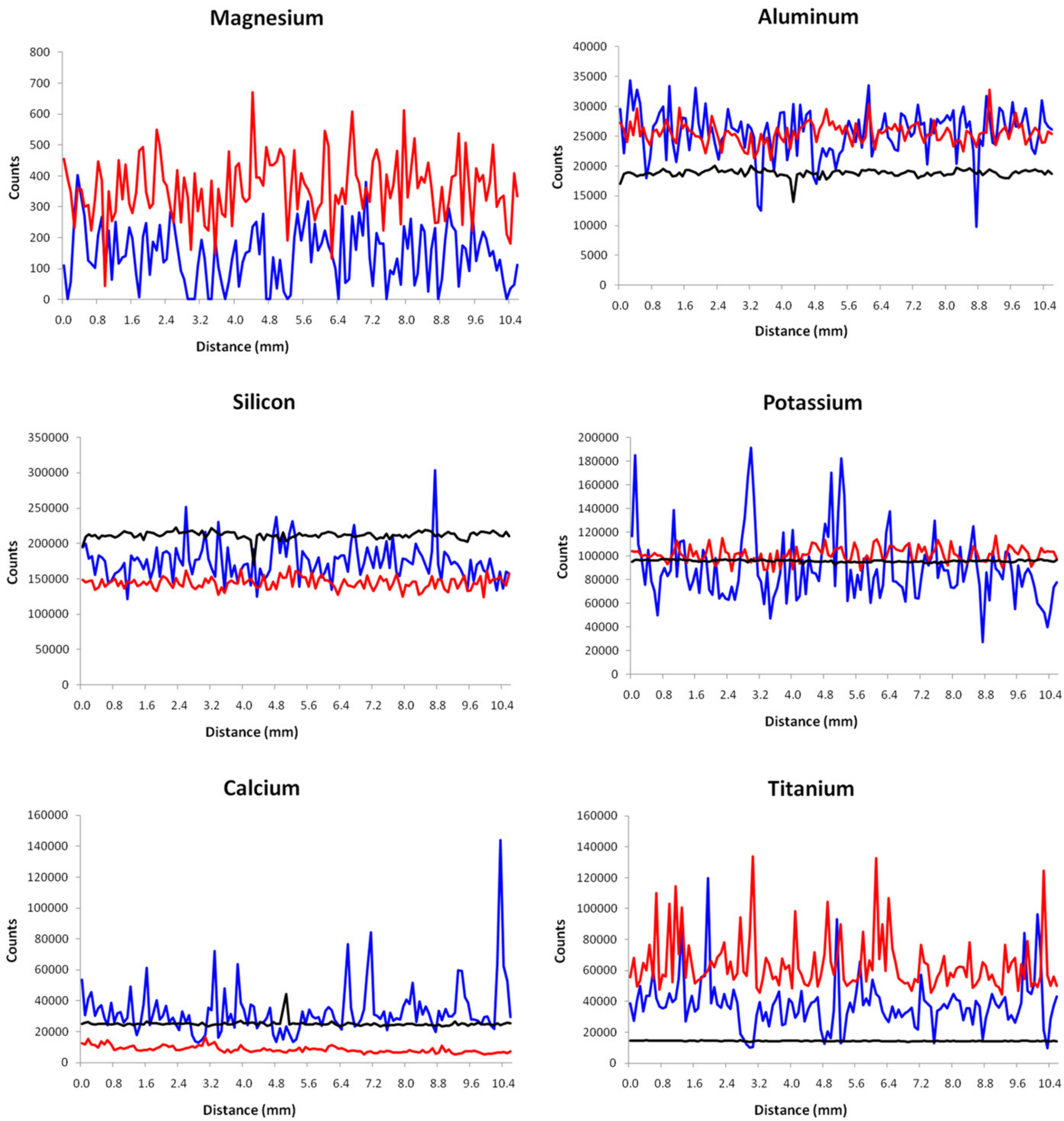

Fig. 3. (*continued*).

manufactured in the Gila Forks area of New Mexico. Unlike other Mimbres Black-on-white pottery which is recognizable as a white-slipped brownware, pottery assigned to Mimbres-3 has a white paste. Mimbres-21 pottery was produced at the Woodrow site which is located along the Gila River in New Mexico, near the Arizona border. The remaining four groups, Mimbres-2a, -4a, -8, and -11 originate from the Mimbres Valley in southwest New Mexico. Mimbres-2a pottery was likely produced in the middle part of the Mimbres Valley, probably at Swarts Ruin. Mimbres-4a pottery is probably from the Galaz site, and Mimbres-8 is believed to represent pottery production at the Mattocks site. Finally, Mimbres-11 currently is believed to represent pottery production at Pruitt Ranch.

3. Analytical methods

3.1. μXRF sample preparation and analysis

The archaeological pottery sample was abraded using a silicon carbide burr to remove the slip, paint, and/or any other materials adhering to the surface. The sample was washed in deionized water and allowed to dry. The Ohio Red Clay sample is a test tile that was produced at MURR and fired to 1100 °C (Cogswell et al., 1996). Because the sample was flat and had been stored in a clean plastic bag since its manufacture, no sample preparation was necessary. The Wiki Peak obsidian sample was prepared by using a lapidary saw with a diamond blade to remove a ca. $2 \times 2 \times 0.5$ cm slice from a larger geological specimen. The sample subsequently was washed with deionized water.

μXRF analyses were conducted using a Bruker AXS ARTAX 800 spectrometer equipped with a rhodium target polycapillary lens X-ray tube that has ca. 80 μm spatial resolution. The X-ray detector is a Si drift detector (SDD) with a 10 mm^2 active area and energy resolution of ca. 142 eV for the Mn K_α peak at 100 kcps. For this experiment, the instrument was programmed to travel along a line ca. 10.4 mm in length. A total of 130 individual measurements occurred on each sample, at 80 μm intervals, at 50 kV and 600 μA, for a live-time count of 60 s at each spot. Analyses were conducted in a helium atmosphere to maximize Mg, Al, and Si measurements.

3.2. INAA sample preparation and irradiation

INAA sample preparation and analysis were conducted at the University of Missouri Research Reactor Center (MURR). The pottery samples were prepared for INAA using standard MURR procedures (Glascock et al., 2007a,b). Fragments of about 1–2 cm were removed from each sample and the surfaces were abraded using a silicon carbide burr to remove the slip, paint, and/or any other materials adhering to the surface, thereby reducing the risk of measuring surface contamination. The samples were washed in deionized water and allowed to dry in the laboratory. Once dry, the individual sherds were ground to a fine homogenized powder using an agate mortar and pestle.

Aliquots of approximately 150 mg of powder were weighed into small polyvials used for short irradiations at MURR. At the same time, 200 mg of each sample were weighed into the high-purity quartz vials used for long irradiations. Along with the unknown samples, reference standards of SRM-1633a (coal fly ash) and SRM-688 (basalt rock) were similarly prepared, as were quality control samples (e.g., standards treated as unknowns) of SRM-278 (obsidian rock) and Ohio Red Clay.

INAA of ceramics at MURR, which consists of two irradiations and a total of three gamma counts, constitutes a superset of the procedures used at most other NAA laboratories (Glascock, 1992; Neff, 2000). As discussed in detail by Glascock (1992), a short irradiation entails the irradiation of each sample for 5 s by a neutron flux of 8×10^{13} cm^{-2} s^{-1}. The 720-second count yields gamma spectra containing peaks for short-lived elements: Al, Ba, Ca, Dy, K, Mn, Na, Ti, and V. The samples encapsulated in quartz vials are subjected to a 24-h irradiation at a neutron flux of 5×10^{13} cm^{-2} s^{-1}. This long irradiation is analogous to the single irradiation utilized at most other laboratories. After the long irradiation, samples decay for seven days, and then are counted for 2000 s (the "middle count") on a high-resolution germanium detector coupled to an automatic sample changer. The middle count yields determinations of seven medium half-life elements, namely As, La, Lu, Nd, Sm, U, and Yb. After an additional three- to four-week day, a final count of 9000 s is carried out on each sample. The latter measurement yields the following 17 long half-life elements: Ce, Co, Cr, Cs, Eu, Fe, Hf, Ni, Rb, Sb, Sc, Sr, Ta, Tb, Th, Zn, and Zr.

3.3. Portable XRF sample preparation and analysis

Portable XRF analyses were conducted on archived sherds retained from the earlier INAA studies. Ceramic fragments of approximately 1–2 cm were abraded using a silicon carbide burr to flatten the surfaces and remove slip, paint, and/or any other materials adhering to the surface. The samples were washed in deionized water and allowed to dry.

Analyses were conducted using a Bruker Tracer III-V handheld XRF spectrometer equipped with a rhodium tube and a Si-PIN detector with a resolution of ca. 170 eV FWHM for 5.9 keV X-rays (at 1000 counts per second) in an area 7 mm^2. The spot size on this specific instrument is ca. 4 mm diameter.

Each sample was measured twice using different excitation conditions. For the first analysis, each sample was analyzed at 40 kV, 15 μA, with a 0.076-mm copper filter and 0.0305-mm aluminum filter placed in the X-ray path for a 200-second live-time count. Peak intensities for the K_α peaks of Mn, Fe, Rb, Sr, Y, Zr, Nb, and L_α peak of Th were calculated as ratios to the Compton peak of rhodium, and converted to parts-per-million (ppm) using

Table 2
μXRF data summary statistics for MRM049, Ohio Red clay, and Wiki Peak obsidian. %rsd (relative standard deviation); Conc. (concentration).

	MRM049			Ohio Red Clay (NOR)			Wiki Peak Obsidian		
	Average Counts	std	%rsd	Average Counts	std	%rsd	Average Counts	std	%rsd
Mg	145	93	64	361	101	28	bdl		
Al	25,642	3980	16	25,513	1776	7	18,819	633	3
Si	174,698	25,104	14	144,248	8320	6	211,946	5538	3
K	89,190	28,381	32	101,414	6439	6	95,718	878	1
Ca	33,225	16067	48	8494	2118	25	25,141	2013	8
Ti	37,917	16,162	43	63,744	17,377	27	14,316	196	1
Cr	1111	1246	112	2227	1421	64	bdl		
Mn	4512	1961	43	6765	2259	33	9052	208	2
Fe	817,290	199,095	24	1,679,301	82,389	5	300,527	8617	3
Ni	1142	2484	217	2900	814	28	37	65	174
Cu	1659	1331	80	1063	395	37	866	248	29
Zn	6479	1895	29	6529	841	13	2508	232	9
Ga	2340	1702	73	833	300	36	2247	190	8
Rb	16,868	2555	15	13,383	576	4	10,073	270	3
Sr	13,138	4282	33	4658	384	8	7960	309	4
Y	207	548	265	506	1208	238	38	146	380
Zr	15,525	7848	51	14,443	8051	56	12,397	328	3
Nb	1197	436	36	880	296	34	554	228	41

std – standard deviation.
%rsd – % relative standard deviation.
bdl – below detection limits.

Table 3
INAA and portable XRF data for individual specimens.

Group	Al (PXRF) %	Al (NAA) %	K (PXRF) %	K (NAA) %	Ca (PXRF) %	Ca (NAA) %	Ti (PXRF) %	Ti (NAA) %	Mn (PXRF) ppm	Mn (NAA) ppm	Fe (PXRF) %	Fe (NAA) %	Th (PXRF) ppm	Th (NAA) ppm	Rb (PXRF) ppm	Rb (NAA) ppm	Sr (PXRF) ppm	Sr (NAA) ppm	ZR (PXRF) ppm	Zr (NAA) ppm	Y (PXRF) ppm	Nb (PXRF) ppm
El Paso Core																						
MRM276	9.07	8.76	3.45	4.40	1.23	1.46	0.53	0.67	563	555	4.44	3.72	14	17	98	99	379	305	399	506	39	38
MRM282	8.66	8.71	2.26	3.11	0.86	1.27	0.48	0.55	517	414	4.41	3.85	13	19	103	113	198	322	421	367	28	28
MRM286	8.73	9.27	2.36	3.50	0.82	1.15	0.36	0.36	440	303	2.84	3.05	16	28	112	138	361	322	308	309	24	31
MRM289	9.32	9.13	1.78	2.94	2.34	1.51	0.46	0.65	627	536	4.73	4.75	20	24	99	100	541	432	483	287	28	41
MRM290	9.24	9.11	2.07	3.10	1.00	1.36	0.40	0.56	453	485	3.80	4.30	12	21	116	112	343	455	361	296	28	31
MRM295	8.45	9.09	2.35	3.21	1.08	1.31	0.38	0.45	847	454	3.40	3.63	12	19	132	134	340	360	303	275	31	26
MRM305	9.59	9.24	3.20	4.05	0.97	1.33	0.56	0.60	625	564	3.56	4.24	14	19	109	112	538	414	544	418	35	38
MRM307	10.11	8.60	2.66	3.28	1.24	1.59	0.38	0.43	604	553	4.33	4.05	12	18	128	109	263	455	338	283	32	22
MRM311	9.78	9.34	2.91	2.82	0.95	1.39	0.35	0.34	663	372	4.63	4.12	21	20	137	132	407	408	298	282	35	33
MRM312	9.37	8.18	2.61	2.91	1.05	1.20	0.42	0.49	610	396	3.90	4.02	13	21	102	105	397	450	295	220	22	31
Mean	9.23	8.94	2.57	3.33	1.15	1.36	0.43	0.51	595	463	4.01	3.97	15	21	114	115	377	392	375	324	30	32
Standard Dev.	0.52	0.37	0.51	0.52	0.44	0.14	0.07	0.11	116	90	0.61	0.45	3	3	14	14	106	60	86	84	5	6
%rsd	5.6	4.1	20.0	15.5	38.0	10.2	16.5	22.2	19.5	19.5	15.2	11.4	21.3	15.2	12.6	12.2	28.2	15.2	23.0	25.8	17.0	18.2
Mimbres-01																						
MRM042	10.18	9.02	3.01	3.73	0.47	0.58	0.26	0.22	341	418	1.62	1.74	34	36	239	259	136	145	157	149	33	18
MRM063	10.14	9.69	2.49	3.30	0.43	0.63	0.20	0.18	135	127	1.19	1.27	36	46	184	205	79	73	145	193	27	18
MRM077	10.16	10.48	2.90	3.47	0.49	0.65	0.12	0.11	189	165	0.94	1.05	48	56	214	232	82	88	173	166	28	22
MRM086	12.11	9.83	2.78	2.72	1.04	0.78	0.16	0.11	333	149	1.08	1.11	40	50	186	195	115	110	159	177	27	23
MRM115	12.54	10.69	2.85	3.01	0.83	0.76	0.18	0.15	290	305	1.41	1.37	62	55	231	241	115	97	140	155	44	25
MRM126	12.00	9.43	2.92	3.43	1.22	0.75	0.39	0.11	156	170	0.82	0.97	39	49	178	196	152	203	113	170	24	22
MRM130	10.90	9.48	2.92	2.89	0.72	0.59	0.45	0.16	205	153	1.02	1.24	37	49	196	221	140	135	158	166	25	22
MRM131	9.68	9.39	2.74	3.42	0.39	0.78	0.19	0.16	172	171	0.82	1.02	40	47	188	195	130	109	132	147	28	24
Mean	10.96	9.75	2.83	3.25	0.70	0.69	0.24	0.15	228	207	1.11	1.22	42	48	202	218	119	120	147	165	30	22
Standard Dev.	1.10	0.57	0.16	0.34	0.31	0.09	0.12	0.04	82	101	0.28	0.25	9	6	23	24	27	41	19	15	7	2
%rsd	10.0	5.8	5.6	10.5	44.2	12.7	47.5	27.5	35.9	48.7	25.6	20.5	21.4	12.9	11.5	11.1	22.4	34.2	12.8	9.3	22.1	11.1
Mimbres-02a																						
MRM026	9.58	9.01	2.45	2.79	0.96	1.24	0.30	0.29	479	395	2.63	2.64	21	21	146	159	301	403	227	151	32	20
MRM033	10.18	9.17	2.38	2.83	0.75	1.16	0.32	0.36	473	315	2.69	2.75	16	20	136	155	277	303	319	194	32	21
MRM035	10.43	9.24	2.20	2.55	0.82	1.27	0.35	0.34	343	315	2.78	2.72	18	20	149	155	284	333	232	163	33	18
MRM043	9.02	8.89	2.25	2.68	0.85	1.15	0.40	0.33	378	251	2.60	2.59	17	19	156	147	299	294	216	154	39	21
MRM049	9.61	9.19	2.54	3.29	0.45	0.61	0.34	0.30	200	193	2.08	2.04	20	24	183	190	149	153	262	173	32	23
MRM050	10.21	9.08	2.40	2.86	0.82	1.17	0.32	0.33	419	364	2.35	2.38	14	19	142	151	367	382	250	180	32	20
MRM052	9.91	9.20	2.16	2.60	0.77	1.22	0.32	0.33	434	299	2.70	2.69	21	20	145	144	283	321	268	218	32	18
MRM053	12.61	8.59	1.89	2.68	3.34	1.26	0.29	0.27	396	320	2.49	2.74	16	19	140	143	279	375	208	169	30	17
MRM054	10.00	9.67	2.19	2.71	0.70	0.98	0.31	0.33	439	356	2.48	2.59	18	20	150	155	328	348	232	181	34	20
MRM087	10.07	8.40	2.31	2.76	0.86	1.21	0.36	0.31	513	533	2.58	2.62	15	20	144	152	335	403	253	187	36	21
Mean	10.16	9.04	2.28	2.77	1.03	1.13	0.33	0.32	407	334	2.54	2.58	17	20	149	155	290	331	247	177	33	20
Standard Dev.	0.95	0.35	0.18	0.21	0.82	0.20	0.03	0.03	88	90	0.21	0.22	2	1	13	13	58	74	32	20	2	2
%rsd	9.3	3.9	8.0	7.4	79.6	17.7	9.7	8.2	21.7	27.1	8.1	8.3	13.4	6.9	8.8	8.7	19.8	22.3	13.0	11.3	7.5	9.0
Mimbres-03																						
MRM150	9.03	8.14	2.51	4.70	0.98	0.82	0.27	0.11	690	535	1.36	1.38	41	38	281	289	100	90	240	193	167	41
OT195	9.74	7.98	5.43	5.24	0.49	0.88	0.12	0.11	655	713	1.16	1.23	42	37	289	304	40	42	209	226	76	29
OT196	11.31	8.39	4.91	5.02	0.71	1.18	0.11	0.15	401	667	0.98	1.35	39	36	277	283	60	63	215	201	66	29
OT197	10.52	8.48	5.12	5.14	0.73	0.29	0.11	0.07	504	672	0.96	1.37	47	37	279	291	69	54	207	206	85	31
OT198	10.07	8.03	4.91	5.05	0.53	0.81	0.11	0.08	557	538	1.06	1.31	39	32	271	278	68	67	183	167	66	27
OT199	10.85	8.31	5.13	5.31	0.53	0.68	0.13	0.06	420	614	1.03	1.39	31	36	300	305	59	49	223	194	113	32
OT200	11.16	8.14	5.31	5.58	0.99	1.26	0.12	0.19	508	651	1.22	1.47	44	35	315	329	52	50	187	186	81	27
OT230	10.30	8.32	4.35	4.56	0.74	1.08	0.13	0.13	696	622	1.22	1.26	38	35	250	258	90	90	275	156	80	30
OT231	11.25	7.84	5.12	5.41	0.92	1.65	0.15	0.23	572	630	1.04	1.22	36	34	280	282	63	68	197	151	103	29
OT233	12.37	8.24	5.95	5.19	0.90	0.87	0.15	0.14	556	663	1.02	1.29	49	37	322	312	74	58	212	187	106	34
OT234	11.25	8.66	5.45	5.01	0.84	1.11	0.11	0.14	469	613	0.98	1.21	44	36	271	286	49	39	194	162	78	31

(continued on next page)

Table 3 (*continued*)

Group	Al (PXRF) %	Al (NAA) %	K (PXRF) %	K (NAA) %	Ca (PXRF) %	Ca (NAA) %	Ti (PXRF) %	Ti (NAA) %	Mn (PXRF) ppm	Mn (NAA) ppm	Fe (PXRF) %	Fe (NAA) %	Th (PXRF) ppm	Th (NAA) ppm	Rb (PXRF) ppm	Rb (NAA) ppm	Sr (PXRF) ppm	Sr (NAA) ppm	ZR (PXRF) ppm	Zr (NAA) ppm	Y (PXRF) ppm	Nb (PXRF) ppm
OT243	12.16	8.37	5.39	4.71	0.70	0.64	0.14	0.18	471	604	1.08	1.33	33	35	263	269	89	54	218	174	94	33
Mean	10.83	8.24	4.97	5.08	0.75	0.94	0.14	0.13	542	627	1.09	1.32	40	36	283	290	68	60	213	183	93	31
Standard Dev.	0.96	0.23	0.86	0.30	0.18	0.35	0.04	0.05	99	52	0.12	0.08	5	1	21	19	18	16	25	22	28	4
%rsd	8.9	2.8	17.4	6.0	23.4	36.9	32.1	38.6	18.3	8.4	11.2	6.0	13.4	3.9	7.3	6.7	26.5	27.3	11.7	12.2	29.9	11.9
Mimbres-04a																						
MRM028	9.13	9.11	1.98	2.69	0.95	1.35	0.36	0.25	516	493	3.06	2.70	18	17	128	137	228	301	296	189	30	19
MRM057	9.60	8.83	1.95	2.79	1.01	1.35	0.30	0.26	540	519	2.86	2.83	17	22	124	126	247	246	237	199	31	20
MRM146	9.47	7.86	2.69	3.20	0.89	1.32	0.14	0.22	570	419	2.46	2.69	20	21	181	181	234	241	225	198	29	16
OT511	8.97	8.80	2.32	2.70	0.61	1.00	0.39	0.36	292	379	2.36	2.47	15	19	134	150	222	257	366	266	27	17
OT512	8.55	8.82	2.31	2.96	0.66	1.10	0.29	0.29	282	203	1.64	1.98	16	20	135	147	246	288	191	180	30	15
OT513	8.31	7.74	2.36	2.78	0.59	0.97	0.35	0.39	329	308	2.30	2.29	16	19	143	153	238	251	271	274	29	17
WCRM003	9.67	8.35	2.35	2.82	0.76	1.01	0.34	0.29	203	248	2.17	2.28	18	19	133	140	251	249	236	168	28	15
WCRM004	8.74	8.99	2.28	2.93	0.53	1.30	0.29	0.27	723	376	2.36	2.37	19	27	174	177	136	234	200	169	38	18
MRM104	9.35	8.97	1.93	2.62	0.83	1.37	0.39	0.39	443	390	3.15	3.08	10	18	113	120	275	303	246	184	28	18
Mean	9.09	8.61	2.24	2.83	0.76	1.20	0.32	0.30	433	371	2.49	2.52	17	20	141	148	231	263	252	203	30	17
Standard Dev.	0.48	0.50	0.25	0.18	0.17	0.17	0.08	0.06	169	104	0.47	0.34	3	3	23	21	39	26	54	40	3	2
%rsd	5.3	5.8	11.1	6.3	22.5	14.3	24.5	21.1	38.9	28.1	19.0	13.4	17.7	15.0	16.1	13.9	16.8	10.1	21.3	19.5	10.8	10.2
Mimbres-08																						
MRM191	8.34	8.46	2.62	3.31	0.56	0.77	0.30	0.30	323	183	1.78	2.11	22	27	193	198	158	152	231	173	27	19
OT102	8.45	8.39	2.38	2.75	0.38	0.61	0.27	0.24	288	195	1.86	2.16	21	31	209	199	114	131	215	165	31	16
OT157	7.71	8.30	2.42	2.92	0.48	0.85	0.26	0.28	399	248	1.99	2.10	22	28	191	193	140	584	201	197	28	16
OT504	8.71	8.49	2.35	2.90	0.45	0.62	0.30	0.28	242	201	1.90	2.15	22	27	156	189	120	119	186	198	25	15
OT506	9.08	8.17	2.83	3.29	0.39	0.60	0.30	0.32	416	497	1.87	1.89	21	26	199	196	130	150	274	208	31	19
WCRM010	9.14	8.07	2.66	3.14	0.54	0.74	0.27	0.22	479	330	1.83	2.03	25	27	198	199	121	112	224	175	27	17
Mean	8.57	8.32	2.54	3.05	0.46	0.70	0.28	0.27	358	275	1.87	2.08	22	28	191	196	131	208	222	186	28	17
Standard Dev.	0.53	0.17	0.19	0.23	0.07	0.10	0.02	0.04	88	121	0.07	0.10	2	2	18	4	16	185	30	17	3	2
%rsd	6.2	2.0	7.5	7.5	15.6	15.0	7.2	13.4	24.7	43.9	3.8	4.8	7.0	5.8	9.5	2.0	12.6	89.0	13.6	9.3	9.2	10.0
Mimbres-11																						
MRM003	10.87	7.85	2.85	2.97	0.88	0.92	0.37	0.26	769	996	2.35	2.15	20	18	191	198	241	199	204	157	32	21
MRM006	10.80	8.48	2.64	3.13	1.12	1.28	0.36	0.38	482	397	2.06	2.08	16	20	177	184	236	221	225	172	32	22
MRM062	10.85	8.90	2.81	3.26	0.76	1.07	0.40	0.36	1134	1088	2.47	2.35	17	19	189	189	234	265	213	143	32	19
MRM081	10.26	8.26	2.66	2.92	1.07	0.71	0.30	0.20	3068	2331	2.11	2.19	18	20	190	200	225	243	191	121	34	18
MRM090	11.76	8.80	2.63	2.89	0.92	0.85	0.37	0.23	929	1155	3.13	3.02	14	19	190	190	190	177	200	165	29	17
MRM094	13.34	8.20	2.81	3.23	2.36	1.09	0.36	0.42	780	741	2.28	2.50	15	19	204	198	224	260	215	165	31	22
MRM116	12.54	8.39	2.85	2.89	0.83	1.05	0.18	0.30	1229	1384	2.52	2.64	15	19	191	199	246	294	212	161	29	19
MRM128	10.41	8.86	2.92	4.15	0.54	1.06	0.12	0.33	2109	2367	2.34	2.41	17	21	202	208	232	223	191	159	32	21
MRM166	11.05	8.13	2.90	3.27	1.02	0.91	0.38	0.37	965	796	1.95	2.21	13	20	181	184	271	247	254	169	28	23
OT174	11.33	8.75	2.90	2.52	0.79	1.00	0.39	0.36	401	338	2.09	2.25	28	22	197	191	233	243	235	155	34	22
WCRM007	11.87	9.02	2.49	3.11	0.86	1.07	0.42	0.59	1405	1663	2.81	2.77	17	18	181	174	262	253	209	136	29	22
Mean	11.37	8.51	2.77	3.12	1.01	1.00	0.33	0.35	1206	1205	2.37	2.42	17	20	190	192	236	239	214	155	31	21
Standard Dev.	0.94	0.38	0.14	0.40	0.47	0.15	0.10	0.11	775	686	0.35	0.29	4	1	9	10	21	32	19	16	2	2
%rsd	8.2	4.4	5.1	12.9	46.8	15.1	28.6	30.6	64.2	56.9	14.7	12.2	23.3	6.4	4.5	5.0	9.0	13.6	8.8	10.1	6.8	9.0
Mimbres-21																						
ANI022	10.48	9.85	2.80	3.07	0.72	0.99	0.33	0.30	851	927	2.63	2.78	9	11	144	153	275	317	246	158	30	11
ANI024	10.81	8.61	2.59	3.02	0.91	1.16	0.29	0.25	771	885	2.38	2.45	8	10	129	133	327	356	258	153	26	14
ANI026	11.27	9.36	2.46	2.34	1.08	1.22	0.31	0.25	904	1180	3.12	3.28	8	9	117	119	374	444	232	147	24	11
ANI029	11.90	9.82	2.61	2.87	1.03	1.36	0.28	0.27	955	1076	2.51	2.91	9	10	121	130	372	385	241	160	25	13
ANI030	10.39	8.78	2.23	2.37	0.81	1.23	0.25	0.25	1105	1225	2.27	2.63	7	10	114	117	368	411	217	148	23	11
OT187	12.49	8.63	2.80	2.75	1.71	1.79	0.23	0.28	734	1073	1.97	2.44	10	10	98	110	351	403	187	147	22	8
OT189	11.83	9.15	2.53	2.57	1.62	2.37	0.23	0.15	912	1145	2.28	2.47	10	9	107	114	400	480	275	143	23	12
OT205	10.37	9.08	2.36	2.72	0.93	1.16	0.28	0.27	988	1154	2.88	3.13	11	10	133	131	354	362	229	172	24	13
OT235	11.34	8.93	2.56	2.84	0.84	1.46	0.27	0.18	1034	1028	2.22	2.39	14	9	126	128	380	265	233	140	24	13
Mean	11.21	9.13	2.55	2.73	1.07	1.41	0.27	0.24	917	1077	2.47	2.72	10	10	121	126	356	380	235	152	25	12
Standard Dev.	0.76	0.47	0.19	0.26	0.35	0.42	0.04	0.05	120	114	0.36	0.33	2	1	14	13	36	65	25	10	2	2
%rsd	6.8	5.1	7.3	9.5	32.9	30.0	12.9	19.7	13.1	10.6	14.4	12.0	20.5	7.2	11.4	10.2	10.2	17.1	10.6	6.7	8.9	13.1

linear regressions derived from the analysis of 15 obsidian reference samples (Phillips and Speakman, 2009). The obsidian calibration was selected to quantify the ceramic data because our initial experiments suggested that it worked quite well. Given that both obsidian and pottery are silicates and given the relative accuracy of the calibration for ceramics, this approach seemed reasonable. Technically it also should be possible to measure zinc using these settings; however, a high instrument background precludes accurate quantification of this element when present in low abundances.

For the second analysis, each sample was analyzed at 12 kV, 15 μA, for a 200-second live-time count. Peak intensities for the K_α peaks Al, K, Ti, and K_β peak of Ca were converted to parts-per-million (ppm) using a quadratic regression model based on the analyses of New Ohio Red Clay (Glascock et al., 2007a,b), Brill Glass A and B, and USGS pressed powder standards (AGV-1, DNC-1, DTS-2, G-2, MAG-1, SDC-1, SDO-1, SGR-1, and W-2). Silicon was observed in all spectra and Cr was observed in some spectra, but no attempts were made to quantify these elements.

4. Results

4.1. μXRF results

Graphical depictions of the μXRF data for 12 of the 18 elements measured are shown in Fig. 3A and B. These line scans—based on measurements of Mg, Al, Si, K, Ca, Ti, Cr, Mn, Fe, Rb, Sr, and Zr—illustrate the heterogeneous nature of the Ohio Red Clay (red line) and archaeological pottery (blue line) relative to the more homogeneous obsidian (black line). In the case of the obsidian sample Cr and Mg were below detection limits. Inspection of the line plots and the mean and standard deviations of the count rates (see Table 2) illustrate the relative homogeneity of the obsidian sample relative to the moderately tempered archaeological specimen and the fine-paste Ohio Red Clay tile. If we exclude Mg, Cr, Ni, Cu, Y, and Nb from consideration for all samples, due to inherently low values in the specimens analyzed and/or instrument sensitivity issues which resulted in greater analytical error, we see the obsidian has an average coefficient of variation of 4% versus 19% for the Ohio Red tile, and 35% for the archaeological sample. Visually, significant variability in the archaeological sample is evident in the plots for Al, K, Ca, Ti, Fe, Sr, and Zr and would seem to support a hypothesis that μXRF is less than adequate for provenance studies of ceramics.

4.2. Portable XRF results

Compositional data for all elements measured by portable XRF and their corresponding INAA data are presented in Table 3. Concentration ratios for portable XRF versus INAA groups are presented in Table 4. In general, some correlation exists between the INAA values and the corresponding portable XRF values (Table 3). Having said this, however, it is clear that some elements are better correlated than others. As shown in Table 4, Rb data for portable XRF and INAA are highly correlated and exhibit low relative standard deviations. Sr and Fe ratios for all groups are greater than 90% and are reasonably well correlated. Mean ratios for Zr are high and exhibit variability that likely reflects heterogeneity in the ceramic samples measured by portable XRF and possibly higher analytical error that is inherent in INAA measurements for this element. Th ratios tend to be systematically low in the portable XRF data which is a reflection of the ability of XRF to accurately measure low ppm Th. Likewise, Al is difficult to measure by XRF and even more challenging for samples not measured under full vacuum. We suspect that differences among K, Ca, and Ti reflect differences

Table 4
Concentration ratios for portable XRF versus INAA.

	El Paso Core			Mimbres-01			Mimbres-02a		
	Mean	std	%rsd	Mean	std	%rsd	Mean	std	%rsd
Al	1.03	0.08	8	1.13	0.10	9	1.13	0.13	12
K	0.77	0.12	16	0.88	0.10	11	0.82	0.05	6
Ca	0.84	0.26	30	1.00	0.38	38	0.90	0.62	69
Ti	0.87	0.11	12	1.71	0.93	54	1.04	0.11	10
Mn	1.32	0.32	25	1.18	0.45	38	1.24	0.19	16
Fe	1.01	0.12	12	0.90	0.08	9	0.99	0.03	3
Th	0.72	0.15	20	0.87	0.12	14	0.86	0.09	10
Rb	0.99	0.09	9	0.93	0.03	3	0.96	0.05	5
Sr	0.97	0.26	27	1.02	0.15	14	0.89	0.09	11
Zr	1.18	0.24	20	0.90	0.13	15	1.40	0.13	10

	Mimbres-03			Mimbres-04a			Mimbres-08		
	Mean	std	%rsd	Mean	std	%rsd	Mean	std	%rsd
Al	1.31	0.11	9	1.06	0.08	8	1.03	0.08	7
K	0.98	0.16	16	0.79	0.06	7	0.83	0.03	4
Ca	0.93	0.53	57	0.64	0.10	16	0.67	0.06	10
Ti	1.19	0.58	49	1.05	0.22	21	1.05	0.12	11
Mn	0.87	0.20	22	1.17	0.35	30	1.39	0.33	24
Fe	0.83	0.09	11	0.98	0.08	8	0.90	0.05	6
Th	1.13	0.14	12	0.83	0.15	18	0.80	0.08	10
Rb	0.97	0.02	2	0.95	0.04	4	0.98	0.08	8
Sr	1.14	0.21	18	0.88	0.14	16	0.85	0.31	37
Zr	1.18	0.22	18	1.25	0.19	15	1.20	0.17	14

	Mimbres-11			Mimbres-21			All Groups		
	Mean	std	%rsd	Mean	std	%rsd	Mean	std	%rsd
Al	1.34	0.13	10	1.23	0.11	9	1.16	0.12	11
K	0.90	0.11	13	0.94	0.07	7	0.86	0.07	8
Ca	1.03	0.46	44	0.76	0.12	15	0.85	0.15	17
Ti	1.02	0.38	38	1.16	0.23	20	1.14	0.25	22
Mn	1.02	0.19	19	0.85	0.09	11	1.13	0.20	18
Fe	0.98	0.06	6	0.91	0.05	6	0.94	0.06	6
Th	0.88	0.17	19	1.01	0.23	23	0.89	0.13	14
Rb	0.99	0.03	3	0.96	0.04	4	0.97	0.02	2
Sr	1.00	0.11	11	0.96	0.19	20	0.96	0.09	10
Zr	1.39	0.14	10	1.55	0.20	13	1.26	0.20	16

std – standard deviation.
%rsd – % relative standard deviation.

between the two type of analyses—bulk (INAA) versus heterogeneous surface analyses (portable XRF). Despite the observed differences between the two analytical techniques, there is some general agreement between the elements common to the INAA and portable XRF analysis.

Following common statistical routines for multivariate compositional datasets (see Glascock, 1992, among others), biplots derived from principal components analysis (PCA) of the elements in common to both the INAA and portable XRF datasets (Al, K, Ca, Ti, Mn, Fe, Rb, Sr, Zr, Th), calculated here as variance-covariance matrices, show more or less the same group structure (Fig. 4A and B). In general, these figures illustrate the elements that can be measured and quantified by portable XRF have similar analytical precision and accuracy, but that these elements as a group are not particularly useful for sourcing archaeological ceramics at a site-specific level. When PCA scores are recalculated to include all elements measured by portable XRF (e.g., the inclusion of Y and Nb in the data matrix) no significant differences are observed. In contrast, a variance-covariance matrix biplot, based on PCA of 5 INAA elements (Cr, Cs, Eu, Ta, Th) known to be good discriminators

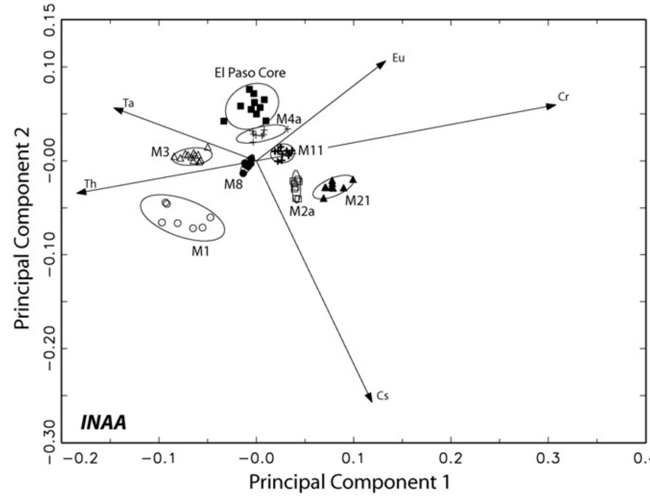

Fig. 5. Variance-covariance matrix PCA biplot based on Cr, Cs, Eu, Ta, Th measurements by INAA that are known to be important discriminating elements of Mimbres and Jornada pottery.

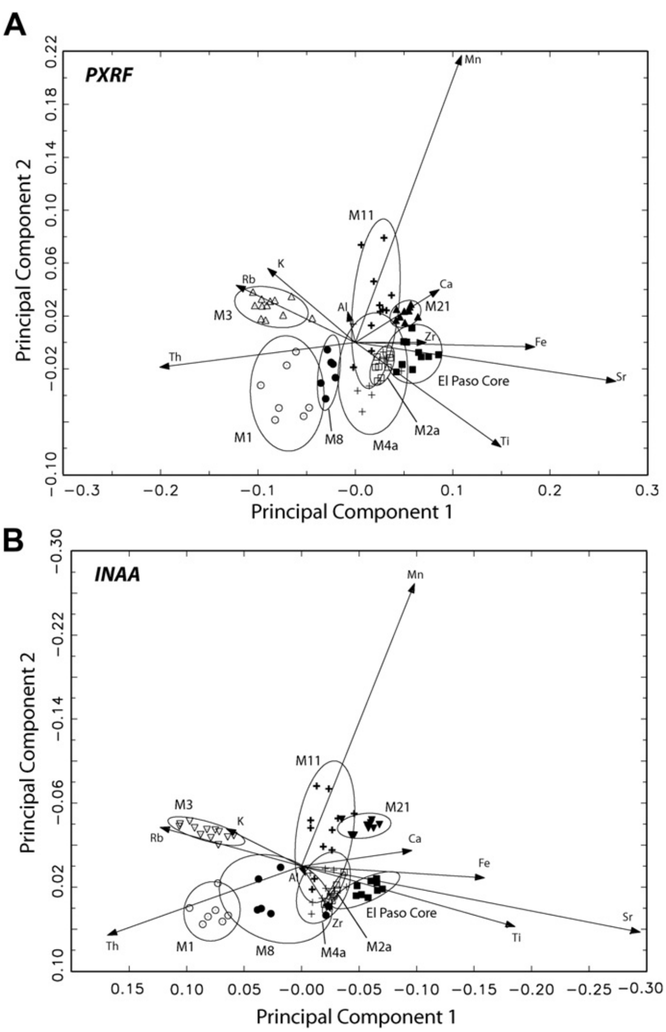

Fig. 4. A and B Biplot derived from PCA of the variance-covariance matrix of the Mimbres and Jornada pottery samples measured by portable XRF (A). Ellipses represent 90% confidence level for membership in the groups. Only elements in common to both portable XRF and INAA (Al, K, Ca, Ti, Mn, Fe, Rb, Sr, Zr, Th) are used to calculate PCA scores. (B) Same as above, but based on INAA data.

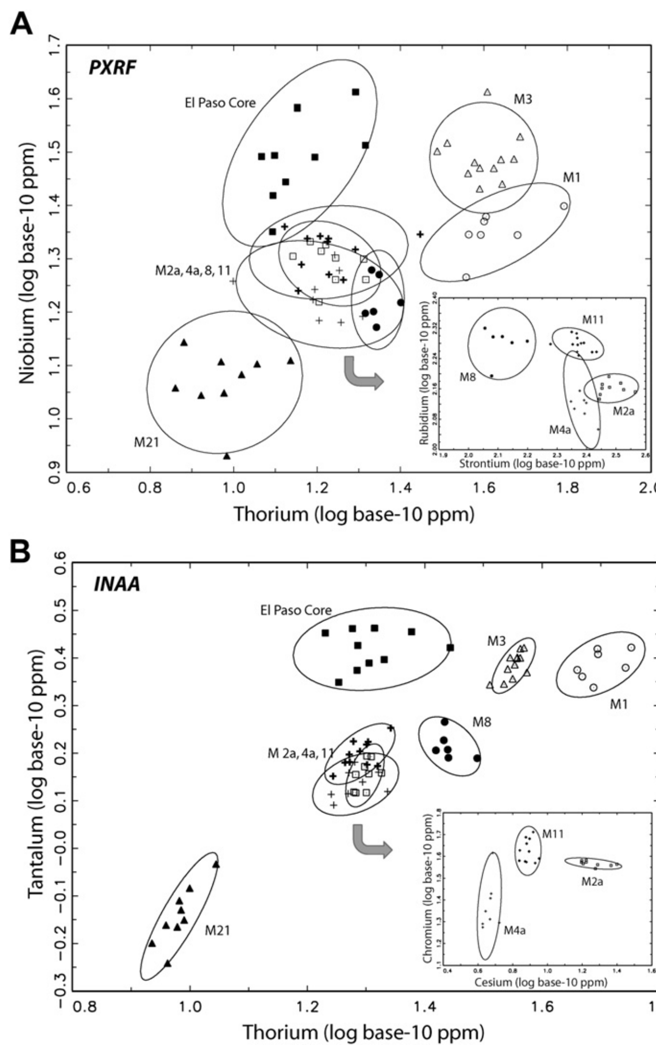

Fig. 6. A and B Elemental plots showing the best separation of groups/samples analyzed by portable XRF (A) and INAA (B).

of the groups in question, show a clear and unambiguous separation of the eight compositional groups (Fig. 5).

In addition to examining the data in multivariate space, attempts were made to show group discrimination using bivariate plots of the elements. The absolute best possible separation of the 8 groups using portable XRF data is shown in Fig. 6A. In this figure Th and Nb show marginal separation of the El Paso Core and groups Mimbres-1, Mimbres-3, and Mimbres-21 from the 4 Mimbres Valley groups (Mimbres-2a, 4a, 8, and 11). The four Mimbres Valley groups can be separated using Sr and Rb (Fig. 6A, inset). In contrast to the portable XRF data, excellent separation of El Paso Core and groups 1, 3, 8, and 21 is observed in a bivariate plot based on Th and Ta INAA concentrations (Fig. 6B). The three remaining Mimbres Valley groups exhibit equally good discrimination using Cs and Cr (Fig. 6B, inset).

5. Conclusions

Portable XRF has demonstrated great potential for quantitative analyses of many material classes, such as obsidian and metals (e.g., Heginbotham et al., 2010; Phillips and Speakman, 2009); however, the application of portable XRF to provenance studies of ceramics is not straightforward. In this study we examined 75 Mimbres and Jornada pottery samples by portable XRF. We carefully prepared the surfaces of the sherds and made every effort to optimize the portable XRF experiment to ensure that we generated the best possible data. The results of the portable XRF analyses were directly compared to INAA data generated from the same sherds. Although there is not a direct 1:1 correlation between the two datasets, data from the portable XRF study are somewhat in agreement with the corresponding INAA data. In particular, portable XRF was found to be suitable for distinguishing between major drainage basins and, to some extent, even short-distance intradrainage variation as shown by our results. Despite the generally acceptable results from portable XRF, it is clear that INAA has significantly greater analytical precision. In addition, the ability of INAA to measure trace and rare earth elements has proved critical to being able to effectively identify compositional groups that are useful for provenance studies. We suspect, based on our knowledge of other studies in the Americas, that the same can be said for most pottery studies—that is to say that analytical precision and the ability to measure trace and rare earth elements is key for discriminating compositional groups at a level required for site-specific (or approximately so) research questions. We are certain that there are some exemptions to this rule, but would argue that a portable-XRF study of ceramics should never be undertaken blindly. It is important to have some *priori* knowledge of the chemical variability and the expected group structure so that meaningful compositional groups can be constructed.

In cases where museums will not permit removal of samples from whole pottery vessels (often referred to as destructive sampling), thus precluding INAA and/or ICP-MS, portable XRF may be the only practical method of chemical compositional analysis currently available. In such cases, some data are better than none even if the results may be less useful for answering some research questions than INAA and/or ICP-MS.

As a final consideration, the μXRF experiments we conducted highlighted significant chemical variability within individual ceramics samples. The heterogeneous nature of ceramics at the μm scale must be considered when initiating provenance studies by μXRF. There is a big difference between the 80 μm diameter spot used in our μXRF experiments and the ca. 4000 μm diameter spot of our portable XRF instrument. Although much of our ability to generate numbers comparable to INAA lies in the preparation of our samples, we must also consider that larger beam sizes will average out some of the spatial chemical variability that occurs in ceramic pastes. It is therefore important to underscore that the ability to generate quantitative μXRF data for archaeological ceramics will be challenging and likely will have limited applicability to ceramic provenance studies.

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