



Assessing the applicability of portable X-ray fluorescence spectrometry for obsidian provenance research in the Maya lowlands

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ABSTRACT

Recent innovations in portable energy-dispersive X-ray fluorescence (PXRF) spectrometry have increased its utility for the geochemical characterization of obsidian artifacts for archaeological provenance research. However, concerns over the utility of PXRF instrumental analyses have been raised, focused on the validity and reliability of the geochemical data produced. Here we adopt the framework of Richard Hughes (*On Reliability, Validity, and Scale in Obsidian Sourcing Research*, 1998), whereby reliability addresses instrument stability and issues of measurement while validity pertains to an instrument's ability to discern geochemical source provenance. This is done in order to test the utility of PXRF instruments for archaeological provenance research. *k*-Means cluster analysis was used to test the accuracy of PXRF through statistical comparison of data acquired via laboratory and portable energy-dispersive XRF instruments. Multivariate analysis was employed to demonstrate obsidian source representation at two Classic Maya archaeological sites in southern Belize – Uxbenká and Ek Xux – and to test the validity of data obtained from a PXRF instrument in answering archaeological research questions pertaining to regional interactions between lowland Maya polities. Results suggest that portable XRF instruments produce internally consistent results. However, data acquired from a PXRF instrument are not statistically equivalent to other XRF instruments. This is to say that while PXRF is not a reliable technique, it is valid for questions pertaining to geochemical source representation.

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1. Introduction

This article discusses the suitability of portable X-ray fluorescence instruments for discerning obsidian procurement from two Classic Maya sites in southern Belize, Uxbenká and Ek Xux (Fig. 1). Sources from which obsidian was obtained by Classic Maya populations were determined through geochemical analysis using both laboratory energy-dispersive X-ray fluorescence (herein LXRF) and portable energy-dispersive X-ray fluorescence (herein PXRF) spectrometry.

Several techniques are currently available for archaeological obsidian provenance research, including neutron activation analysis (NAA or INAA), destructive and non-destructive X-ray fluorescence (XRF), proton-induced X-ray emission and proton-induced gamma-ray emission (PIXE-PIGME), and inductively coupled plasma mass spectrometry (ICP-MS) (Harbottle, 1982; Pollard et al., 2007; Shackley 1998a). Among these, X-ray fluorescence (XRF) spectrometry has often been utilized for obsidian provenance studies for

several reasons. For instance, while INAA can analyze for many elements with relatively high precision, it cannot analyze for barium (Ba), strontium (Sr), and zirconium (Zr) as well as XRF (Shackley, 2005: 90). Additionally, XRF is capable of non-destructive analysis with minimal sample preparation, making it preferable for several types of samples, including museum specimens and culturally sensitive materials. Low costs and short analysis time are further advantages of XRF instruments (Moens et al., 2000).

The recent development of PXRF technology has ushered in a new era in the archaeological application of XRF technology by allowing researchers to perform geochemical analyses of artifacts in a variety of circumstances in situ or in other field situations. This new technology still requires initial exploration of the strengths and weaknesses of the technique. It is the concern for understanding these limitations that forms the basis of this paper. PXRF has become an increasingly important tool for archaeologists (Morgenstein and Redmount, 2005) and has found ready use in obsidian provenance research. PXRF technology has been tested (to varying degrees of success) on obsidian materials from Turkey (Frahm, 2007), the Petén Lakes area of the Maya lowlands (Cecil et al., 2007), Peru (Craig et al., 2007), and the Russian Far East (Phillips and Speakman, 2009). One recent study (Craig et al., 2007)

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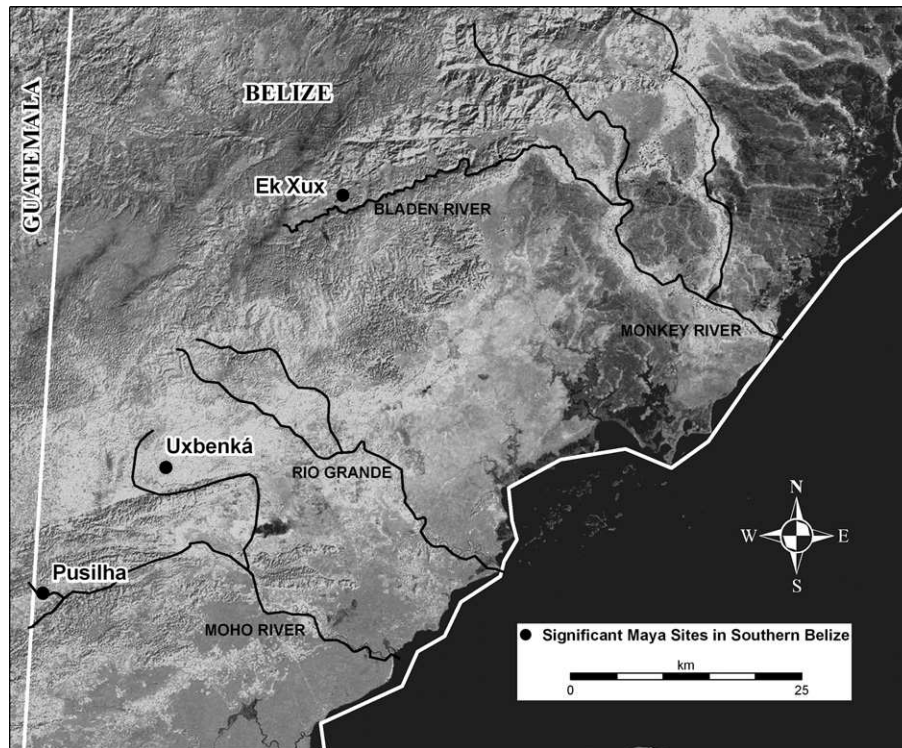


Fig. 1. Map showing the location of the study area in southern Belize and regional sites discussed in this article.

sought to examine the utility of a PXRF instrument for the geochemical source assignment of obsidian artifacts recovered from the site of Jiskairumoko, Peru. Sixty-eight artifacts were analyzed with both LXRF and PXRF instruments in order to test the data produced via PXRF against that acquired from the laboratory instrument. Through such a comparative approach, Craig et al., (2007) were able to determine that data produced via PXRF were suitable for identifying obsidian sources in southern Peru.

The study presented here has two goals. First, we test the comparability of the geochemical data acquired via LXRF and PXRF instruments. Second, we demonstrate the utility of PXRF instruments for archaeological provenance research by presenting data on obsidian source representation at the sites of Uxbenká and Ek Xux, and possible interactions with other regional polities based on obsidian geochemical source representation at each site. Identifying these sources helps us to understand the spatial distribution of obsidian from distinct geochemical groups during the Classic period, as well as potential relationships between regional polities.

1.1. What is an archaeological source?

The definition of an archaeological *source* is crucial to any provenance investigation. Considering that the various facets of this paper seek to determine the ability of a particular instrument in identifying the source of obsidian material used in the manufacture of an artifact, and to extend such ability to understanding source use by prehistoric populations, a cryptic definition will not suffice. Furthermore, because our research pertains to the geochemical characterization of rhyolitic glass, our definition of source will reflect this material and its occurrence in the archaeological record. This requires a definition distinct from provenance studies which focuses on multi-composite objects such as ceramics – because ceramic materials often comprise several different materials from various locations (cf. Whitbread, 2001), the definition of source will differ from that of obsidian.

Concerning obsidian, the material from which an object is manufactured originates from a single source.

Discussions concerning the meaning of the term *source* have differentiated between a spatial and genetic definition prominent in the discipline of geology (Harbottle, 1982; Neff, 1998), and one of geochemistry (Hughes, 1998; Shackley, 2008). Specifically, Harbottle takes the term *source* to mean the “ultimate starting point” (Harbottle, 1982: 16) from which a material is procured. He continues that it is therefore “Where one goes to procure and thus initiate the chain of processing and/or distribution” (Harbottle, 1982: 16). Neff (1998) also refers to a source as the physical point on a landscape from which a material is procured; a discrete geologic formation in space.

Concerning efforts of a geochemical nature, several individuals (e.g., Harbottle, 1982; Hughes, 1998; Shackley, 2008) have clarified that no obsidian object is ever truly sourced. It has been challenged that the submission of archaeological samples to be sourced “implies that whatever is submitted to the archaeometrist will return with a bona fide and certified source provenance that is not probabilistic at all, but confidently determined” (Shackley, 2008: 196). Rather, what occurs is a chemical characterization of an object and a likely fit to a known geochemical source group. The known geochemical group, it is assumed, has previously been established through field sampling, which has determined to a greater or lesser degree of certainty the range of chemical variability within a specific formation, thus defining the ‘fingerprint’ and the corresponding geochemical source group. It is these geochemical source groups which define material sources – not the spatial distribution of geologic materials (Hughes, 1998: 104). It follows that in order for an instrument to assign objects to a geochemical source, it must be able to chemically differentiate between various geochemical groups. The term ‘source’, as used here, refers to these geochemical groups as defined by specific concentrations of elements.

A related issue is the suite of elements chosen for source discrimination. The diagnostic suite of elements used in a given

geographic region to differentiate geochemical groups may not be adequate for differentiation in another region. The variation among specific elements of different geochemical groups will vary between and within geographic regions. Therefore, a researcher must discover a distinct suite of elements in discriminating among sources in each region of study (Glascock et al., 1998; Harbottle, 1982; Shackley, 1998a,b).

1.2. Reliability and validity of PXRF instruments as an archaeological technique

In order to measure the reliability and validity of PXRF instruments for obsidian provenance research in the Maya Lowlands, 56 samples – 32 from the site of Uxbenká, and 24 from the site of Ex Xux – were chemically characterized using both LXRF and PXRF instruments in order to provide the basis for a comparative study between the two instruments. Previous research (see for instance Davis et al., 1998; Moens et al., 2000; Shackley, 2005) has demonstrated the validity of LXRF instrumentation for archaeological provenance research. It follows that data produced from the University of California at Berkeley will make a suitable control for which to test the applicability of PXRF analysis for archaeological sourcing studies. Analysis of 124 additional obsidian artifacts using solely PXRF instrumental analysis offered a larger data set for an assessment of the instruments' validity in geochemical source assignment.

Here we test both the reliability and validity of PXRF instrumental analysis for the geochemical source identification of various obsidian objects recovered from two Mesoamerican archaeological contexts. Fig. 2 depicts the concepts of reliability and validity as they pertain to archaeological provenance research (per Hughes, 1998). According to Hughes (1998) reliability involves issues of measurement and instrumentation, “in geochemistry, reliability involves consideration of both precision and accuracy – precision directing attention to repeatability and stability of measurement, and accuracy concerning the degree to which measurements conform to ‘correct’ values (e.g., those recommended for international reference standards)” (Hughes, 1998: 108 emphasis added). Here we discuss precision in the context of the repeatability of measurement for each sample. An instrument's precision is measured by its ability to produce similar geochemical data each time it analyzes the same physical sample. The accuracy of PXRF analysis will be statistically evaluated by a comparison of data

acquired via PXRF to data produced from a LXRF instrument using the same sample population.

Hughes (1998: 109) identifies two distinct levels of validity pertaining to geochemical provenance research of obsidian in archaeology. The first is whether or not an instrument can identify geochemical variation of obsidian and match objects to these varieties. This study assesses the first level of validity by using multivariate and *k*-means cluster analyses to identify distinct geochemical clusters from the data produced by the PXRF instrument. The second level of validity focuses on the ability of the data to answer archaeological questions. Concerning obsidian research in southern Belize specifically, our archaeological question deals with the geochemical source varieties of obsidian present at the sites of Uxbenká and Ek Xux, and the implications of such source representation in a more broad cultural landscape.

If PXRF instrumentation were determined to be a reliable and valid technique for sourcing studies in Mesoamerica, there are a number of implications which would result for archaeological research. First, PXRF machines are portable, meaning they can be brought into the field allowing for in situ analysis of obsidian, or transported between institutions. However, because some PXRF instruments contain radioactive materials, difficulties may arise when transporting across state lines, much less from one country to another (Frahm, personal communication). Second, PXRF data are available to the archaeologist immediately, unlike LXRF or INAA. For large projects PXRF may be more cost effective. Even for smaller projects, using PXRF avoids the complicated bureaucracy of exporting and repatriating artifacts (Cecil et al., 2007: 506). Finally, PXRF instruments can be used in situations where cultural sensitivities may not allow artifacts to be removed from institutions or communities.

2. Archaeological context

Chemical sourcing studies demonstrate that long-distance trade of obsidian was an important aspect of Maya economies starting in at least 400 BC (e.g., Brown et al., 2004; Fowler et al., 1989; Hammond, 1981; Kovacevich et al., 2006; Moholy-Nagy, 2003; Masson and Chaya, 2000). Three Highland Guatemalan sources dominated obsidian assemblages in the Maya Lowlands: El Chayal, Ixtapeque, and San Martin Jilotepeque, with other sources such as San Barolome Milpas in Guatemala, and Pachuca in central Mexico minimally represented (Glascock et al., 1998). In

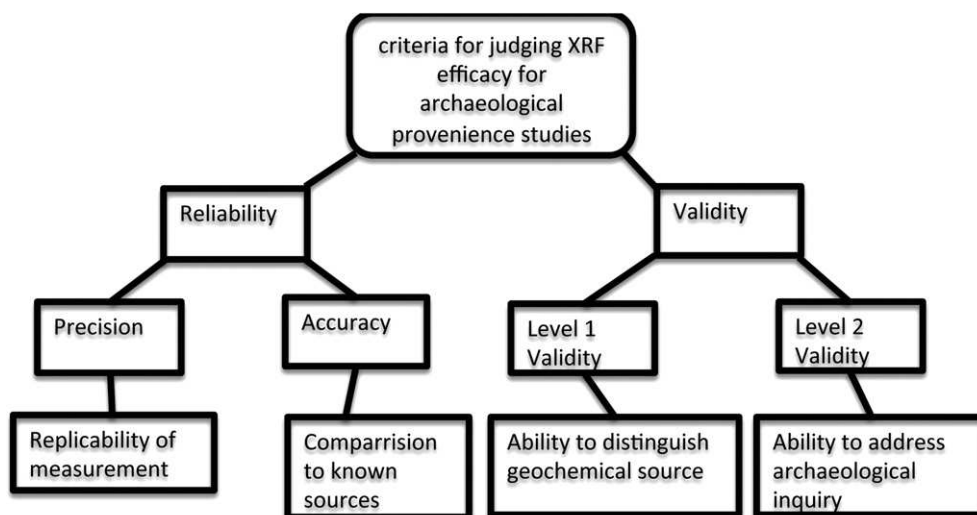


Fig. 2. Depiction of criteria to judge the effectiveness of XRF instruments for archaeological provenance research (per Hughes, 1998).

general in the southern Maya Lowlands (see Nelson, 1985; Rice et al., 1985), San Martín Jilotepeque was commonly traded during the Middle Preclassic (100–400 BC), but declined in use during the Late Preclassic through the Terminal Classic periods (400 BC to AD 900) when El Chayal became the dominant source, only to be overshadowed by Ixtepeque during the Postclassic (AD 900–1500).

Our research focuses on southern Belize, an important but underreported area of the Maya Lowlands that has, in recent decades, been the focus of numerous discussions of resource exploitation and exchange. During its apogee between AD 500 and AD 800 the region was involved in significant economic interactions that were facilitated by a range of mineral and biotic resources (Abramiuk and Meurer, 2006; Dunham and Prufer, 1998; Graham, 1987), and productive agricultural lands (Prufer, 2005; Wright et al., 1959). Though clearly marginal to the central Petén in terms of the size scale of polities, ceramic, lithic, and epigraphic data from the region indicate that it participated fully in regional economies.

The samples selected from Uxbenká and Ek Xux were all assigned to dates between AD 300–700 using a combination of AMS radiocarbon dating of archaeological contexts and comparative ceramic analysis (Prufer, 2002; Prufer et al., 2008). This time period spans the growth of several large polities in the region (Braswell and Prufer, 2009). Uxbenká and Ek Xux are the two oldest known polities in southern Belize, and both are located along what are thought to be regional trade routes. Uxbenká is located in a fertile valley with easy access to the central Maya 'heartland' via routes through a low pass in the southern Maya Mountains (Prufer et al., 2008). Ek Xux is located in the interior of the Maya Mountains along a tributary of the upper Bladen Branch of the Monkey River, a seasonally navigable waterway in an area of economically important mineral and biotic resources (Dunham, 1996) (Fig. 3). Both sites appear to have continuous occupation throughout the Early and Late Classic periods.

Archaeological research in southern Belize shows that inhabitants displayed a preference for obsidian for the manufacture of prismatic blades and other tools such as (less frequently) projectile points. Movement of obsidian into southern Belize likely took two forms. Both Uxbenká and Ek Xux both had easy access to coastal routes that were routinely plied during the Classic period. Data from Wild Cane Caye, located directly off the coast of Southern Belize, suggest robust trade in obsidian, salt, and marine resources (McKillop, 2002: 12). Coastal and island sites were utilized as trade stations throughout the Early and Late Classic and continued to be important long-distance nodes well into the Postclassic (McKillop, 2005: 46–49), well after the abandonment of Uxbenká and Ek Xux. The easily traversable coastal routes would have facilitated movement of obsidian from Highland Guatemalan sources down the Motagua River and up the Caribbean Coast, protected from the open sea by the Atlantic Barrier Reef. Movement of resources up rivers to political centers would likely have facilitated local trade. Access to Uxbenká would have been via the Rio Grande, which is navigable to within 13 km of the site. Ek Xux is located approximately 22 km above the navigable portions of the Bladen Branch.

Inland trade routes also could have facilitated movement of obsidian to southern Belize. Uxbenká is situated near important north–south trade routes that linked the central Petén to Copan (Sharer, 2003: 320, 322). Its location in a low corridor bisecting the Maya Mountains may have facilitated overland trade with the central Petén (Hammond, 1978), where obsidian may have moved via the Usumacinta and Pasión Rivers (Dreiss et al., 1993; Hammond, 1972), following the movement of jade (Kovacevich et al., 2001).

3. Method

3.1. Sampling procedure

Archaeological samples for comparative analysis were selected from the larger obsidian assemblage using a random number generator. Davis et al. (1998) have demonstrated that obsidian objects submitted for LXRF analyses which have a diameter less than 10 mm are unable to produce reliable data for geochemical source assignment. As a result, samples which did not meet this initial standard were discarded.

3.2. Laboratory EDXRF analysis

The sample population was first analyzed by Dr M. Steven Shackley in the Geoarchaeological XRF Laboratory, Department of Anthropology, University of California, Berkeley, using a Thermo/ARL *Quant'X* energy-dispersive X-ray fluorescence spectrometer. The instrument contains a peltier-cooled solid-state Si(Li) X-ray detector, with an ultra-high-flux end window bremsstrahlung rhodium (Rh) X-ray target with a 125- μ m beryllium (Be) window, an X-ray generator that operates from 4 to 50 kV/0.02 to 1.0 mA at 0.02 increments, using an IBM PC based microprocessor and WinTrace™ 4.1 software. Data were acquired with a pulse processor and analog-to-digital converter. This is a noteworthy improvement in analytical speed and efficiency over the former Spectrace 5000 and *QuanX* analog systems (see also Davis et al., 1998; Shackley, 2005).

Dr Shackley at the Berkeley laboratory conducted analyses of all archaeological samples whole. The results presented here have been derived from 'filtered' intensity values as a ratio to the appropriate X-ray continuum regions through a least-squares fitting formula (McCarthy and Schamber, 1981; Schamber, 1977). Moreover, through the analysis of international rock standards, the data derived from LXRF allow for comparison between instruments with a predictable degree of certainty (Hampel, 1984) (Table 1).

The X-ray tube was operated at 30 kV for 200 live seconds, using a 0.05-mm (medium) Pd primary beam filter in an air path to generate X-ray intensities at the $K\alpha_1$ -line data for elements titanium (Ti), manganese (Mn), iron (as Fe^T), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), gallium (Ga), rubidium (Rb), strontium (Sr), yttrium (Y), zirconium (Zr), niobium (Nb), lead (Pb), and thorium (Th) (Shackley, personal communication). Conversion of raw spectra produced from the Thermo/ARL *Quant'X* EDXRF spectrometer to trace elemental intensities (reported here in ppm) was achieved at the Berkeley laboratory through a least-squares calibration line for each element from the analysis of international rock standards certified by the National Institute of Standards and Technology (NIST), the US Geological Survey (USGS), Canadian Centre for Mineral and Energy Technology, and the Centre de Recherches Pétrographiques et Géochimiques in France (Govindaraju, 1994). A series of 17 standards used for the best fit regression calibration for elements Ti – Nb, Pb, Th, and Ba included G-2 (basalt), AGV-2 (andesite), GSP-2 (granodiorite), SY-2 (syenite), BHVO-2 (hawaiite), STM-1 (syenite), QLO-1 (quartz latite), RGM1 (obsidian), W-2 (diabase), BIR-1 (basalt), SDC-1 (mica schist), BCR-2 (basalt), TLM-1 (tonalite), SCO-1 (shale), all US Geological Survey standards, BR-1 (basalt) from the Centre de Recherches Pétrographiques et Géochimiques in France, and JR-1 and JR-2 (obsidian) from the Geological Survey of Japan (Govindaraju, 1994).

The data derived from the WinTrace software were converted directly into Excel 2007 format for Windows software for further statistical manipulation and geochemical source assignment at the University of New Mexico by one of the authors (Nazaroff). Geochemical source determinations were achieved through

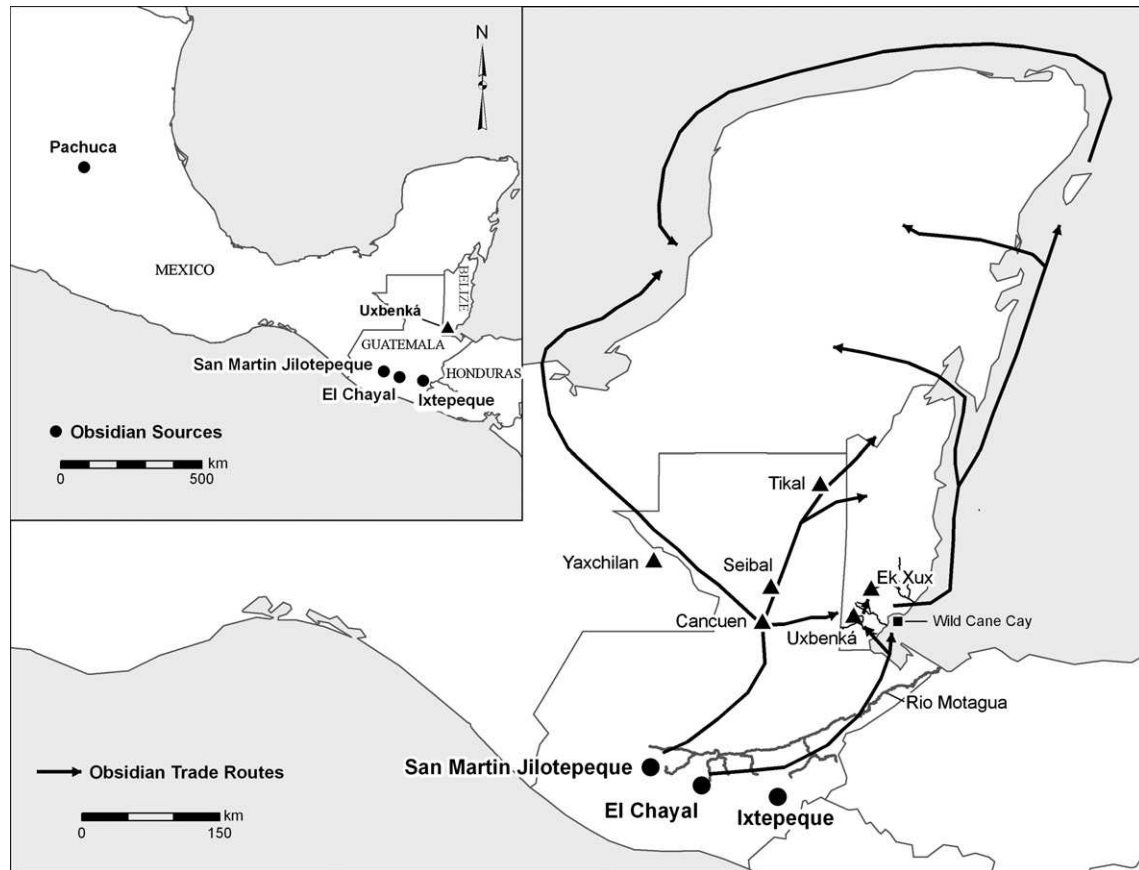


Fig. 3. Geographic locations of obsidian sources correlating with source groups discussed in the paper as well as likely trade routes.

multivariate analysis and by comparison to published (Barker et al., 2002; Shackley, 1997) and unpublished (Glascok, unpublished data 1996) (Table 2) references using trace-element concentrations of Rb, Sr, and Zr, as this suite of elements was able to distinguish between obsidian geochemical source groups located in Mesoamerica (cf. Cecil et al., 2007). Concentrations of Fe, Rb, Sr, Y, Zr, and Nb derived from the Berkeley analysis are reported in parts per million (ppm) in Table 1.

3.3. Portable EDXRF analysis

Following geochemical analysis at Berkeley, the same sample population was analyzed using a Bruker AXS Tracer 3-V Portable EDXRF analyzer, equipped with a rhodium tube from which X-rays are emitted, and a peltier-cooled, silicon PIN diode detector, operating at 40 kV and 9.0 μ A from an external power source for 300 live seconds using a filter composed of 6 mil copper (Cu), 1 mil titanium (Ti), and 12 mil aluminum (Al). The Bruker instrument produces an X-ray beam at a 45° angle from the center of the analyzer's tip (Fig. 4). In order to make sure that analysis of each sample included the bulk of the X-rays produced, each sample was placed so as to cover the 45° angle beam path. Furthermore, samples were positioned with as much contact as possible with the instrument's surface; irregularly shaped samples were placed with the smoothest side positioned for analysis. This was done to ensure that the greatest amount of X-rays possible would bombard the sample, which would optimize the count rate and mitigate the effects of irregular sample surface structure on X-ray scatter. During analysis, the instrument was mounted in a Bruker-designed plastic hold, which allowed for fixed positioning during

analysis and standardized the distance of each sample from the analyzer.

X-ray counts were processed using the S1PXRF spectra program developed by Bruker, and converted to parts per million concentrations using a Bruker-designed calibration program (S1CalProcess) which utilizes the Compton's scatter derived from rhodium backscatter. Seventeen analyses of eight archaeological obsidian samples, whose trace-element concentrations were known from previous LXRF analysis (FS 0002, 0008, 0042, 0109, 0136, 0150, this study; and AC 0001, 0006, Huckell, unpublished data 2008) (Table 1) were used in order to empirically calibrate the instrument by comparing expected values with those produced by instrumental analysis for elements tin (Ti), manganese (Mn), iron (Fe), rubidium (Rb), strontium (Sr), zirconium (Zr), niobium (Nb), zinc (Zn), yttrium (Y), and barium (Ba). Only samples which were large enough to completely cover the X-ray beam path and met the infinite thickness requirement set by Bruker AXS – 3 mm – were utilized for calibration. Furthermore, the aforementioned samples were chosen because of their known geochemistry, which would span the range of variability for the Mesoamerican geochemical obsidian sources expected to appear in the Uxbenká and Ek Xux assemblages. This is to say that the calibration curve produced when using these samples should be capable of addressing the geochemical variation present in our archaeological assemblages. In addition, a single archaeological obsidian sample of known geochemistry (FS 0153, this study) was run each day in order to ensure the stability (precision) of instrument measurement (Table 3). Analysis was conducted at the $K\alpha_1$ -line for the above elements; concentrations of Fe, Rb, Sr, Y, Zr, and Nb are reported in Table 1 for comparison with LXRF analysis.

Table 1
Geochemical data reported in this study. Top: ppm concentrations for iron (Fe), rubidium (Rb), strontium (Sr), yttrium (Y), zirconium (Zr), and niobium (Nb) acquired from LXRF (left) and PXRF (right) instruments for the comparative sample population. Middle: PXRF geochemistry for samples AC 0001, 0006 utilized in calibration. Bottom: LXRF data for RGM1-S4, a US Geological Survey rhyolite (obsidian) standard in order to allow for comparison between instruments.

FS no.	Laboratory XRF analyses						Portable XRF analyses					
	Fe	Rb	Sr	Y	Zr	Nb	Fe	Rb	Sr	Y	Zr	Nb
FS 0001	11820	112.3	165.3	19.31	161.5	8.26	10510	92.34	150.9	32.23	152.7	12.06
FS 0002	10680	100.4	150.4	19.46	153.8	18.16	10600	98.96	152.9	23.35	157.8	14.71
FS 0008	8162	147.2	143.5	17.78	103.3	6.65	8143	141.2	140.2	32.98	100.8	8.86
FS 0016	8715	153.6	150.7	20.07	109.9	12.20	8719	151.2	156.9	-10.59	100.0	2.32
FS 0018	8526	157.0	151.0	19.78	109.6	10.81	8135	141.2	149.5	10.31	100.4	7.47
FS 0021	8260	149.4	147.3	20.11	108.2	5.78	8155	141.6	145.0	20.79	99.95	8.72
FS 0028	8122	148.8	147.8	18.04	103.1	3.63	8207	136.8	138.2	39.86	94.86	7.28
FS 0032	8537	156.9	154.0	20.45	109.5	9.38	8012	148.1	140.2	29.69	101.1	7.42
FS 0039	9337	151.1	144.6	15.99	104.9	15.57	8270	143.7	144.9	18.29	97.98	4.88
FS 0040	9300	162.2	155.7	17.39	107.4	7.44	8928	145.7	144.6	19.91	102.5	6.73
FS 0041	19850	233.2	10.3	113.9	975.4	101.2	14590	288.7	6.10	163.1	889.3	61.91
FS 0044	9088	157.7	160.4	20.23	112.2	11.01	8122	142.3	151.4	4.70	106.8	7.64
FS 0047	8035	152.0	149.1	17.62	109.7	7.66	8413	144.1	150.4	8.44	99.66	7.74
FS 0051	8630	157.8	156.0	17.74	107.0	9.22	8325	148.5	143.4	26.54	104.4	7.73
FS 0052	8343	152.7	150.7	21.63	105.7	5.68	8353	144.4	146.9	15.68	98.55	8.21
FS 0053	8375	156.9	156.7	18.81	106.1	8.69	8445	138.0	148.9	16.75	97.66	8.64
FS 0057	8639	158.3	154.2	21.76	107.6	11.31	8253	145.4	141.0	29.39	102.9	9.21
FS 0060	8788	162.1	159.6	20.77	109.0	7.36	8636	150.3	150.1	3.03	96.96	3.14
FS 0061	7857	146.6	145.6	20.68	103.1	8.04	8272	145.7	150.4	9.77	95.83	9.03
FS 0062	8440	153.7	153.1	20.57	108.4	8.38	8379	142.7	153.1	3.19	98.59	6.71
FS 0067	8860	155.1	159.8	17.77	111.1	5.96	8279	138.2	142.1	29.09	100.8	9.04
FS 0071	9275	166.3	166.5	19.36	109.3	9.36	8443	145.4	145.0	23.20	103.0	11.34
FS 0080	9577	160.0	161.2	19.35	112.0	14.17	9399	142.7	150.9	5.98	99.83	8.40
FS 0082	8131	131.0	128.0	16.97	101.2	11.23	8095	138.7	139.9	35.92	99.29	10.50
FS 0083	8998	156.1	152.6	20.37	109.4	10.20	9363	143.3	150.4	6.34	102.3	6.12
FS 0087	9293	160.2	155.3	21.41	106.4	12.21	8495	146.7	151.7	5.65	97.04	4.92
FS 0088	8643	152.3	150.4	18.10	106.5	9.28	8523	143.6	140.4	31.67	102.5	10.25
FS 0092	8970	149.0	151.6	19.58	108.5	11.53	8579	142.0	150.4	10.39	104.2	11.15
FS 0095	8631	153.3	152.3	18.01	109.1	10.65	8107	137.9	138.4	39.95	101.8	12.45
FS 0098	8157	147.6	146.0	17.71	101.8	11.45	8121	146.3	138.3	35.02	104.2	8.41
FS 0102	8715	144.8	149.0	20.48	108.8	7.38	8473	144.5	147.5	14.59	102.0	10.52
FS 0108	7998	147.2	145.0	23.41	108.9	6.31	8122	145.6	140.3	28.39	107.6	10.48
FS 0109	8127	146.7	147.2	17.92	105.8	10.35	7725	135.5	130.1	60.54	99.43	10.05
FS 0113	8562	154.1	152.0	21.80	106.8	10.58	8516	143.1	143.7	24.07	102.3	9.95
FS 0122	8625	150.0	154.9	20.88	106.7	11.97	8364	145.5	143.7	25.05	99.53	7.49
FS 0123	7910	148.4	145.2	17.23	106.6	11.69	8165	141.5	144.6	20.28	100.5	8.76
FS 0131	8123	147.5	145.6	16.85	109.0	11.81	8612	137.5	142.1	25.30	102.5	7.57
FS 0137	8307	158.9	157.1	19.12	107.2	13.26	8204	143.9	145.6	15.02	108.7	5.99
FS 0141	10800	98.6	151.4	18.60	156.9	8.72	10710	98.07	160.5	12.31	154.3	17.41
FS 0142	11050	106.5	164.4	15.00	162.9	6.67	10650	94.55	159.5	10.65	159.3	11.24
FS 0143	10840	104.0	156.6	12.58	157.9	10.43	11670	102.5	156.9	14.45	151.2	12.45
FS 0144	8130	154.4	150.8	19.96	105.1	7.27	8054	151.4	147.1	13.28	101.2	8.29
FS 0145	11460	108.1	159.6	18.08	164.3	5.65	10920	99.20	144.7	40.61	156.1	13.63
FS 0147	10940	103.3	157.5	20.29	160.6	12.16	10640	95.55	157.3	14.65	155.3	13.94
FS 0150	7923	145.0	146.8	20.66	107.1	7.96	8046	146.7	137.2	36.17	106.2	10.65
FS 0167	7799	145.3	143.6	21.42	106.1	7.35	8219	145.5	140.0	31.17	106.5	10.21
FS 0168	8523	160.1	153.1	19.66	109.6	7.89	8409	149.3	147.7	12.30	106.3	6.74
FS 0178	8502	159.3	157.5	22.18	111.4	12.65	7904	140.5	137.6	38.41	100.4	8.46
FS 0180	8308	150.4	150.9	17.28	101.3	4.69	8305	147.1	142.1	24.39	102.9	4.93
FS 0182	9430	166.1	164.5	20.37	114.5	10.52	7869	140.4	139.1	36.84	99.40	8.20
FS 0184	8197	147.7	143.6	18.29	108.4	12.26	8187	139.2	144.1	24.79	99.20	11.97
FS 0186	9413	167.0	163.3	20.22	108.1	3.59	7984	139.5	146.1	19.30	98.00	2.97
FS 0187	8999	161.7	159.3	19.65	108.8	12.36	8512	148.4	147.8	14.66	98.21	9.91
FS 0189	8775	157.7	156.5	18.76	108.0	9.75	8103	150.0	139.2	30.18	100.4	7.41
FS 0190	8665	156.8	150.4	20.22	110.6	9.25	8353	149.4	142.6	27.22	104.3	7.73
	Ti	Mn	Fe	Zn	Rb	Sr	Y	Zr	Nb			
AC 0001	1204	334.44	8432	191.4	320.6	12.69	232.8	153.3	11.52			
AC 0006	1230	471.62	8783	161.8	310.5	13.21	239.1	150.7	14.65			
RGM1-S4	1585	293.8	13112	32.18	152.4	107.0	23.91	217.5	11.35			
RGM1-S4	1569	274.2	12971	32.56	154.6	105.5	25.13	216.1	8.94			
RGM1-S4	1495	302.8	13032	31.84	153.9	104.6	24.73	223.2	11.51			
RGM1-S4	1602	307.3	13041	32.20	150.6	105.8	25.30	222.5	7.89			

3.4. Statistical analysis

Two-sample *t*-tests and *k*-means cluster analysis were employed to partition clusters (geochemical source groups) of data produced via PXRF and thus test for systematic error. The

geochemical data and source assignments achieved through multivariate analysis acquired from the Berkeley instrument acted as a test for PXRF data by generating a hypothesis as to how many source groups (clusters) the PXRF should find if its results are as reliable as the laboratory instrument. Precision was determined by

Table 2

LXRF (Barker et al., 2002; Shackley 1997) and NAA (Glascock unpublished data 1996) source standard data utilized for provenance assignment.

	Laboratory XRF analyses								NAA analyses			
	Ti	Mn	Fe	Rb	Sr	Y	Zr	Nb	Mn	Rb	Sr	Zr
<i>Ixtepeque</i> (n = 4)												
Mean	1553	455.0	11801	104.7	160.4	17.97	164.2	8.35	453.0	95.00	155.0	159.0
SD	106.5	42.58	515.6	3.76	3.96	0.93	5.93	2.56	10.00	2.10	8.00	7.00
Min.	1450	405.5	11324	100.8	157.0	17.19	155.3	5.38	443.0	92.91	147.4	152.3
Max.	1670	508.0	12328	108.9	166.0	19.24	167.9	11.57	163.0	97.09	162.6	165.7
<i>El Chayal</i> (n = 2)												
Mean	1001	593.6	8578	149.0	150.2	20.65	109.4	12.40	644.0	139.0	152.0	112.0
SD	3.32	35.96	136.8	9.27	6.02	2.98	0.64	3.20	17.00	2.00	13.00	26.00
Min.	999.0	568.1	8482	142.5	146.0	18.54	108.9	10.19	627.3	136.9	138.9	86.35
Max.	1003	619.0	8675	155.6	154.5	22.75	109.8	14.67	660.7	141.1	165.1	137.6
<i>Pachuca</i> (n = 7)												
SD	96.00	48.00	-	4.00	7.00	3.00	7.00	2.00				
Min.	897.0	923.0	-	202.0	5.0	107.00	892.0	87.00				
Max.	1152	1188.0	-	214.0	9.0	114.00	931.0	91.00				

the repeated analysis of a standard mentioned above. For accuracy, a two-standard deviation confidence level was generated for the laboratory-derived source clusters and overlain onto the PXRF-derived geochemical clusters in order to test for variation within the PXRF instrument's data (Fig. 5).

Two-sample *t*-tests were conducted between the data acquired from the laboratory XRF and PXRF instruments for each cluster using each of the elements reported in Table 1. These tests were employed in order to further test the accuracy of PXRF in identifying the correct chemical concentrations as defined by source standards. Cluster analysis was used in order to assess the ability of the PXRF instrument to produce geochemical clusters indicative of those generated by Mesoamerican obsidian sources, as well as to assess whether error introduced by the PXRF instrument was systematic (predictable) or random (not predictable). The *k*-means algorithm was employed to partition a hypothetical number of clusters within a vector space based on Eq. (1):

$$V = \sum_{i=1}^k \sum_{x_j \in s_i} (x_j - \mu_i)^2 \quad (1)$$

The input of *k* clusters was noted by Lloyd (1982) to be most effective when given a random value, which is subsequently

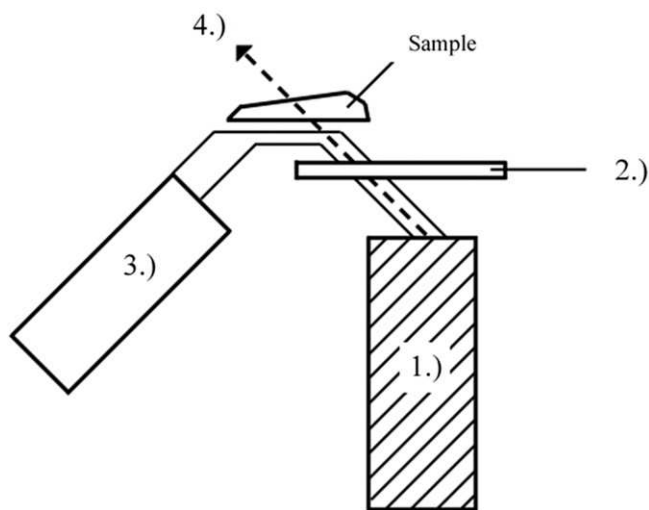


Fig. 4. Schematic of PXRF, including: (1) X-ray source (rhodium tube); (2) filter (6 mil Cu, 1 mil Ti, 12 mil Al); (3) detector (Si(Li) X-ray detector); as well as (4) beam path at 45° angle.

modified by multiple iterations to move closer to a point (centroid) of least variation within a vector space. For obsidian provenance research, the vector space is defined as the combined possibilities of values for comparable trace elements.

In order to test for systematic error, *k*-means cluster analysis was used to generate a centroid per source per instrument. Centroids were determined for each of the source groups determined from the LXRF data in an Rb and Zr vector space, and confidence levels were generated to the second standard deviation. These measures of variance for LXRF were then transposed onto the vector space for PXRF, allowing for direct quantitative comparison of source clusters within the vector space (Figs. 5 and 6). That is to say, a geochemical source is represented by a centroid within a defined vector space to the first or second standard distribution. The Rb and Zr distances between the central points of each confidence interval for each geochemical source cluster were measured. These values were then subtracted from the data acquired from the portable instrument in order to produce a "treatment" which created a closer correlation between the laboratory XRF and PXRF data sets (Fig. 7). The overlapping confidence intervals were then used to determine the presence of systematic error, as seen in Figs. 5 and 6.

4. Results

4.1. Obsidian provenance determination and a comparison of laboratory and portable EDXRF instruments

Both instruments provided geochemical data from the comparative sample population which indicated that seven samples best fit the Ixtepeque obsidian geochemical group, 47 the El Chayal group, and one from the Pachuca group (Fig. 6, Table 4). However, two-sample *t*-tests performed at the 95% confidence level between the LXRF and PXRF data for elements Fe, Rb, Sr, Y, Zr, and Nb demonstrate several differences in the data produced by each instrument. Based on the two-sample *t*-tests for the El Chayal geochemical group, Fe, Rb, Sr, Zr, and Nb all demonstrate significant differences in the geochemical values produced between the two instruments; *p*-values for these elements were 0.004, 0.000, 0.000, 0.000, and 0.013 respectively. Only yttrium was comparable at a *p*-value greater than 0.050 – specifically 0.224 – which demonstrates a lack of significant difference in the geochemistry for Y produced between the two instruments. Results were more favorable for the Ixtepeque geochemical group, with only *t*-tests for Rb and Zr producing *p*-values below 0.050 (0.005 and 0.027

Table 3
Repeated analyses ($n = 6$) of a single archaeological sample (FS 0153, this study) utilized as a standard in order to assess instrument stability. Note only minimal fluctuations in ppm readings for elements iron (Fe), rubidium (Rb), strontium (Sr), yttrium (Y), zirconium (Zr), and niobium (Nb), those primarily of interest here.

	Ti	Mn	Fe	Zn	Rb	Sr	Y	Zr	Nb
S1	1112	650.5	8084	60.26	141.6	141.3	30.77	100.6	9.34
S2	1256	578.9	7941	56.47	140.3	142.8	24.13	98.47	4.95
S3	1240	594.1	8046	61.13	146.7	137.2	36.17	106.2	10.65
S4	1228	624.9	8128	56.78	145.8	142.2	26.14	102.4	8.71
S5	1431	593.8	8056	61.15	142.2	141.5	28.80	104.5	9.21
S6	1229	632.7	8115	58.30	145.2	141.6	27.78	102.7	10.81
Mean	1249	612.9	8062	59.02	143.6	141.1	28.97	102.5	8.95
SD	102.8	27.65	67.20	2.12	2.60	1.99	4.19	2.74	2.13
Min.	1112	578.9	7941	56.47	140.3	137.2	24.13	98.47	4.95
Max.	1431	650.5	8128	61.15	146.7	142.8	36.17	106.2	10.81

respectively); while Fe, Sr, Y, and Nb had p -values of 0.241, 0.308, 0.438, and 0.062 respectively.

Interestingly, treatment of the data using k -means cluster analysis creates a closer fit between the readings produced from the portable and laboratory instruments. This is to say that although laboratory and PXRF produce significantly different datasets for several of the elements within each geochemical group, statistical treatment can increase the closeness of fit between the PXRF and LXRF techniques, allowing the geochemical data acquired to be more similar to those of laboratory XRF. The ability to create a treatment strongly supports the notion that the low accuracy witnessed in PXRF compared to an established LXRF instrument is due to systematic, not random, error. This is essential. It is because of systematic error that a treatment can be created in order to correct for the differences between the geochemical readings acquired from the different instruments. This is important if a researcher desires to produce geochemical data comparable with other instruments. However, as will be discussed below, this does not influence the ability of the PXRF instrument in geochemical source discrimination.

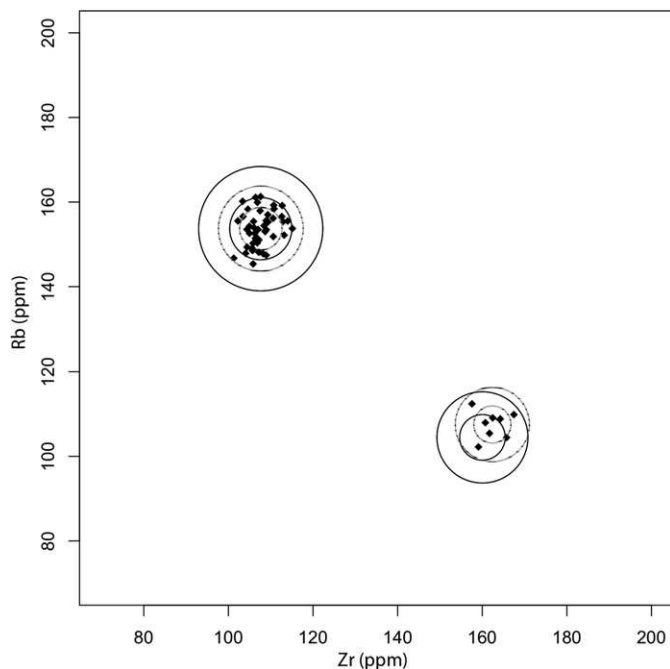


Fig. 5. El Chayal (upper left) and Ixtepeque (lower right) geochemical source centroids as determined by k -means cluster analysis from data acquired via LXRF (solid circles) and PXRF (dashed circles) instruments. Data points depict individual PXRF measurements. Both LXRF and PXRF instruments are able to distinguish geochemical source clusters, though it can be seen that despite intra-instrument consistency there is inter-instrument error (Drake et al., 2009, Fig. 3).

4.2. Archaeological results and interpretations

The validity of an instrument used for geochemical sourcing in archaeology, as discussed above, is measured on one level by its ability to differentiate geochemical source groups, and on another by how this differentiation adequately answers an archaeological question posed.

The Bruker AXS Tracer 3-V analyzer used in this study demonstrated the ability to differentiate between the Ixtepeque, El Chayal, and Pachuca obsidian geochemical groups. Indeed, multivariate analysis of geochemical data acquired from the PXRF instrument for the sample population ($n = 56$) correctly distinguished which samples belonged to each group. This warranted further analysis of additional obsidian artifacts ($n = 124$) acquired from the Uxbenká and Ek Xux archaeological sites. In total, 103 artifacts were analyzed from Uxbenká: 85 were assigned to the El Chayal group, 11 to the Ixtepeque group, two to the Pachuca group, and five were not identified as belonging to any of these. Seventy-seven artifacts were analyzed from the site of Ek Xux, with 64 being identified as having geochemistry indicative of the El Chayal group, and 13 identified as belonging to the Ixtepeque group (Fig. 8, Table 4).

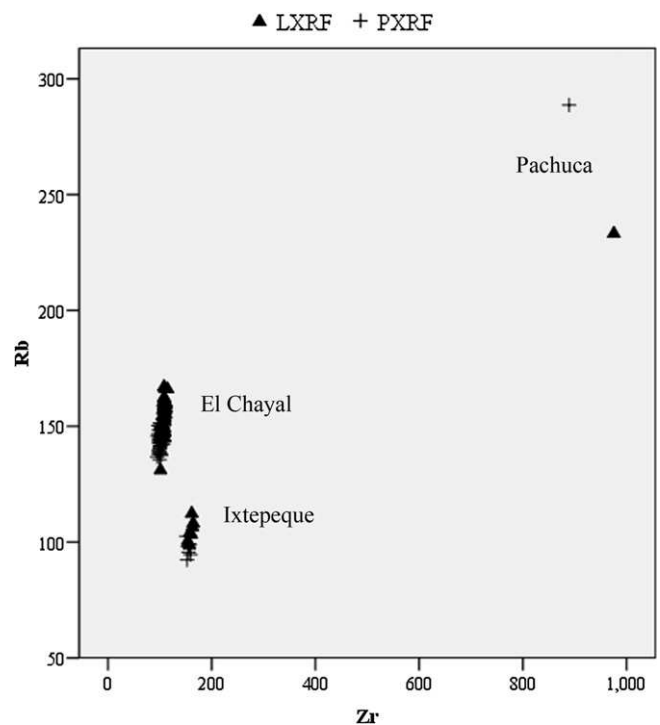


Fig. 6. Bivariate plot of data obtained for comparison sample from LXRF (triangles) and PXRF (crosses). All quantities reported in parts per million (ppm).

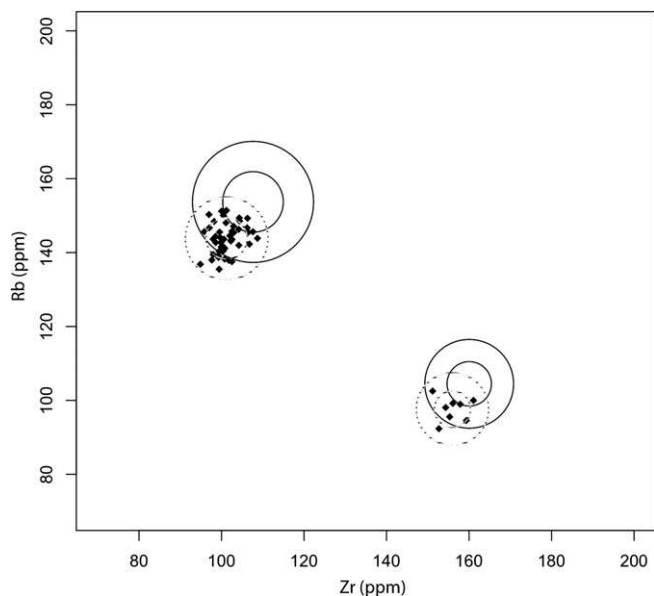


Fig. 7. El Chayal (upper left) and Ixtepeque (lower right) geochemical source centroids as determined by *k*-means cluster analysis from data acquired via laboratory XRF (solid circles) and portable XRF (dashed circles) instruments. PXRF centroids are depicted after statistical treatment based on PXRF treatment of samples assigned to the El Chayal geochemical source group. Two observations can be made. First, the data assigned to the Ixtepeque geochemical source group increases in accuracy – as measured against LXRF data – along with the El Chayal data. This is consistent with the argument for systematic error; the instrument is shifting data with the same quantity and trajectory. Second, precision is unaffected by treatment (Drake et al., 2009, Fig. 3).

Regarding the second level of validity, PXRF data can be used to address an archaeological question pertaining to regional interaction between polities based on obsidian geochemical source representation at different lowland Maya sites; here Uxbenká and Ek Xux. We posit that Uxbenká and Ek Xux were engaged in larger regional economic interactions. The ability of PXRF to discern geochemical source representation helps to support archaeological interpretations which pertain to these interactions. The role of Uxbenká and Ek Xux in significant regional exchange throughout the Maya lowlands, as discussed below and by Dunham and Prufer (1998), is further supported by obsidian data presented here. Locally, the data suggest similar interactions for both sites in the obsidian economy based on the correlation of obsidian source representation at both Uxbenká and Ek Xux.

Both the Ek Xux and Uxbenká obsidian assemblages are dominated by obsidian materials sourced to El Chayal, Guatemala, representing 83% of the Ek Xux total and 85% of the Uxbenká materials (Table 2). The second most common source is Ixtepeque, which was represented in 16.9% of the Ek Xux material and 10.7% of the Uxbenká samples. These percentages can be compared with two nearby sites for which sourcing data are available: Pusilha and Wild Cane Caye. At Pusilha (Braswell et al., 2008: 57–58) visual sourcing suggested that 94% of the Early Classic obsidian originated from El Chayal with only 6% from Ixtepeque ($n = 83$). During the Late Classic 95% of the obsidian originated from El Chayal, with 0.5% coming from Ixtepeque ($n = 884$). At Wild Cane Caye, which is part of the coastal trade network (Fig. 3), chemical sourcing suggests that Ixtepeque was the dominant source for artifacts in Late Classic assemblages at 52%, with El Chayal only present in 41% of samples (McKillop, 2005: 44).

High proportions of El Chayal are consistent with chemical characterization studies from Classic period contexts from Trinidad de Nosotros (Cecil et al., 2007: Fig. 6) and in the Tikal Yaxha corridor (Ford et al., 1997: 103), both in the central Petén. However, in both

of those studies Ixtepeque formed a smaller percentage of the assemblages (<5%) than at Ek Xux or Uxbenká. In this regard, our sources suggest slightly more affinity with Colha in northern coastal Belize, where Classic period assemblages consisted of 51% El Chayal and 47% Ixtepeque (Brown et al., 2004: Table 2).

The dominance of El Chayal as the primary source for obsidian during the Classic period is consistent with other studies in the southern Lowlands. The higher proportion of Ixtepeque relative to the central Petén and Pusilha may suggest a higher degree of articulation with coastal trade networks, where El Chayal and Ixtepeque are both well represented. Overall, however, lack of a good fit with the coastal trade areas may be an indicator of overland and marine trade playing a role in obsidian procurement at the two sites examined.

5. Discussion

The testing of the applicability of PXRF instrumental analysis for the geochemical source assignment of Mesoamerican obsidian artifacts through measures of reliability and validity has returned some intriguing results.

5.1. Reliability

In order to assess the reliability of PXRF instruments, we must discuss both the precision and accuracy of the technique. Concerning precision, the continued analysis of a single sample ensured consistent geochemical readings by the instrument over the period of analysis. Indeed, Table 3 illustrates six separate analyses of this sample throughout the course of our research with only minimal fluctuations in the elemental concentrations of interest here (Fe, Rb, Sr, Zr, and Nb). Such variation may be the result of minor variation within the sample itself. As to the accuracy of the instrument, two-sample *t*-test results conclusively show that the PXRF instrument, when compared with a LXRF instrument, is not statistically accurate for each element within each obsidian geochemical group in that a significant difference is present between the data produced from a previously determined reliable method – LXRF – and those of PXRF. Indeed, it shows significant differences at the 95% confidence level in Fe, Rb, Sr, Zr, and Nb concentrations for the El Chayal group. PXRF also demonstrates significant differences in Rb and Zr for the Ixtepeque group. This demonstrates that there exists a low accuracy in the geochemical readings produced by the PXRF instrument when compared with laboratory XRF analysis. More specifically, *k*-means cluster analysis

Table 4

Geochemical source assignments for artifacts from Uxbenká and Ek Xux, Belize, for the 56 obsidian artifacts analyzed at the UC Berkeley Geoarchaeological XRF Laboratory and derived from geochemical analysis of 180 artifacts analyzed with the Bruker AXS Tracer 3-V PXRF analyzer.

Source	Uxbenká		Ek Xux	
	Number	Percent	Number	Percent
<i>UC Berkeley Geoarchaeological XRF Laboratory</i>				
El Chayal	28	87.5	19	79.2
Ixtepeque	2	6.3	5	20.8
Pachuca	1	3.1	0	0
Unknown	1	3.1	0	0
Total	32	100	24	100
<i>Bruker AXS Tracer 3-V PXRF analyzer</i>				
El Chayal	85	82.5	64	83.1
Ixtepeque	11	10.7	13	16.9
Pachuca	2	1.9	0	0
Unknown	5	4.9	0	0
Total	103	100	77	100

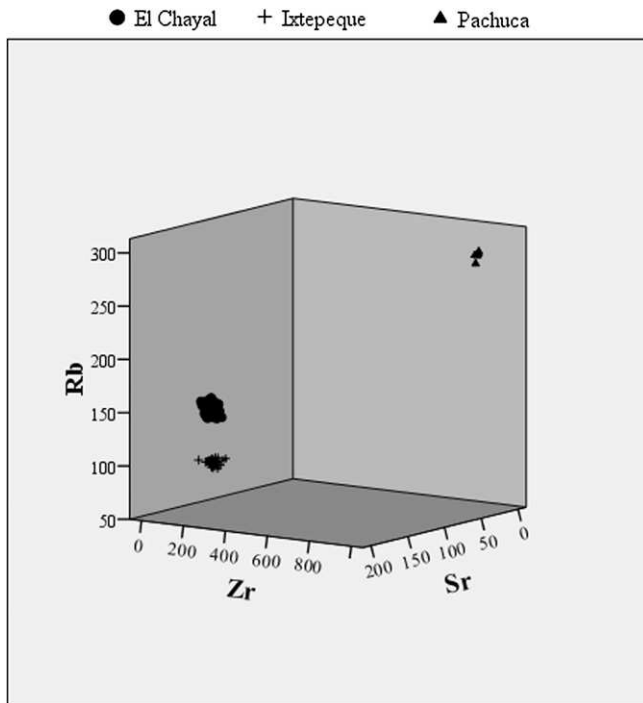


Fig. 8. Multivariate plot of all artifacts recovered from Uxbenká and Ek Xux sites which have been assigned to geochemical sources via PXRF instrumental analysis. Triangular symbols, Pachuca geochemical obsidian source; circles, El Chayal geochemical obsidian source; crosses, Ixtepeque geochemical obsidian source. All quantities reported in parts per million (ppm).

distilled variation in source data to centroids that generate a mathematical definition of the source within a predetermined vector space. This enabled quantitative comparison of laboratory and PXRF data by using the confidence levels to the second standard deviation. The differences between the data acquired from laboratory and portable XRF instruments suggests that systematic error is introduced by PXRF, and, furthermore, that this error can be corrected through *k*-means cluster analysis if laboratory-sourced standards are available. What can be deduced then is that, based on statistical comparison to a previously established reliable technique, PXRF is itself not a reliable technique. Admittedly, additional comparative analyses must be conducted with other forms of geochemical analysis in order to further test the reliability of PXRF instruments.

5.2. Validity

Measurement of validity has been set forth here to include two levels: the first is the ability of an instrument to differentiate between different geochemical source groups, and the second is how well a technique can answer an archaeological question. We conclude that the first level of validity is indeed met by the PXRF instrument used in this study. As Fig. 8 depicts, the data produced by the PXRF instrument results in distinct clustering utilizing concentrations of Rb, Zr, and Sr. These clusters are diagnostic of the Ixtepeque, El Chayal, and the Pachuca geochemical source groups (Table 2). Indeed, samples were assigned to these groups using the portable data with the same accuracy as when using the laboratory data. However, as the statistical analyses above demonstrate, the actual data between the two techniques is not statistically comparable. What can be said is that the data acquired via PXRF meet the first level of validity put forth by Hughes (1998) for obsidian provenance

research, specifically among Mesoamerican geochemical source groups, in that it can successfully differentiate the El Chayal, Ixtepeque, and Pachuca geochemical groups. The second level of validity is satisfied by allowing us to further posit regional interactions in southern Belize and elsewhere in the Maya lowlands as represented by obsidian source representation. Though portable X-ray fluorescence instrumental analysis may not be a reliable – that is, comparable – technique, it is in fact a valid technique for obsidian provenance research.

A similar conclusion to that presented here was reached by Craig et al. (2007), who state that “[r]aw data generated by one instrument may not be directly comparable to untransformed results produced by another. Regardless, internal consistency is sufficient such that source determinations were identical in all cases” (Craig et al., 2007: 9). Using *k*-means cluster analysis, we were able here to distinguish between inter-instrument systematic and random error. Our study supports a statement similar to that of Craig et al. (2007) for the El Chayal, Ixtepeque, and Pachuca Mesoamerican obsidian geochemical sources.

6. Conclusion

Research presented here demonstrates that intra-instrument consistency is present in the Bruker AXS Tracer 3-V PXRF instrument, as it is able to effectively distinguish between the El Chayal, Ixtepeque, and Pachuca geochemical source groups. In this regard, our PXRF instrument is a valid technique for obsidian provenance studies. However, systematic error is introduced that influences the accuracy, and therefore reliability, of the instrument. The PXRF data are therefore not comparable, statistically, with the LXRF machine utilized in this study. This is to say that for our PXRF instrument there is intra-instrument consistency, but there is also inter-instrument variation when comparing our PXRF and the Berkeley LXRF instruments. Given that PXRF technology has yet to mature, there could remain several differences between various instrument manufactures.

Data from the PXRF instrument, despite inter-instrument variation, has sufficient intra-instrument consistency to distinguish the El Chayal, Ixtepeque, and Pachuca geochemical sources. The use of these sources indicates two primary spheres of interaction: one along the coast and another further inland. This is supported by our geochemical data and is consistent with other research pertaining to regional interactions in Belize during the Classic Maya period.

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