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Testing the accuracy of portable X-ray fluorescence to study Aztec and Colonial obsidian supply at Xaltocan, Mexico

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ABSTRACT

This article demonstrates the accuracy of non-destructive portable X-ray fluorescence (*p*XRF) for the study of obsidian in central Mexico. Obsidian sources were identified for a sample of 103 artifacts from the site of Xaltocan, which spanned the rise and fall of the Aztec empire and the first centuries of Spanish colonial rule (AD 900–1700). Sources were assigned by comparing *p*XRF measurements with previously published source data and were verified using the standard techniques of laboratory XRF (*l*XRF) and instrumental neutron activation analysis (INAA). Additional tests of potentially confounding factors show that neither length of read time, presence of surface residue, nor incomplete detector coverage due to small artifact size compromised our ability to attribute sources to artifacts. Concave surfaces did decrease the accuracy of readings because of the greater distance between the artifact and the detector. Our results provide new insight into the stability of supply networks and markets well into the Colonial period as well as the homogenizing tendencies of the Aztec market system.

1. Introduction

Obsidian was a necessity in Mesoamerican economies—blades and other tools made of this volcanic glass were ubiquitous in households from the earliest sedentary villages until well after the Spanish conquest. Because each source of obsidian has a distinct chemical fingerprint and because obsidian artifacts are chemically stable on an archaeological time-scale, chemical characterization of obsidian artifacts is central to studies of long-distance trade (Hammond, 1972; Moholy-Nagy et al., 1984; Zeitlin, 1982), centralized production and resource monopolization (Healan, 1993; Santley, 1984; Spence, 1987), and the development of market systems (Hirth, 1998, 2008; Smith et al., 2007). Such research relies on sampling strategies that are spatially broad and temporally deep, but can be limited because reliable chemical characterization techniques are often expensive and destructive.

This article tests the accuracy of an inexpensive and non-destructive technique, portable X-ray fluorescence (*p*XRF), for the study of obsidian in central Mexico. Our data include 103 obsidian artifacts from excavated contexts at the site of Xaltocan spanning the rise and fall of the Aztec empire and the first centuries of Spanish colonial rule (ca. AD 900–1700). Given the limited number of obsidian sources present in central Mexico (Fig. 1) (Cobean, 2002), and that only a fraction of these were economically significant (Braswell, 2003), we need only to establish that *p*XRF is reliable and precise enough to differentiate between these sources for it to be useful. By comparing *p*XRF with the standard techniques of laboratory XRF (*l*XRF) and instrumental neutron activation analysis (INAA), we demonstrate that *p*XRF is sensitive enough to differentiate these sources and provide new insight into the stability of supply networks and market systems over centuries of political and social change. As *p*XRF becomes more widely applied, such inter-laboratory and inter-instrument comparisons are needed to guarantee the accurate attribution of artifacts to sources (Shackley, 2010). Furthermore, we show that researchers who lack comparative collections of geological source materials can accurately link artifacts to sources by comparing their *p*XRF results to previously published source data.

2. The choice of techniques for the sourcing of Mesoamerican obsidian

Current best practice for identifying sources of Mesoamerican obsidian involves first separating artifacts into groups based on macroscopic characteristics. This is followed by the chemical

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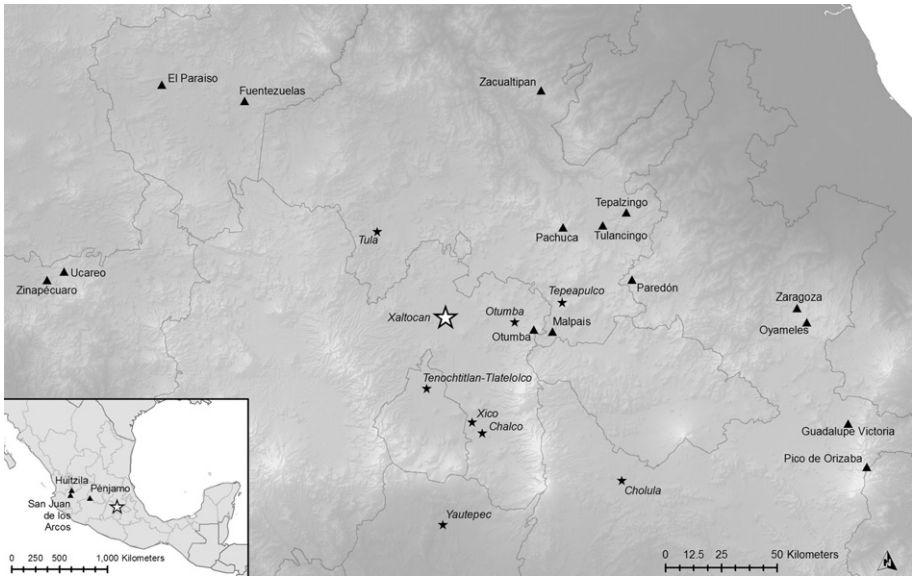

Fig. 1. Map of obsidian sources and archaeological sites mentioned in the text. State boundaries provided by the Instituto Nacional de Estadística y Geografía (INEGI) of Mexico. Digital elevation model data were distributed by the Land Processes Distributed Active Archive Center (LP DAAC), located at the U.S. Geological Survey (USGS) Earth Resources Observation and Science (EROS) Center (lpdaac.usgs.gov).

characterization of random samples of artifacts from those groups that cannot be accurately assigned to a source by visual qualities (Braswell et al., 2000; Cobean, 2002; Moholy-Nagy, 2003; Smith et al., 2007). In central Mexico, two of the most common sources are visually unmistakable: the Pachuca source in Hidalgo is most often a translucent green color with a golden sheen, while the obsidian of Pico de Orizaba, in southeastern Puebla, is nearly bottle-glass clear (Charlton and Spence, 1982; Cobean, 2002; Pastrana, 1998; Stocker and Cobean, 1984). The identification of three chemical sub-sources of Pachuca obsidian (Cobean et al., 1991: 78–79; Cobean, 2002) begs a finer-grained study of its distribution, although these sub-sources have not yet been linked to particular mines or workshops. The rest of the obsidian artifacts found in Mesoamerican archaeological contexts are variations of black, gray, and reddish-brown, for which no single source can be assigned based on visual criteria alone. Chemical characterization therefore is a valuable method for answering archaeological questions about obsidian distribution and consumption (Moholy-Nagy, 2003).

When choosing a method of chemical characterization, one must balance accuracy, speed, and cost with the goal of minimizing the number of artifacts that are damaged or destroyed. The most widely used techniques are XRF and INAA. XRF has been successfully employed in studies of sources and artifacts across Mesoamerica (Andrews et al., 1989; Clark and Lee, 1984; Cobean et al., 1971; Ford et al., 1997; Hammond, 1972; Healan, 1993; Hester et al., 1972, 1973; Jack and Heizer, 1968; Moholy-Nagy et al., 1984; Pollard and Vogel, 1994; Rice, 1984; Smith et al., 2007). INAA has been a successful alternative to XRF because of its accuracy, the wide range of elements that can be measured, and long-term investment by the University of Missouri Research Reactor (MURR) to develop a database of obsidian sources and archaeological samples (Cobean, 2002; Glascock, 1999, 2002; Glascock et al., 1999). While INAA is optimal for highly precise studies and samples too small for analysis by XRF, it cannot measure barium (Ba), strontium (Sr), or zirconium (Zr) with the same accuracy as XRF (Shackley, 2005: 90). Furthermore, INAA is time-consuming, destructive, and involves the handling of radioactive material. Currently at MURR, INAA is used more often to resolve very fine distinctions between sources that cannot be identified by XRF.

An attractive feature of XRF is that it can be non-destructive. XRF spectrometry measures the quantities of multiple rare and trace elements by exposing the sample's surface to a narrow beam of X-rays and measuring either the wavelength (WXRF) or energy (EDXRF) of the subsequent X-rays released by the bombarded sample (Jenkins, 1999). It is possible to conduct non-destructive XRF analysis on objects as long as they meet the following four criteria: (1) the internal composition of the object is homogenous, at least within the width of the X-ray beam; (2) the object's surface has not been weathered or modified in a way that significantly alters its chemical composition; (3) the artifact's physical surface is relatively smooth and flat; and (4) the sample is large enough to cover the beam (Davis et al., 1998; Giauque et al., 1993). On an archaeological time-scale, obsidian meets all of these criteria (Shackley, 2005).

2.1. The application of pXRF to archaeological obsidian studies

Within the last fifteen years, advances in XRF and microprocessor technology have made portable, handheld XRF (*p*XRF) analyzers commercially available. Using *p*XRF addresses current and long-standing limitations in archaeological provenance studies—namely the need to transport materials back to the lab (often crossing international borders) and the cost of analysis. To date, the only portable and non-destructive technique available is *p*XRF (but see Pappalardo et al., 2003 for efforts to develop portable PIXE). Standard *p*XRF equipment is small enough to fit in carry-on luggage. By bringing the tools to the artifacts and outcrops, *p*XRF represents a potential revolution in chemical composition analyses. The method has been effectively used to study obsidian in the Peruvian Andes (Craig et al., 2007, 2010), China (Jia et al., 2010), Russia (Phillips and Speakman, 2009), Oceania (Golitko et al., 2010; Sheppard et al., 2010), New Zealand (Sheppard et al., 2011), and the Maya lowlands (Meierhoff et al., 2010; Nazaroff et al., 2010). From a sampling standpoint, using *p*XRF means that more comprehensive and representative samples can be analyzed in a timely and inexpensive manner. Those artifacts that cannot be attributed to a known source by *p*XRF can then be analyzed by more sensitive methods.

Table 1
Time periods and primary obsidian sources in the Basin of Mexico.

Date AD	Phase	Xaltocan	Major (minor) obsidian sources
1521–1700	Early Colonial	Colonial	Pachuca (Otumba)
1430–1521	Late Postclassic	Phase 4	Pachuca (Otumba)
1300–1430	Middle Postclassic	Phase 3	Pachuca (Otumba)
1100–1300	Early-to-Middle Postclassic transition	Phase 2	Pachuca (Otumba)
900–1100	Early Postclassic	Phase 1	Pachuca (Otumba) (Ucareo-Zinapécuaro)
700–900	Epiclassic	Epiclassic	Oyameles-Zaragoza Ucareo-Zinapécuaro

3. The archaeological context

Visual and chemical characterization studies of obsidian in Postclassic and Colonial central Mexico have revealed a remarkable consistency among households in their reliance on obsidian from Pachuca and Otumba (Fig. 1) over all other available sources (Brumfiel, 1986; Elam et al., 2008; Glascock et al., 1999; Neff et al., 2001; Smith et al., 2007). During the Postclassic, obsidian entered the Basin of Mexico through both trade and tribute, but market exchange rather than elite redistribution was the primary mechanism for supply and distribution (Blanton, 1996; Charlton and Spence, 1982; Pastrana, 1998). The consistency of obsidian supply is even more remarkable when we consider the entire Basin of Mexico before, during, and after the Aztec empire, when consumers acquired obsidian through a mix of venues including regional and local markets, trips to workshops, and itinerant peddlers (Berdan et al., 2003; Hirth, 1998). Less formal economic activity is often difficult to identify archaeologically, but chemical characterization provides the most effective method for examining how smaller-scale and local patterns of trade fared under different political regimes.

Xaltocan provides a valuable opportunity for exploring such long-term change in obsidian consumption. Xaltocan is a small town located about 35 km north of Mexico City. What we know of the Postclassic and Colonial community there is based on over twenty years of surface collections, controlled excavations, and ethnohistoric research (Brumfiel, 2005a; Rodríguez-Alegría, 2009). Xaltocan was settled circa AD 900 on an island near the western shore of a saline lake of the same name. Brumfiel (2005b) has divided the pre-conquest occupation of Xaltocan into four phases roughly corresponding to the rise of Xaltocan as an independent polity (Phases 1, 2, and 3 – AD 900–1100, 1100–1300, and 1300–1430 respectively) and its eventual conquest and inclusion into the Aztec empire (Phase 4, AD 1430–1521) (Table 1). Despite the hardships of the Conquest and its aftermath, during the early Colonial Phase (AD 1521–1700) Xaltocan began to prosper again, with an economy based on hunting waterfowl, fishing, and the production of salt, soap, and reed mats (Gibson, 1964; Rodríguez-Alegría, 2008). Xaltocan remains a vibrant township today.

The obsidian collections from Xaltocan reveal a pattern of consistent local production of stone tools from the Early Postclassic through the Colonial period, punctuated by a significant decline in local production under Aztec control (Phase 4). By count and weight, obsidian represents 95% and 75% of the chipped stone artifacts found in excavations of pre-Hispanic and Colonial contexts (Millhauser, 2005; Rodríguez-Alegría, 2008). Green obsidian increased from 69%, by weight, of household obsidian in Phase 1 to 89% in Phase 3 and 95% in Phase 4 (Millhauser, 2005). During the

Table 2
*p*XRF sample tabulated by color and time period.

Phase	Green	Black	Gray	Red	Total
Colonial	26	3	24	–	53
Phase 4	5	1	4	–	10
Phase 3	7	2	4	1	14
Phase 2	7	–	4	–	11
Phase 1	9	2	3	1	15
Total	54	8	39	2	103

Table 3
Comparison of INAA and *p*XRF for SPHM and GBO standards. INAA results are reported from Glascock (1999). The INAA measurements of Fe, K, and Na were reported as wt.% oxides. The conversion factors to ppm are as follows: Fe_2O_3 to Fe using 6988; K20 to K using 8299; and Na_2O to Na using 7418.

Element (ppm)	SPHM		GBO	
	INAA ($n=5$)	*p*XRF ($n=$ l)	INAA ($n=5$)	*p*XRF ($n=1$)
Ag		47 ± 13		
Ba	30 ± 12	340 ± 66	1270 ± 20	776 ± 61
Ca		593 ± 130		5134 ± 138
Ce	92.0 ± 1.6		48.4 ± 1.0	
Cl	1460 ± 150		113 ± 29	
Co	054 ± 0.011	184 ± 47	0.39 ± 0.01	124 ± 26
Cr		43 ± 9		21 ± 7
Cs	3.92 ± 0.06		3.40 ± 0.05	
Cu		43 ± 10		39 ± 8
Dy	15.8 ± 0.8		3.6 ± 0.3	
Eu	1.59 ± 0.03		0.58 ± 0.01	
Fe	11,041 ± 139	15,375 ± 259	4333 ± 70	5408 ± 87
Hf	27.0 ± 0.4		3.67 ± 0.06	
K	31,370 ± 1992	33,376 ± 789	29,212 ± 1327	30,168 ± 656
La	38.6 ± 0.9		25.8 ± 0.4	
Lu	1.85 ± 0.04		0.44 ± 0.01	
Mn	1149 ± 20	991 ± 27	327 ± 6	277 ± 12
Mo		14 ± 4		
Na	28,188 ± 668		21,067 ± 445	
Nb		75 ± 3		6 ± 2
Nd	33.0 ± 2/4		18.7 ± 4.9	
Pb		39 ± 6		20 ± 5
Rb	192 ± 3	217 ± 6	95 ± 1	101 ± 4
Sb	0.264 ± 0.022		0.20 ± 0.01	
Sc	3.21 ± 0.04		2.81 ± 0.05	
Sm	9.90 ± 0.22		3.66 ± 0.05	
Sr			78 ± 20	73 ± 3
Ta	4.87 ± 0.07		0.66 ± 0.01	
Tb	2.25 ± 0.06		0.55 ± 0.03	
Th	17.9 ± 0.3		8.48 ± 0.13	
Ti		874 ± 81		572 ± 70
U	6.9 ± 2.1		4.1 ± 0.6	
V		297 ± 79		240 ± 70
Yb	12.3 ± 0.3		2.77 ± 0.10	
Zn	191 ± 12	212 ± 10	31 ± 7	32 ± 4
Zr	888 ± 40	965 ± 13	118 ± 7	91 ± 3

Table 4
Sensitivity and accuracy of *p*XRF measurements for those elements most consistently measured, based on instrumentally reported error ranges.

Element	Range of concentrations	*p*XRF no. observations	Average error in *p*XRF
K	27,850–65,890 ppm	125	2%
Fe	6380–18,370 ppm	125	2%
Ca	380–10,800 ppm	111	12%
Ti	280–1800 ppm	125	4%
Mn	140–1070 ppm	125	2%
Zr	100–1040 ppm	125	2%
Ba	150–800 ppm	80	18%
Rb	110–290 ppm	125	3%
Zn	20–260 ppm	125	9%
Nb	10–90 ppm	125	8%
Sr	7–190 ppm	59	6%

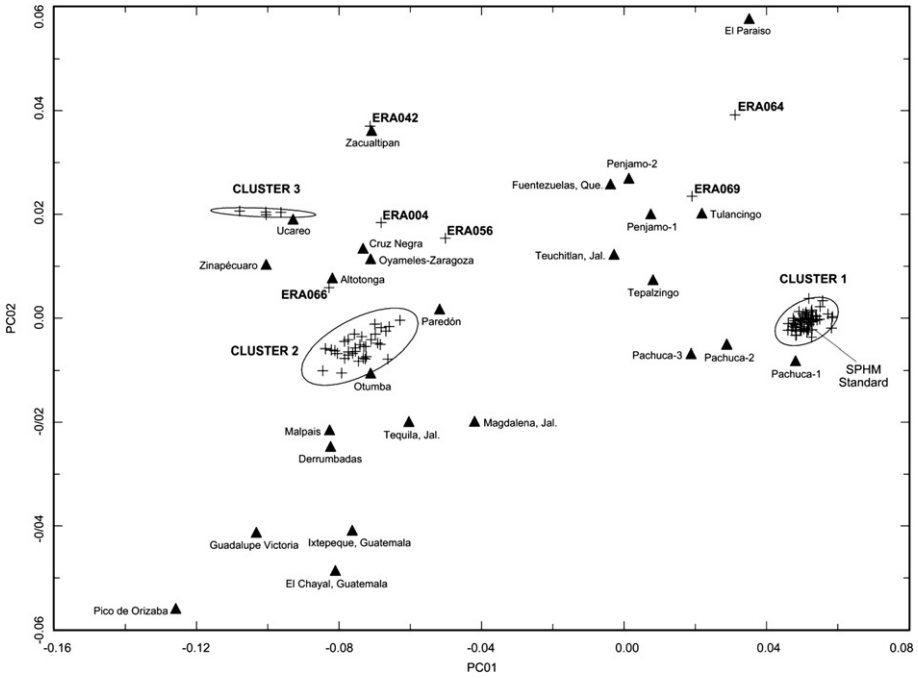

Fig. 2. Results of the principal components analysis of all 103 obsidian artifacts from Xaltocan, based on log10-transformed measurements (ppm) of Fe, Mn, Rb, Zn, and Zr. Ninety percent confidence ellipses are provided for the three clusters of artifacts. Sources are plotted based on averages reported in Cobean (2002) and Cobean et al. (1991). Artifacts are marked with a plus sign, sources are marked with triangles, and outliers are labeled.

Colonial period, green obsidian remained dominant, declining slightly to 90% of all obsidian artifacts (Rodríguez-Alegría and Obledo, 2009: Table 1). Chemical characterization allows us to answer persistent questions about the distribution and consumption of obsidian before, during, and after the Aztec empire. For example, was Otumba the only source of non-green obsidian used at Xaltocan? Did consumers have access to different sources of obsidian, and did this access change over time? On a regional scale, when we compare patterns of consumption at Xaltocan with its contemporaries, do we find the same kinds of small-scale sources or different patterns? More broadly, what do the locations of these sources suggest about local exchange networks that may have existed outside, or parallel to, the Aztec market system? Our results provide preliminary answers to these questions and confirm the validity of using *p*XRF as one part of a strategy to answer them.

4. Methodology

4.1. Sampling strategy

In selecting the sample of artifacts for chemical characterization, our primary goal was to identify the range of sources and subsources of obsidian used during all phases of occupation at Xaltocan. We selected samples of obsidian from Colonial ($n = 53$) and Postclassic ($n = 50$) contexts covering all phases of occupation as well as the range of visual variation. When possible, we selected artifacts from the early stages of production, such as prismatic cores, to better represent patterns of acquisition (Table 2). We must stress that this was not a random sample. Our goal was to identify the range of sources present in the collection rather than determine the frequency of these sources relative to one another. However, the presence and diversity of minor sources of obsidian still provides valuable information both for testing the accuracy of *p*XRF and our study of the site's local economy. Finally, in order to facilitate interlaboratory comparisons, we included two obsidian standards: SPHM (Sierra Pachuca, Hidalgo, Mexico) and GBO (Little Glass Buttes, Oregon) (Glascock, 1999) which are presented in Table 3.

4.2. pXRF analysis

We conducted the *p*XRF analysis with an Innov-X Alpha Series instrument at the Elemental Analysis Facility of the Field Museum of Natural History. The Alpha Series uses an X-ray tube with a tungsten anode as an excitation source and an Si PiN diode detector with an energy resolution of less than 230 eV FWHM at 5.95 keV Mn Kα line. We operated the device in soil mode using fundamental parameters and the Light Element Analysis Program (LEAP), which corresponds to a voltage of 40 kV and a current of 20 μA (following Williams et al., in press). We mounted it on an integrated stand that allows individual artifacts to be set above the detector in an optimal location and includes a safety lid to avoid the risk of exposure to X-rays. We ran the device remotely with a laptop using Innov-X software, but it can also be used with an integrated field computer and rechargeable batteries. The Innov-X software generates comma-delimited files that include metadata (reading time and mode) along with internally calculated error ranges. It has internal standards and requires no external calibration. While the device can potentially measure 32 elements, in this trial only 9 had a self-reported degree of accuracy greater than 90%: potassium (K), titanium (Ti), manganese (Mn), iron (Fe), zinc (Zn), gallium (Ga), rubidium (Rb), strontium (Sr), yttrium (Y), zirconium (Zr), and niobium (Nb) (Table 4).

All artifacts were cleaned using distilled water and acetone and read for 60 s for light elements and 60 s for heavy elements. We reran a random subset of 13 artifacts for 120 s to test whether additional time increased the accuracy or consistency of measurements. Following Davis et al. (1998) we addressed the effects of sample thickness, incomplete coverage of the detector, and surface irregularities or contamination. As we ran each analysis, we recorded the following additional information: percentage of the area of the

Table 5
Eigenvalues of the principal components analysis of the *p*XRF analysis. Simultaneous R-Q factor analysis based on variance–covariance matrix.

Eigenvalues and percentage of variance explained					
Eigenvalue	%Variance	Cumulative	%Var.		
1	0.4062	97.3994	97.3994		
2	0.0071	1.7104	99.1098		
3	0.0019	0.4494	99.5592		
4	0.0014	0.3356	99.8948		
5	0.0004	0.1052	100		
Eigenvectors (largest to smallest)					
Rb	0.1479	0.3153	0.8704	0.0857	−0.3373
Fe	0.2214	0.1329	−0.4232	0.4067	−0.7674
Mn	0.4017	−0.8619	0.2102	0.225	−0.0301
Zn	0.5958	0.0543	−0.1101	−0.7755	−0.169
Zr	0.6424	0.3702	−0.0839	0.4186	0.5176
Scaled factor loading matrix (largest to smallest component)					
Rb	0.0943	0.0266	0.0377	0.0032	−0.0071
Fe	0.1411	0.0112	−0.0183	0.0152	−0.0161
Mn	0.2561	−0.0728	0.0091	0.0084	−0.0006
Zn	0.3797	0.0046	−0.0048	−0.029	−0.0035
Zr	0.4095	0.0313	−0.0036	0.0157	0.0108

detector covered by the artifact (estimated to the nearest 10% with most covering 85% to 100% and a minimum of 33%), the presence of surface residues or encrustations, the roughness of the surface, and the shape of the surface (convex, concave, or flat). We were careful to cover as much of the detector as possible with the cleanest, flattest surface. In three cases with pronounced curvature and four cases with surface residues or encrustations, we ran multiple assays, switching between dorsal and ventral surfaces or covering multiple locations along the sample. Using this technique, we were able to take 151 measurements on the 103 archaeological samples and two standards in a single 8-h day.

4.3. *l*XRF and INAA

Non-destructive elemental analysis of obsidian artifacts was performed using an ElvaX desktop EDXRF spectrometer, following procedures described by Blomster and Glascock (2011: 25–26) and Knight et al. (2011: 1076). The analysis permitted quantification of eleven elements: the same nine as the *p*XRF with the addition of gallium (Ga) and yttrium (Y). In two cases (samples ERA056 and ERA066), it was not possible to assign a source based on the *l*XRF data alone. Both samples subsequently underwent the standard procedure for abbreviated INAA described by Glascock (2002).

4.4. Data analysis

All statistical analysis was conducted using GAUSS Runtime following procedures described by Glascock (2002).[1] For the samples analyzed at MURR, sources were determined by comparison with their database of Mesoamerican obsidian sources using RQ-Mode principal components analysis (PCA). For the *p*XRF data, we compared the artifacts to published summaries of INAA measurements of source materials (Cobean, 2002; Cobean et al., 1991) using the multivariate techniques of PCA as well as Euclidean-distance hierarchical clustering analysis (HCA) of log10-transformed data to identify the most likely source of each artifact. The only elements that overlapped between INAA and *p*XRF were K, Mn, Fe, Zn, Rb, Sr, and Zr. We excluded K based on Glascock's (2002) assessment of its poor accuracy. We also removed Sr because it fell below the level of detection in 57 artifacts measured by *p*XRF. We maintain that Sr is a significant marker of sources, however, because very low levels of Sr are characteristic of certain sources of obsidian (Altotonga, Paredón, Pachuca, Tulancingo, Zinapécuaro, El Paraiso, and Pénjamo) and can therefore serve to clarify ambiguous source determinations.

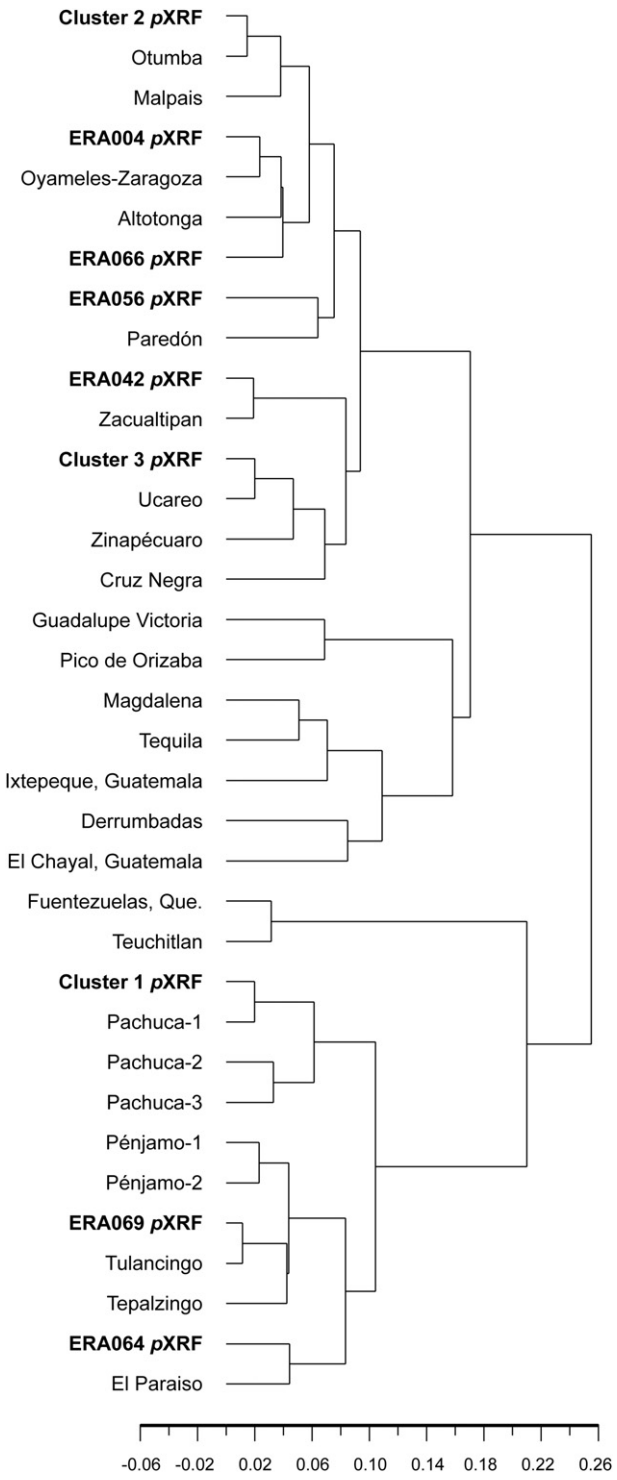

Fig. 3. Results of the Euclidean-distance hierarchical clustering analysis of groups of artifacts identified with principal components analysis, outlying artifacts, and obsidian sources based on averages reported in Cobean (2002) and Cobean et al. (1991). Variables included log10-transformed measurements (ppm) of Fe, Mn, Rb, Zn, and Zr.

[1] GAUSS Runtime is available for free at http://archaeometry.missouri.edu/datasets/distribution/GAUSS_Download.html.

Table 6
Results of the *p*XRF for the archaeological sample. All elements are measured in ppm. Values for artifacts measured more than once are averages that exclude poor readings from concave surfaces or surfaces with heavy residues. The "blade production" category includes plunging blades, crested blades, and platform preparation flakes.

Sample	Color	Type	Phase	Final source	Fe	Mn	Nb	Rb	Sr	Zn	Zr
ERA001	Black (red)	Blade	Colonial	Pachuca-1	14,919	957	80	215	–	230	982
ERA002	Gray	Blade	Colonial	Otumba	7896	357	16	132	143	39	139
ERA003	Black (red)	Blade production	Colonial	Pachuca-1	15,222	995	80	215	–	219	965
ERA004	Gray	Blade	Colonial	Oyameles-Zaragoza	8500	227	23	154	35	37	212
ERA005	Gray	Flake	Colonial	Otumba	7708	326	18	146	152	53	154
ERA006	Gray	Blade	Colonial	Otumba	7741	321	16	125	136	34	143
ERA007	Gray	Bifacial tool	Colonial	Otumba	7480	313	10	116	125	35	127
ERA008	Green	Prismatic core	Colonial	Pachuca-1	14,812	971	75	210	9	221	949
ERA009	Gray	Blade	Colonial	Ucareo	6510	158	14	152	15	33	117
ERA010	Gray	Chunk	Colonial	Otumba	8347	341	13	125	143	38	145
ERA011	Gray	Blade	Colonial	Otumba	8393	332	11	131	148	42	140
ERA012	Green	Blade	Colonial	Pachuca-1	15,376	1022	77	207	–	212	936
ERA013	Green	Blade	Colonial	Pachuca-1	15,489	1030	81	221	–	217	988
ERA014	Gray	Blade	Colonial	Otumba	7976	337	12	129	134	35	133
ERA015	Green	Blade production	Colonial	Pachuca-1	15,202	977	78	217	–	220	998
ERA016	Green	Blade	Colonial	Pachuca-1	14,381	928	75	198	–	216	906
ERA017	Green	Blade production	Colonial	Pachuca-1	15,624	985	83	211	7	238	962
ERA018	Green	Blade	Colonial	Pachuca-1	15,389	1003	80	218	–	228	995
ERAO19	Green	Blade	Colonial	Pachuca-1	14,776	951	70	199	–	213	895
ERA020	Gray	Bifacial tool	Colonial	Otumba	8308	328	14	130	148	37	145
ERA02I	Green	Prismatic core	Colonial	Pachuca-1	15,251	977	78	200	–	205	923
ERA022	Gray	Blade	Colonial	Otumba	7774	318	12	120	137	32	129
ERA023	Gray	Blade	Colonial	Otumba	7913	336	14	119	132	35	131
ERA024	Gray	Flake	Colonial	Otumba	8393	331	8	119	133	37	128
ERA025	Gray	Blade	Colonial	Otumba	8182	350	9	117	137	27	129
ERA026	Gray	Flake	Colonial	Otumba	8119	346	12	122	137	40	129
ERA027	Gray	Blade	Colonial	Otumba	8094	318	17	129	148	36	142
ERA028	Gray	Blade	Colonial	Otumba	7655	329	14	129	141	40	136
ERA029	Green	Blade	Colonial	Pachuca-1	15,561	1013	77	216	–	234	969
ERA030	Green	Blade	Colonial	Pachuca-1	15,406	995	80	207	–	213	952
ERA03I	Green	Blade	Colonial	Pachuca-1	15,110	977	76	201	–	214	951
ERA032	Green	Blade	Colonial	Pachuca-1	15,135	982	79	201	–	235	945
ERA033	Green	Bezote	Colonial	Pachuca-1	15,236	980	81	211	–	214	984
ERA034	Green	Unifacial tool	Colonial	Pachuca-3	15,609	1004	73	195	7	202	925
ERA035	Black (red)	Prismatic core	Colonial	Pachuca-1	15,257	986	76	199	–	205	915
ERA036	Green	Blade	Colonial	Pachuca-1	15,634	958	76	210	–	213	953
ERA037	Gray	Flake	Colonial	Otumba	7S81	366	18	140	133	38	137
ERA038	Green	Blade	Colonial	Pachuca-1	14,992	978	73	195	–	198	938
ERA039	Green	Blade production	Colonial	Pachuca-1	15,433	1002	80	213	–	219	981
ERA040	Green	Blade production	Colonial	Pachuca-1	15,791	1029	73	201	–	217	954
ERA041	Green	Blade	Colonial	Pachuca-1	15,689	1026	83	221	–	232	987
ERA042	Gray	Chunk	Colonial	Zacualtipan	9525	172	17	281	39	33	210
ERA043	Green	Blade	Colonial	Pachuca-1	15,269	979	75	209	–	208	938
ERA044	Green	Flake	Colonial	Pachuca-1	16,054	1063	76	201	–	224	931
ERA045	Gray	Flake	Colonial	Otumba	8101	320	18	128	148	49	152
ERA046	Gray	Chunk	Colonial	Otumba	7974	329	10	119	127	39	130
ERA047	Gray	Flake	Colonial	Otumba	8347	341	20	145	164	39	160
ERA048	Gray	Flake	Colonial	Otumba	8349	341	19	142	157	43	154
ERA049	Gray	Blade	Colonial	Ucareo	6609	158	17	159	13	28	115
ERA050	Green	Blade	Colonial	Pachuca-1	15,992	999	75	209	–	193	937
ERA051	Green	Blade	Colonial	Pachuca-1	15,034	993	82	217	–	219	970
ERA052	Green	Blade	Colonial	Pachuca-1	14,764	913	84	216	14	222	1017
ERA053	Green	Blade	Colonial	Pachuca-1	15,275	967	79	212	–	214	971
ERA054	Green	Blade production	Phase 4	Pachuca-1	14,826	944	77	205	–	225	967
ERA055	Green	Blade production	Phase 4	Pachuca-1	15,470	1003	77	200	–	207	951
ERA056	Gray	Bifacial tool	Phase 4	Unknown	14,564	276	14	130	185	46	255
ERA057	Gray	Blade	Phase 4	Otumba	7724	313	17	138	156	45	144
ERA058	Gray	Flake	Phase 4	Otumba	7895	326	11	121	141	39	134
ERA059	Green	Prismatic core	Phase 4	Pachuca-1	15,642	1005	75	202	–	221	962
ERA060	Green	Prismatic core	Phase 4	Pachuca-1	15,314	955	73	191	–	192	932
ERA061	Green	Blade	Phase 4	Pachuca-1	15,018	957	79	198	–	204	936
ERA062	Black (red)	Blade	Phase 4	Pachuca-1	15,750	1028	76	197	–	216	948
ERA063	Gray	Blade	Phase 4	Otumba	8711	354	18	135	146	41	148
ERA064	Green	Biface	Phase 1	Unknown	18,201	350	69	211	–	179	995
ERA065	Red	Bifacial tool	Phase 1	Otumba	7312	327	14	125	131	34	129
ERA066	Red	Bifacial tool	Phase 3	S. Juan de los Arcos	7423	247	16	112	59	29	167
ERA067	Black (red)	Macroblade	Phase 1	Pachuca-1	15,422	1002	76	188	–	210	903
ERA068	Gray	Flake	Phase 3	Otumba	7762	349	15	139	151	42	147
ERA069	Black (red)	Blade	Phase 1	Tulancingo	17,303	379	38	127	14	179	699
ERA070	Gray	Flake	Phase 3	Otumba	8029	309	9	113	131	31	128
ERA071	Green	Blade	Phase 3	Pachuca-1	14,876	1006	85	225	–	260	993
ERA072	Black (red)	Blade	Phase 3	Pachuca-1	15,489	1006	76	212	–	222	977
ERA073	Green	Blade	Phase 3	Pachuca-1	15,528	1027	75	205	–	222	933

Table 6 (*continued*)

Sample	Color	Type	Phase	Final source	Fe	Mn	Nb	Rb	Sr	Zn	Zr
ERA074	Green	Blade	Phase 3	Pachuca-1	15,566	1023	73	195	–	199	921
ERA075	Green	Blade production	Phase 3	Pachuca-1	15,640	1016	72	200	–	210	926
ERA076	Black (red)	Blade	Phase 3	Pachuca-1	15,226	1003	74	199	–	190	937
ERA077	Green	Blade	Phase 3	Pachuca-1	15,613	991	80	212	–	200	968
ERA078	Gray	Blade	Phase 3	Ucareo	6382	149	14	156	16	24	107
ERA079	Gray	Blade	Phase 3	Otumba	7920	329	15	120	141	41	139
ERA080	Green	Prismatic core	Phase 3	Pachuca-1	15,412	1006	73	205	–	208	892
ERA081	Green	Prismatic core	Phase 3	Pachuca-1	15,369	1001	75	197	–	212	925
ERA082	Green	Blade production	Phase 2	Pachuca-1	14,675	966	71	189	–	202	895
ERA083	Gray	Blade	Phase 2	Otumba	8471	341	14	127	140	36	136
ERA084	Green	Prismatic core	Phase 2	Pachuca-1	15,626	1033	74	205	–	228	943
ERA085	Green	Blade	Phase 2	Pachuca-1	16,258	1049	84	231	–	251	1009
ERA086	Green	Prismatic core	Phase 2	Pachuca-1	15,836	1026	78	208	–	217	936
ERA087	Green	Blade	Phase 2	Pachuca-1	15,543	995	80	205	–	230	953
ERA088	Gray	Blade	Phase 2	Otumba	8014	355	16	127	140	38	139
ERA089	Gray	Flake	Phase 2	Otumba	8467	361	11	118	134	32	129
ERA090	Gray	Flake	Phase 2	Otumba	8642	373	12	133	141	46	140
ERA091	Green	Blade	Phase 2	Pachuca-1	15,519	989	79	214	–	225	981
ERA092	Green	Prismatic core	Phase 2	Pachuca-1	14,546	919	76	201	–	220	944
ERA093	Green	Prismatic core	Phase 1	Pachuca-1	15,539	1010	79	214	–	220	978
ERA094	Green	Prismatic core	Phase 1	Pachuca-1	15,720	1065	86	210	–	259	994
ERA095	Gray	Blade	Phase 1	Ucareo	6507	150	13	139	15	32	109
ERA096	Green	Blade	Phase 1	Pachuca-1	14,875	991	82	211	–	201	980
ERA097	Green	Blade production	Phase 1	Pachuca-1	15,059	959	91	228	–	239	1041
ERA098	Green	Prismatic core	Phase 1	Pachuca-1	15,578	999	79	213	–	216	965
ERA099	Green	Blade	Phase 1	Pachuca-1	15,096	993	84	213	–	214	969
ERA 100	Green	Blade	Phase 1	Pachuca-1	14,996	960	80	217	–	243	1011
ERA101	Green	Blade	Phase 1	Pachuca-1	15,503	1027	79	216	–	260	1016
ERA 102	Gray	Flake	Phase 1	Otumba	7846	325	14	142	144	47	134
ERA 103	Gray	Flake	Phase 1	Otumba	7569	316	10	128	128	36	132

5. Results

5.1. pXRF source attribution

By comparing our *p*XRF data with published measurements of obsidian sources, we were able to attribute sources in 98% of the cases, or for 101 of the 103 artifacts. The PCA differentiated three clusters of artifacts and six outliers (Fig. 2). The first two principal components explained 99% of the variation in the archaeological sample (Table 5). Plotting known sources of obsidian on the first two principal components, we made the following preliminary links between artifacts and sources: Cluster 1 with Pachuca-1, Cluster 2 with Otumba or Paredón, Cluster 3 with Ucareo, ERA042 with Zacualtipan, ERA066 with Altotonga, ERA069 with Tulancingo or Pénjamo-1, and ERA004 with Cruz Negra or Oyameles-Zaragoza. We confirmed the link to Pachuca-1 by plotting our reading of the SPHM standard, which fell squarely within Cluster 1. The level of Sr in our samples supported the links to Pachuca-1, Ucareo, and Zacualtipan; distinguished Otumba over Paredón as the source of Cluster 2; and ruled out Cruz Negra as the source of ERA004 and Altotonga as the source of ERA066. The HCA – which was based on source averages, cluster averages, and individual outliers – provided additional confirmation as well as clarification of the outliers (Fig. 3). For the outliers, the best links were between ERA004 and Oyameles-Zaragoza, ERA042 and Zacualtipan, ERA064 and El Paraiso, and ERA069 and Tulancingo. No clear associations could be drawn for ERA056 or ERA066 based on the *p*XRF data. Our final selection of sources was based on comparing the results of *all* techniques and is presented, along with our measurements, in Table 6.

5.2. Comparison of source attributions based on pXRF and lXRF/INAA

The fit between the sources identified by *p*XRF, *l*XRF, and INAA was remarkable—our source attributions matched in 97% of the cases (100 out of 103). At MURR we were able to attribute sources to 101 of the 103 artifacts by using *l*XRF and comparing the results to MURR's source database. Using INAA, we were able to link one of the two remaining outliers, ERA066, to the San Juan de los Arcos source in Jalisco. The second outlier, ERA056, could not be attributed to any source in MURR's database. When comparing the *p*XRF and *l*XRF/INAA results, there were only three mismatches. The first, ERA034, was identified as Pachuca-1 by *p*XRF and Pachuca-3 by *l*XRF. The fine-grained differences used to distinguish the three Pachuca sub-sources fell outside the sensitivity of the *p*XRF instrument. In this case, we followed MURR's attribution of Pachuca-3. The second mismatch, ERA064, was tentatively identified as El Paraiso by the *p*XRF analysis (see Fig. 3, HCA results) and Pachuca-1 by *l*XRF. The Pachuca attribution is surprising because the levels of Fe and Mn for sample ERA064 fell well below the published range of variation for this source. Here, we take a conservative approach and call this an outlier without assigning a source. The final mismatch, ERA066, was unidentifiable with *p*XRF and *l*XRF and only attributable to the San Juan de los Arcos source through INAA. We follow MURR's attribution in this case.

6. Discussion

6.1. Explaining the variation between pXRF and lXRF measurements of individual elements

How is it that, given the absolute differences between the amounts of individual elements measured by *p*XRF and the published source data against which we compared this data (Table 3), we were still able to accurately attribute sources to artifacts in 97% of the cases? The simplest explanation is that observed inter-method variation (the difference in the amounts of elements *measured* for individual sources or artifacts using different techniques) was less than inter-source variation (the difference between the amounts of elements present in different geological sources). By combining the

multivariate techniques described above (PCA and HCA), we were able to distinguish among all of the potential sources based on a limited set of consistently measured elements. Only in the cases of the sub-sources of Pachuca was the inter-method variation greater than the inter-source variation, which precluded our identification of sub-sources based on our *p*XRF measurements.

Measurements for K were excluded because they were not normally distributed. We limit the following discussion of inter-method discrepancies to artifacts from Pachuca and Otumba because they represent the largest groups in the sample (33 from Otumba and 59 from Pachuca, which represent 89% of the sample). Comparing inter-method variability across all 103 samples at once is not feasible because of the bimodal distribution of measurements, for which the best solution is to split known groups apart for more detailed investigation (Drennan, 2004: 218).

In comparing our *p*XRF and *l*XRF results, we have two primary questions: 1) are the differences the result of random chance and, 2) if not, are there regular and easily correctable patterns in the differences? To answer these questions, we compared the element-by-element results of the *p*XRF and *l*XRF using paired *t*-test and least-squares regression analysis. Although our data were not all normally distributed, given that each of our sample groups had more than 30 members a *t*-test was still applicable (Drennan, 2004: 161). The paired *t*-test indicated non-random differences ($p < .05$) for Fe, Mn, Nb, and Rb in the Otumba sample and for Fe, Nb, Rb, Zn, and Zr in the Pachuca sample (Table 7). In the cases of Sr, Zn, and Zr in the Otumba sample and Mn in the Pachuca sample, the differences are small enough that they are likely to be the result of random chance ($p > .1$). The answer to our first question appears to be inconsistent—for some elements our use of different methods created no appreciable discrepancies while for others the discrepancies were noteworthy. While a *t*-test can identify significant differences between sample means (i.e. whether or not the difference is the result of random chance), it cannot identify the cause of non-random differences.

A least-squares regression analysis of Fe, Mn, Nb, Rb, K, Sr, Zn, and Zr for the groups of artifacts from Otumba and Pachuca showed that the only strong and significant correlations ($r > 0.5$, $p < .001$) were for the elements Rb, K, Sr, and Zr among the Otumba artifacts and only K among the Pachuca artifacts (Table 8). For all other elements there were weakly positive correlations, with the exception of Mn, which was weakly negative. The inconsistency of these results suggests that there was no uniform pattern of over- or under-reading of elements in our *p*XRF methodology.

Table 7
Results of paired *t*-tests of normally distributed measurements of elements from the Otumba and Pachuca sources. Note that Zn for Otumba excludes one outlier reading for ERA047.

Element	*p*XRF		*l*XRF		*t*	Significance
	$\bar{x}$	S.D.	$\bar{x}$	S.D.		
Otumba ($n = 33$, d.f. $= 32$)						
Fe	8030.1	336.4	8723.3	815.2	−5.096	$.001 > p$
K	33,428.9	7755.6	36,378.2	7151.5	−4.794	$.001 > p$
Mn	335.1	16.3	224.9	36.9	14.736	$.001 > p$
Nb	13.8	3.3	12.7	1.7	2.068	$.05 > p$
Rb	128.1	8.9	121.3	9.0	5.004	$.001 > p$
Sr	140.8	9.1	138.2	12.8	1.489	$.2 > p > .1$
Zn*	38.6	5.5	37.1	8.6	0.987	$.5 > p > .2$
Zr	138.2	8.9	140.9	12.7	−1.665	$.2 > p > .1$
Pachuca ($n = 59$, d.f. $= 58$)						
Fe	15,332.212	374.412	15,909.64	1013.609	−4.227	$.001 > p$
K	37,001.4	7393.3	36,949.2	6995.1	0.130	$p > .5$
Mn	993.017	31.834	1006.587	101.816	−1.006	$.5 > p > .2$
Nb	77.924	4.008	89.342	4.625	−14.753	$.001 > p$
Rb	207.682	9.283	192.307	10.599	9.506	$.001 > p$
Sr	–	–	–	–	–	–
Zn	218.864	15.585	197.022	45.981	3.567	$.001 > p$
Zr	957.212	32.557	902.026	81.372	5.022	$.001 > p$

Table 8
Results of the least-squares regression analysis of artifacts from the Otumba and Pachuca sources. $X = l$XRF measurements. $Y = p$XRF measurements.

Element	*a*	*b*	r^2	*r*	*F*	*p*	*p* range
Otumba ($n = 33$, d.f. $= 31$)							
Fe	6934.324	0.126	0.093	0.304	3.17	0.085	$.1 > p > .05$
K	−1709.955	0.966	0.793	0.891	118.99	0.000	$.001 > p$
Mn	352.709	−0.078	0.031	−0.177	1.01	0.324	$.5 > p > .2$
Nb	3.997	0.771	0.164	0.404	6.06	0.020	$.05 > p$
Rb	54.689	0.606	0.374	0.611	18.50	0.000	$.001 > p$
Sr	79.106	0.446	0.394	0.628	20.18	0.000	$.001 > p$
Zn	33.856	0.123	0.073	0.270	2.44	0.128	$.2 > p > .1$
Zr	72.264	0.468	0.449	0.670	25.31	0.000	$.001 > p$
Pachuca ($n = 59$, d.f. $= 57$)							
Fe	14,816.187	0.032	0.008	0.088	0.44	0.508	$p > .5$
K	1474.157	0.962	0.828	0.910	273.63	0.000	$.001 > p$
Mn	962.203	0.031	0.010	0.098	0.55	0.461	$.5 > p > .2$
Nb	73.508	0.049	0.003	0.057	0.19	0.668	$p > .5$
Rb	169.869	0.197	0.050	0.225	3.03	0.087	$.1 > p > .05$
Sr	–	–	–	–	–	–	–
Zn	212.103	0.034	0.010	0.101	0.59	0.445	$.5 > p > .2$
Zr	919.373	0.042	0.011	0.105	0.63	0.429	$.5 > p > .2$

An element-by-element comparison of our *l*XRF and *p*XRF results for the Pachuca and Otumba groups showed inconsistent results—some differences were significant but these were not the same for each group. In a similar inter-laboratory comparison, Craig et al. (2007) found that a similar element-by-element inconsistency did not interfere with their ability to accurately identify sources. While it is worthwhile to identify sources of inter-method variation, we reiterate that *p*XRF need only be accurate enough to accurately identify sources in order for it to be useful in archaeological provenance studies. Potential causes for the observed inter-method variation could be broadly instrumental (the sacrifice of precision for portability in the Innov-X alpha series, differences in excitation source), narrowly instrumental (the particular instrument we used may have been poorly calibrated), or methodological (differences in sample preparation, proximity to the detector, or the selection of reading surface between laboratories). The first two cases are beyond the scope of this study to assess, as they would involve conducting further readings using additional devices. We consider the third potential source of difference, the extent to which possible laboratory-based sources of error could have influenced our readings, in the following section.

6.2. Factors influencing accurate and consistent pXRF readings

Doubling the length of the reading for both light and heavy elements to 120 s allowed us to consistently measure four more elements than did the shorter read time: barium (Ba), calcium (Ca), chromium (Cr), and lead (Pb). We also noted a small but consistent improvement in the instrumentally reported accuracy of measurements for all elements but Ca (Table 9). However, given our successful identification of sources using the 60-s data, we do not deem these improvements significant enough to recommend using the longer read time except for ambiguous cases.

The presence of a residue on artifact surfaces did not adversely affect our ability to attribute sources to artifacts. Of the eight artifacts with residues that resisted our efforts at cleaning, only four had fresh breaks or clean areas that could be used as a basis for comparison (ERA001, ERA056, ERA069, and ERA099). For each artifact, we compared the range measured for each element (the measured value +/− the instrumentally reported error) on the different surfaces.

Table 9
Comparison of the sensitivity and accuracy of *p*XRF based on read time. Artifacts were not moved between readings, so all variation is instrumental.

Element	60-s runs		120-s runs		Improvement
	Number	Average error	Number	Average error	
Fe	125	1.7%	13	1.2%	0.5%
K	125	2.3%	13	1.6%	0.7%
Mn	125	3.6%	13	3.1%	0.6%
Nb	125	8.4%	13	6.7%	1.7%
Rb	125	3.2%	13	2.3%	0.9%
Ti	125	9.1%	13	7.3%	1.8%
Zn	125	8.5%	13	7.5%	1.0%
Zr	125	1.9%	13	1.6%	0.3%

We interpreted overlapping ranges as evidence that any error caused by surface residue was less than the standard instrumental error and the natural range of variation combined. We found higher than expected amounts of K, Nb, and Zn associated with residues in one out of four cases, and higher than expected amounts of Ca and Zr in two out of four cases, otherwise all other elements used in source attribution (Fe, Mn, Rb, and Sr) were unaffected (Table 10). Thus it is still best practice to use the cleanest surface possible.

In terms of the effects of incomplete coverage of the detector, we found that, as long as an artifact was flat, we could accurately measure samples that covered as little as 33% of the detector. If an artifact was not flat, our readings were more accurate for the convex side, which allowed placement closer to the detector. In the three prismatic blades we tested (ERA026, ERA029, and ERA031), we found that readings on the ventral (concave) side of the blade were lower than expected for the elements K, Ca, Fe, Zn, and Zr in all cases and for Ti, Rb, Sr, and Nb in some cases (Table 11). The best practice is to maximize coverage of and proximity to the detector, with proximity taking priority.

6.3. Associations between color and source

With the exception of obsidian from Pachuca, the colors of obsidian artifacts matched our expectations for each source. We found that one particular kind of obsidian (glassy and almost opaque black with reddish-brown edges when backlit) was associated with Pachuca in seven out of eight cases. The eighth artifact came from Tulancingo. Based on studies of the geological sources, we know that Pachuca produces small quantities of brown and gray obsidian (Charlton and Spence, 1982: 20; Pastrana, 1998: 87–88), but this is rarely reported in archaeological contexts. One piece of gray obsidian from Pachuca has been reported at Tikal (Moholy-Nagy et al., 1984) and two have been reported at Yautepec (Smith et al., 2007). Because obsidian from Pachuca is so commonly identified with green obsidian, in many studies a simple division between green and non-green obsidian serves as a proxy for the prevalence of pachuca relative to other sources. Our findings suggest that this division under-represents the frequency and variety of obsidian from Pachuca found in archaeological collections.

Table 10
Comparison of *p*XRF measurements of surfaces with and without residues on four artifacts (ERA001, ERA056, ERA069, and ERA099). Overlap was determined by using the instrumentally reported measurement error for each reading.

Element	Number of cases	
	Measurements on residues overlap with clean surfaces	Measurements on residues are higher than clean surfaces
K	3	1
Ca	2	2
Ti	4	
Mn	4	
Fe	4	
Zn	3	1
Rb	4	
Sr	4	
Zr	2	2
Nb	3	1

Table 11
Comparison of *p*XRF measurements of convex and concave blade surfaces for three artifacts (ERA026, ERA029, and ERA031).

Element	Number of cases	
	Measurements are the same on convex and concave side	Measurements are lower on concave side
K		3
Ca		3
Ti	1	2
Mn	3	
Fe		3
Zn		3
Rb	2	1
Sr	2	1
Zr		3
Nb	2	1

6.4. Archaeological interpretation

We identified seven obsidian sources in a sample of 103 artifacts from Xaltocan (Table 12). Our archaeological interpretations are based on the presence and absence of different sources in different phases of occupation rather than relative frequencies, as our sample was non-random. Our analysis of artifacts from Pachuca suggests remarkable stability in the extraction and distribution of obsidian over the span of 800 years. Pachuca-1 was the only subsource in the entire Postclassic sample. We identified one piece of obsidian from Pachuca-3 in the Colonial sample: a scraper on a macroblade that was indistinguishable in form or color from any of the other Pachuca materials. The significance of the exclusivity of Pachuca in Postclassic central Mexico has been hotly debated, especially in terms of whether it reflects state-sponsored control (Spence and Parsons, 1972; Pastrana and Dominguez, 2009) or less centrally organized commercial enterprises (Clark, 1986). While our findings do not resolve the debate, they suggest that if states did control sources or markets, they did so by exploiting and intensifying traditions of mining and networks of supply that had already existed for centuries.

The presence of non-green obsidian from Otumba and Ucareo is not surprising when compared to other contemporary sites. Otumba, located 44 km east of Xaltocan, was the closest source to consumers in the Basin of Mexico and was a center of obsidian tool and lapidary production (Otis Charlton, 1993; Parry, 2001). Ucareo, along with the nearby source of Zinapécuaro, is located in northern Michoacan about 170 km west of Xaltocan (Healan, 1997). It was a major source of obsidian at Early Postclassic Tula (Healan, 1993) and the primary source in the Late Postclassic Tarascan empire (Pollard, 2003; Pollard and Vogel, 1994). In central Mexico, small quantities of obsidian from Ucareo and Zinapécuaro obsidian have been identified in Early Postclassic Chalco (Elam et al., 2008), Xico (Brumfiel, 1986), and Yautepec (Smith et al., 2007).

Only a single artifact each from the sources of Tulancingo, San Juan de los Arcos, Zacualtipan, and Oyameles-Zaragoza were found in the Xaltocan sample. While limited in explanatory power, they may direct our attention to less formal or extensive supply systems. Tulancingo is located 75 km northeast of Xaltocan, near the Pachuca source, although it was of negligible commercial importance outside of its immediate area (Gaxiola and Guevara, 1989;

Table 12
Results of *p*XRF tabulated by color and time period.

Phase	Pachuca-1		Pachuca-3	Otumba		Tulancingo	Ucareo	Zacualtipan	San Juan de los Arcos	Oyameles-Zaragoza	Unknown		Total
	Green	Black	Green	Gray	Red	Black	Gray	Gray	Red	Gray	Gray	Green	
Colonial	25	3	1	20			2	1		1			53
Phase 4	5	1		3							1		10
Phase 3	7	2		3			1		1				14
Phase 2	7			4									11
Phase 1	8	1		2	1	1	1					1	15
Total	52	7	1	32	1	1	4	1	1	1	1	1	103

Charlton and Spence, 1982). In Early Postclassic collections, small amounts of Tulancingo have been found at Otumba (Neff et al., 2001), but none has been identified at Tula, the largest northern center of the time (Healan, 1993; Hester et al., 1973). The single artifact from San Juan de los Arcos found in the Phase 3 sample is unique. This source is located in central Jalisco near the Tequila Volcano, over 500 km west of Xaltocan. During Phase 3, Xaltocan was the capital of a significant polity and may have served as a center for the movement of goods into and throughout the region. Postclassic trade between central and west Mexico more commonly involved copper (Hosler, 2003), but a small amount of obsidian may have also found its way east.

The artifacts from Zacualtipan and Oyameles-Zaragoza date to the Colonial period. Zacualtipan, located over 100 km northeast of Xaltocan, was of little economic importance outside of its immediate vicinity (Braswell, 2003; Charlton and Spence, 1982). Zacualtipan has not, to our knowledge, been found at other Postclassic sites in Central Mexico. Oyameles-Zaragoza consists of two chemically indistinguishable sources located in northeastern Puebla, 150 km east of Xaltocan (Cobean, 2002: 169). In the Postclassic, Oyameles-Zaragoza may have been a primary source of obsidian in Cholula (Hester et al., 1972). Small quantities have been identified at Xico in the Early Postclassic (Brumfiel, 1986), Chalco in the Early and Late Postclassic (Elam et al., 2008), and Yautepec in the Early and Late Postclassic and Colonial period (Smith et al., 2007).

The timing and variety of sources found at Xaltocan fit the patterns of contemporary sites in and around the Basin of Mexico. These patterns involve an emphasis on sources located to the north and west of the Valley of Mexico (Pachuca, Otumba, Ucareo, San Juan de los Arcos, Zacualtipan, and Tulancingo) and contrast with a shift in decorated ceramic consumption at Xaltocan, beginning in the Early Postclassic, to exchange spheres connected to the southern basin of Mexico and Puebla-Tlaxcala Valley to the east (Brumfiel, 2005c; Nichols et al., 2002). Such a pattern has been confirmed through provenance studies of ceramics and obsidian from sites across the Valley of Mexico (Crider et al., 2007; Hodge and Neff, 2005; Minc et al., 1994; Neff et al., 2001; Nichols et al., 2002, 2009; Smith, 1990: 162–3). Despite these broad trends, sources found at other sites are noticeably absent from our sample. These sources include: El Paraíso, Fuentezuelas, Paredón, Pico de Orizaba, Tepalzingo, and Malpais (Brumfiel, 1986; Glascock et al., 1999; Neff et al., 2001; Smith et al., 2007). Both the spatial and temporal variation of these minor sources suggest that smaller-scale supply systems were both local and resilient.

Perhaps the most surprising outcome of our study is the great diversity of sources present in the Colonial sample. Obsidian arrived from typical sources (Pachuca and Otumba) as well as sources to the east and west previously blocked by political barriers (Ucareo and Oyameles-Zaragoza) and a single source to the north (Zacualtipan). Even obsidian from Pachuca shows greater than expected diversity, with the presence of one artifact from the Pachuca-3 sub-source. The Colonial period was a time of new demands and hardship for many indigenous communities, but it also brought new commercial opportunities as well as new technologies of production and transportation (Gibson, 1964; Hassig, 1985) and the reshaping of previous political and social boundaries to commerce. Our findings suggest that during the Colonial period, merchants, miners, and craftspeople continued to make, move, and consume a wide range of obsidian.

7. Conclusions

Our results demonstrate that *p*XRF is accurate enough to identify the major and minor sources of obsidian used in central Mexico and provide consistent data for the examination of archaeological questions. Our method involved using the cleanest and flattest portion of each artifact and comparing the results of multivariate statistical analyses to confirm strong associations and identify weaker links that required further investigation. While we were able to accurately identify sources by comparison with previously published data, we maintain that the first step in using new instrumentation should involve a careful comparison with established techniques. For fine-grained analysis of sources and outlier samples, a combination of *l*XRF and INAA is still best practice. Because *p*XRF analysis can take as little as two minutes per reading, large samples can be rapidly assessed and errors and outliers identified for retesting or more intensive study. However, with artifact collections that number in the thousands to hundreds of thousands, careful sampling is still of utmost importance. We agree that *p*XRF should only be used in association with "clearly defined sampling procedures, both in the field and in the lab, that allow these characterizations to be generalized from a series of samples to whole populations" and with explicit research goals (Smith et al., 2007: 446–7).

Our data suggest long-term stability in the provisioning of obsidian at Xaltocan from the Early Postclassic through the Colonial period and support the conclusion drawn by Hirth (1998: 452) that the crucial provisioning role of markets "produced an institution more durable than the political system in which it operated." Given the success of our initial study, we can now expand our work to better consider social, economic, and temporal differences among the households in our sample as well as functional differences in the use of different sources of obsidian. Obsidian artifacts often moved through many hands before they were ultimately discarded. Existing at several of those stages – from the quarry to the workshop and from the market to the home – were economic, social, and political relations that may only be hinted at by the identification of a source. Thus, obsidian provenance analysis is only one of many threads in any examination of economic processes.

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