

Comparison of XRF and PXRF for analysis of archaeological obsidian from southern Perú

Nathan Craig ^{a,*}, Robert J. Speakman ^b, Rachel S. Popelka-Filcoff ^{c,d,1}, Michael D. Glascock ^c, J. David Robertson ^d, M. Steven Shackley ^e, Mark S. Aldenderfer ^f

^a Department of Anthropology, The Field Museum of Natural History, 1400 South Lakeshore Drive, Chicago, IL 60605, USA

^b Smithsonian Institute, Museum Support Center, 4210 Silver Hill Road, Suitland, MD 20746, USA

^c Archaeometry Laboratory, Research Reactor Center, University of Missouri, Columbia, MO 65211, USA

^d Department of Chemistry, University of Missouri, 125 Chemistry, 601 South College Avenue, Columbia, MO 65211, USA

^e Department of Anthropology, University of California, Berkeley, CA 94720-3710, USA

^f Department of Anthropology, University of Arizona, Emil W. Haury Building, P.O. Box 210030, Tucson, AZ 85721-0030, USA

Received 15 December 2006; received in revised form 29 January 2007; accepted 31 January 2007

Abstract

Chemical sourcing is becoming an increasingly important component of archaeological investigation. Instruments used for elemental analysis generally must be operated in a controlled laboratory environment. Further, many methods require destruction of a small portion of the objects under investigation. These facts inhibit the application of chemical sourcing studies in a number of research contexts. Use of portable non-destructive instruments would resolve these issues. Sixty-eight obsidian artifacts from the site of Jiskairumoko, in southern Perú, were examined by X-ray fluorescence spectrometry (XRF) and portable X-ray fluorescence spectrometry (PXRF). Results were compared for consistency in terms of source determination and individual element concentrations. Both instruments determined that the same sixty-six artifacts derived from the Chivay obsidian source and both identified the same two artifacts that could not be assigned to source. Individual element comparisons showed significant differences, but these can be resolved through instrument cross calibration, and differences had no bearing on source identification. PXRF was found suitable for determining obsidian sources in southern Perú and for identifying specimens that require more sensitive analytical methods such as, instrumental neutron activation analysis (INAA). Regular use of Chivay at Jiskairumoko suggests consistent trade relationships developed during the Archaic.

© 2007 Elsevier Ltd. All rights reserved.

Keywords: XRF; PXRF; Obsidian; Peru

1. Introduction

This paper examines the application of portable X-ray fluorescence spectrometry (PXRF) for non-destructive *in situ*

source analysis of archaeological obsidian from southern Peru. To accomplish this, data generated by PXRF are compared to results generated by laboratory X-ray fluorescence (XRF).

Chemical characterization of archaeological materials is a routine component of provenance and/or technological studies of obsidian (Burger et al., 2000), pottery, metal, ochre (Hovers et al., 2003), monumental stone (Ogburn, 2004), and other inorganic archaeological materials. Comparing trace element compositions of archaeological artifacts to those obtained from known geologic source samples form the basis for identifying raw material sources (Cann and Renfrew,

* Corresponding author. Tel.: +1 312 714 4785.

E-mail addresses: ncraig@fieldmuseum.org (N. Craig), speakmanj@si.edu (R.J. Speakman), rachel.popelka-filcoff@nist.gov (R.S. Popelka-Filcoff), glascockm@missouri.edu (M.D. Glascock), robertsonjo@missouri.edu (J.D. Robertson), shackley@berkeley.edu (M.S. Shackley), aldender@email.arizona.edu (M.S. Aldenderfer).

¹ Current Address: NIST, 100 Bureau Drive, Stop 8395, Gaithersburg, MD 20899-8395, USA.

1964). A number of analytical methods have been used in provenance studies during the past 50 years. Among these, the most successful are instrumental neutron activation analysis (INAA), XRF, and inductively coupled plasma-mass spectrometry (ICP-MS). INAA has a longer history and its advantages include: precision, accuracy, and reliable bulk analysis of the sample. In the majority of cases, INAA is more sensitive than XRF. INAA is also more matrix independent and less susceptible to geometric effects than XRF. However, INAA requires access to a nuclear reactor, a longer analytical time, additional sample preparation, and the destruction of a small fragment of the artifact for irradiation. XRF has the advantage of non-destructive analysis for a given sample, but has limited detection capability compared to INAA. ICP-MS of solutions has the advantage of sensitivity, on the order of that for INAA, but requires sample dissolution which can be difficult for many inorganic materials, especially those with high silica content like obsidian. In contrast, while laser ablation ICP-MS requires minimal sample preparation and the analysis is minimally invasive to the artifact, the analysis is frequently semi-quantitative at best.

In provenance studies, non-destructive analytical techniques are preferable to destructive methods provided that the method allows enough resolution in the final data to characterize possible groups. *In situ* non-destructive analysis is clearly preferable for museum and other protected collections, especially if the collections are in the process of repatriation. Portable methods are also preferable in foreign research contexts. Intra- and inter-national artifact transport to laboratories often entail elaborate bureaucratic procedures and mandatory fees. Artifact transport can heighten the chance of theft, and increase the risk of damage. Ideally, equipment for conducting chemical characterization studies would be mobile, thus permitting data collection where the artifacts are stored. In addition, the non-destructive method would allow precise and accurate measurement, leaving the artifact intact. Non-destructive portable analytical instrumentation would comply with curation and conservation desires in museums and institutes of many developing nations.

Research reported here is part of a larger effort to understand ancient patterns of regional trade in the Andean region through chemical sourcing. Obsidian is an ideal archaeological material for examining resource procurement patterns and exchange networks because artifacts made from obsidian can usually be linked to their sources with a high degree of reliability. Provenance studies of obsidian have several advantages over most other archaeological materials such as ceramics. First, obsidian sources are restricted to areas where volcanic activity occurred, or to locations where secondary deposits were created by other erosional and depositional processes. Second, obsidian sources tend to be chemically homogeneous, and at the same time, the individual sources have chemical “signatures” that are characteristic of the source. Measurements and analysis of trace element abundances have demonstrated that individual sources can be differentiated from one another. However, the characteristic elements for each group of sources are likely to differ in

a given geographic region (Glascock et al., 1998). With sufficient field and laboratory work, the spatial extent of a particular geochemical type of obsidian can be established such that a “source” can be defined. Finally, obsidian artifacts are nearly indestructible in most archaeological contexts. Thus, it is possible to compare the compositional fingerprints of artifacts to those of sources and successfully determine the correct source for each artifact with nearly 100% confidence.

Among the various analytical methods employed in obsidian provenance studies, X-ray fluorescence spectrometry has been widely used since the 1960s (Heizer et al., 1965; Jack and Heizer, 1968; Parks and Tieh, 1966), and has emerged as a powerful analytical tool for determining the chemical compositions of a variety of archaeological materials. The vast majority of archaeometric-based XRF studies have focused on compositional analyses of obsidian and metals (Carter, 1971; Cobean et al., 1971; Heizer et al., 1965; Shackley, 1988, 1990, 1991, 1992, 1995, 1998, 1994, 2002a,b; Shackley et al., 1996; Shackley and Tucker, 2001) and to a lesser extent pottery (Adan-Bayewitz et al., 1999; Culbert and Schwalbe, 1987; Garcia-Heras et al., 1997; Hedges and Moorey, 1975; Kuhn, 1987; Poole and Finch, 1972; Trigger et al., 1980).

In most obsidian provenance studies, the ability to use compositional differences to discriminate between different sources depends, to a certain extent, on the number of elements measured. Conventional analytical techniques, such as INAA and XRF are capable of measuring 10–30 elements in obsidian with excellent precision, therefore numerous combinations of trace and major elements are available for comparing differences between sources. However, the main requirements for success in any obsidian provenance study is that all sources have been located and characterized, and that the internal variation measured within the sources be smaller than the compositional differences measured between the sources (Glascock et al., 1998).

Studies of Mesoamerican (Glascock et al., 1994) and New Mexican (Glascock et al., 1999) and Andean (Burger and Asaro, 1977, 1978, 1993; Burger et al., 1994, 1998, 2000) obsidian have consistently demonstrated that laboratory-based XRF can produce results analytically comparable to abbreviated INAA. Comparative research has revealed that in the central Andes the more rapid and non-destructive XRF instrumentation can measure a sufficient number of elements to discriminate sources.

Advances in analytical instrumentation during the last several years have facilitated the development of small PXRF instruments. A major advantage of PXRF is that instruments can be transported easily into the field or to museums, thereby permitting multi-element analyses of archaeological materials in non-traditional laboratory environments. PXRF has witnessed extensive geological and environmental applications since at least the early 1980s (Nissenbaum et al., 1981; Pandey et al., 1983; Rhodes and Rautala, 1983) and its use has proliferated since the mid-1990s (Bachofer, 2004; Bernick and Campagna, 1995; Clark et al., 1998; Kalnicky and Singhvi,

2001; Potts et al., 1995, 1997; Thomsen and Schatzlein, 2002). Nonetheless, relatively few archaeological applications exist (Morgenstein and Redmount, 2005; Romano et al., 2005; Wager et al., 2002; Williams-Thorpe et al., 2003). Additionally, many earlier applications of PXRF used radioactive isotopes as the excitation source, which hinders transportation of the equipment by commercial airlines and across international boundaries. However, developments in high-precision thermoelectrically-cooled detectors and miniature X-ray tubes have greatly enhanced the potential of PXRF for applications in archaeology and in other disciplines. If PXRF can be developed such that the results are comparable to standard laboratory XRF, it could greatly stimulate chemical characterization and sourcing studies by facilitating *in situ* and on-site analysis.

2. Archaeological context

Previous chemical sourcing studies reveal that long-distance transport of obsidian is an important aspect of Andean cultures as early as 8015–7581 cal BCE at the site of Asana in the Rio Osmore drainage (Aldenderfer, 1999, 1998; Burger et al., 2000). By the Middle Horizon (A.D. 600–1000) regular formalized trade routes that incorporated the distribution of obsidian had developed throughout vast areas of the Peruvian Andes.

The distribution of obsidian during the Archaic is far from uniform (Burger and Asaro, 1978). In the northern highland regions from Lake Junín and beyond, the recovery of obsidian artifacts is a rare occurrence. To the south in the Huancayo/Ayacucho region, obsidian artifacts appear more abundant in Archaic contexts. Obsidian artifacts are found in Archaic contexts at Jiskairumoko in the Rio Ilave of the southwestern Lake

Titicaca Basin (Craig, 2005), at Ch'uxuquilla on the Island of the Sun (Stanish et al., 2002), and at Qillqatani in the Rio Chila (Frye et al., 1998) and at Asana in the Rio Osmore (Aldenderfer, 1999, 1998).

The expansion of XRF chemical sourcing studies has resulted in a greater understanding of regional patterns. Chivay appears to have been an important obsidian source for most of southern Perú and the Titicaca Basin (Burger et al., 2000; Stanish et al., 2002).

Jiskairumoko is an Archaic-Formative transition site located in the upper Rio Ilave drainage of the Lake Titicaca Basin, Perú (Craig, 2005) (Fig. 1). The site chronology has been determined by 30 radiocarbon dates that demonstrate it was occupied from as early as 3300 B.C.E. to as late as 1300 B.C.E.

The initial occupation of Jiskairumoko currently represents the earliest evidence for reduced residential mobility in the region. The site occupation spans a period during which there was an increasing reliance on domesticated plants and animals (Aldenderfer, 1998, 2002; Eisentraut, 1998; Murray, 2005). Temporally sensitive projectile point forms suggest a decrease in the rate of point production during this time (Craig, 2005; Craig and Aldenderfer, *in press*). A similar pattern has been observed during the Terminal Archaic in the Salar de Atacama where it was interpreted to reflect an increasing reliance on animal husbandry and a declining investment in hunting (Nuñez, 1982: 151–152). Excavation at Jiskairumoko indicates that during this period of decreased projectile point production in the Rio Ilave there is a marked increase in the number of obsidian artifacts (Craig, 2005). Sixty-eight obsidian tools were recovered from excavations at Jiskairumoko. Fewer projectile points were produced overall, but a significantly greater

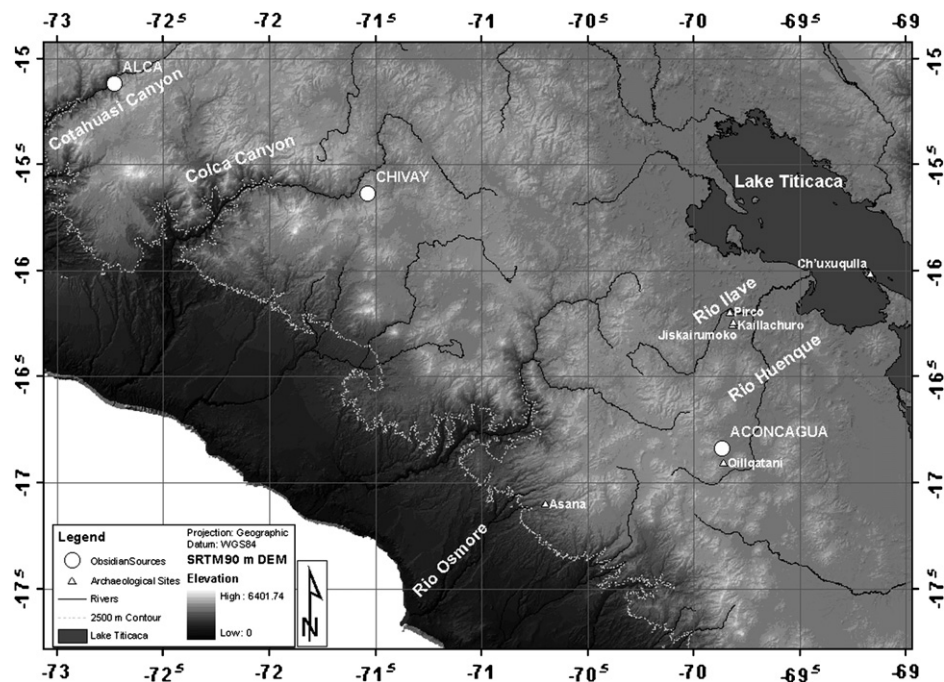


Fig. 1. Relevant obsidian sources and key south-central Andean archaeological sites mentioned in the text.

proportion of them were made out of obsidian. If Chivay was used exclusively then it suggests the formation of regular trade routes. If the artifacts derive from a variety of sources like Aconcagua and Alca it suggests more varied regional economic articulation.

Seeking to determine the sources for obsidian artifacts, all sixty-eight obsidian tools from Jiskairumoko were temporarily exported from Perú to the United States. While in the U.S. these artifacts were analyzed by Shackley et al. (2004) using a laboratory XRF at the University of California, Berkeley. In 2005, as part of a collaborative program to expand materials characterization studies in the Titicaca Basin, Speakman and Popelka-Filcoff visited Puno, Perú with PXRF equipment and reanalyzed the same sixty-eight obsidian artifacts from Jiskairumoko. Are these two methods of materials characterization comparable?

3. Sample preparation and analysis

3.1. Laboratory XRF

All archaeological samples were analyzed whole. The results presented here are quantitative in that they are derived from “filtered” intensity values as a ratio to the appropriate X-ray continuum regions through a least squares fitting formula rather than plotting the proportions of the net intensities in a ternary system (McCarthy and Schamber, 1981; Schamber, 1977). Through the analysis of international rock standards these data allow for inter-instrument comparison with a predictable degree of certainty (Hampel, 1984).

The trace element analyses were performed in the Archaeological XRF Laboratory, Department of Earth and Planetary Sciences, University of California, Berkeley, using a Spectrace/ThermoNoran™ QuanX energy dispersive X-ray fluorescence spectrometer. The spectrometer is equipped with an air cooled Cu X-ray target with a 125 micron Be window, an X-ray generator that operates from 4–50 kV/0.02–2.0 mA at 0.02 increments, using an IBM PC based microprocessor and WinTrace™ reduction software. The X-ray tube was operated at 30 kV, 0.14 mA, using a 0.05 mm (medium) Pd primary beam filter in an air path at 200 s livetime to generate X-ray intensity $K\alpha$ -line data for elements titanium (Ti), manganese (Mn), iron (as FeT), thorium (Th) using $L\alpha$ line, rubidium (Rb), strontium (Sr), yttrium (Y), zirconium (Zr), and niobium (Nb). Trace element intensities were converted to concentration estimates by employing a least-squares calibration line established 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). Line fitting is linear (XML) for all elements but Fe where a derivative fitting is used to improve the fit for the high concentrations of iron and thus for all the other elements. Further details concerning the petrological choice of these elements in obsidian is available in Shackley (Glascok et al., 1998; Hughes and Smith, 1993; Mahood and Stimac, 1990; Shackley, 1995, 2004). Specific standards used for the best fit regression calibration for elements Ti through Nb include G-2 (basalt), AGV-1 (andesite), GSP-1, SY-2 (syenite), BHVO-1 (hawaiite), STM-1 (syenite), QLO-1 (quartz latite), RGM-1 (obsidian), W-2 (diabase), BIR-1 (basalt), SDC-1 (mica schist), TLM-1 (tonalite), SCO-1 (shale), all US Geological Survey standards, BR-N (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). In addition to the values reported here, Ni, Cu, and Ga were measured, but these are rarely useful in discriminating glass sources and are not generally reported.

The data from the WinTrace software were translated directly into Excel for Windows software for manipulation and import into SPSS for Windows for statistical analyses. In order to evaluate these quantitative determinations, machine data were compared to measurements of known standards during each run. RGM-1 is analyzed during each sample run for obsidian artifacts to check machine calibration (see Table 1). Source assignments were made with reference to the source standard library at Berkeley and published and unpublished data, mostly supplied by Glascok at MURR, University of Missouri.

3.2. PXRF

As with the Berkeley analysis, the archaeological samples were analyzed whole. The PXRF instrument is comprised of several components including: an X-ray source (Amptek Eclipse II, Ag anode, 0–30 keV, 1–100 μ A with an external power source), a detector (Amptek XR-100CR, 13 mm² area, 300 μ m thickness, with an external power source), a MCA (Amptek MCA8000A), sets of silver-plated copper X-ray collimators, an aluminum collimator for the detector, a laptop computer, and two small laser pointers (used to align the sample with the X-ray beam). The detector is

Table 1
Elemental concentrations for the measurements of the RGM1 standards

Sample	Ti	Mn	Fe	Zn	Rb	Sr	Y	Zr	Nb	Source
RGM1-H1	1530	339	13175	31	156	110	19	222	10	standard
RGM1-H1	1573	341	13258	36	151	111	21	219	11	standard
RGM1-H1	1480	337	13341	38	151	114	19	225	5	standard
RGM1-H1	1585	344	13231	39	151	111	19	224	9	standard

All measurements in parts per million (ppm).

thermoelectrically cooled, and the X-ray source also is cooled internally. The total system is relatively compact and weighs about 8 kg.

The X-ray tube was operated at 30 kV, 0.02 mA in an air path for 200 s livetime to generate X-ray intensity $K\alpha$ -line data for elements manganese (Mn), iron (as FeT), rubidium (Rb), strontium (Sr), yttrium (Y), zirconium (Zr), and niobium (Nb).

Due to the irregularity of the sample sizes and shapes, the experimental setup is mounted to a specially fabricated table to hold the components together in a fixed geometry and at a distance consistent for each measurement. Through experiments with standards completed prior to the analysis of artifacts, the optimum angle between the X-ray source and the detector was determined to be 45 degrees. Samples were mounted 20 mm from the X-ray beam in a sample holder that can be adjusted in the x and y direction for the optimal positioning of the sample. For each analysis, the smoothest part of the sample was selected to minimize surface effects and X-ray scatter and optimize the count rate. The area analyzed on each sample is approximately 10 mm in diameter. Obsidian samples were analyzed at 25 keV, at 20 micro-amperes for 200 s each.

Thin film standards of single and multiple elements deposited on mylar (Micromatter, Inc.) were used for the energy calibration of the instrument. Standards used in the analysis included polished samples of obsidian from known sources (Alca, Chivay and Quispisisa). These standards were used at the beginning and end of the daily sample collection to assure stability of the system and monitor instrument drift as well as to determine the precision and accuracy of the measurements. The XRF-FP software, provided by Amptek and CrossRoads Scientific, identifies peaks and calculates quantitative data for the elemental compositions of the samples. The XRF-FP software uses a fundamental parameters method to calculate the concentrations of the elements in the samples. Within the software, values for each analysis were constrained to 100%.

4. Results

4.1. Archaeological results

Both laboratory XRF (Table 2) and PXRF (Table 3) analyses arrived at identical conclusions. Each instrument determined that the same sixty-six ($n = 68$) obsidian artifacts were derived from material obtained from the Chivay source (Figs. 2 and 3). Two samples (171 and 695) produced ambiguous results in both XRF and PXRF sourcing programs. Initially, it appeared that the two samples might be from the Alca-2 source (Shackley et al., 2004) located in the Cotahuasi Valley (Jennings and Glascock, 2002). Additional examination of the data showed these samples fell outside the known range of variation for Alca-2. Small fragments of both artifacts were analyzed by INAA at MURR to characterize a broader range of elements (Table 4). INAA results indicate that sample 171 is most similar to the Alca-3 source, but it is nonetheless a poor match. Sample 171 may represent unknown variation

in the Alca volcanic field or the sample may originate from a previously undocumented source. Sample 695 was a perfect match with a single artifact from Khonko Wankane, Bolivia (Giesso, 2000). The source of this obsidian remains unknown, and both non-Chivay artifacts originate from sources that apparently were not exploited at a large scale in prehistory. Chivay obsidian was used in the earliest contexts of reduced residential mobility and dominated the assemblage throughout the site's occupation, which lasted from the end of the Late Archaic to the Early Formative.

4.2. Method comparison results

The most archaeologically critical criterion is assignment to source. Several quantitative comparisons of instrument results were also performed for exploratory purposes since PXRF remains a developing analytical technique.

XRF and PXRF values were compared for six elements (Mn, Fe, Rb, Sr, Zn, and Zr) that were quantified by both instruments for the sixty-eight obsidian artifacts that were analyzed. Principal components and Varimax rotated factor analysis (Padilla et al., 2006: Table 4) were used to explore multivariate patterning. Consistency between XRF and PXRF was evaluated by means of: linear regression of individually paired element comparisons (Padilla et al., 2006: 287, Fig. 2), the paired t -test (Westgard, 1998; Westgard and Hunt, 1973), and Z -scores.

PCA of XRF shows that most of the variance is explained by components one through three (Tables 5 and 6). PC1 eigenvectors show the highest loading for Sr with positive correlations with Zr, Fe, and Zn and negative correlations with Rb and Mn. PC2 shows high loadings for Mn with positive correlations with Rb and Fe. PC3 shows a negative correlation between Zn and Zr. Varimax factor rotation (Table 7) strengthened the negative correlations between Sr and Rb in Factor 1, and strengthened the positive correlations between Zr and Fe in Factor 2.

PCA of PXRF shows most of the variation is explained by components one through four (Tables 8 and 9). PC1 shows a strong correlation between Mn and Rb and negative correlations with Fe and Sr. PC2 shows a strong correlation with Zr and Sr and a negative correlation with Fe. PC3 shows a negative correlation with Sr and Zr, while PC4 is dominated by Zn. Varimax factor rotation (Table 10) strengthened negative correlations between Rb and Fe in Factor 1.

Correlation analysis of individual element to element comparisons between XRF and PXRF were weakly positive in four cases (Table 11). Zn produced a weak negative correlation, but this could be due to chance ($p > 0.05$). Zr produced an exceptionally weak positive correlation but this could very easily be due to chance ($p > 0.5$). Element by element paired t -tests comparing concentrations between XRF and PXRF showed significant difference in all elements ($p < 0.001$) except for Mn (Table 12). Z -scores also indicated significant differences between XRF and PXRF in all elements except for Mn (Table 13).

Correlation, and formal hypothesis testing by means of paired t -tests and Z -scores, show that elemental concentrations

Table 2
Elemental concentrations for the archaeological obsidian samples characterized by XRF

ID	Ti	Mn	Fe	Zn	Rb	Sr	Y	Zr	Nb	Source
14	971	637	6489	40	243	47	16	83	23	Chivay
33	909	770	6749	41	247	44	21	86	24	Chivay
83	925	653	6455	40	249	49	17	85	22	Chivay
104	866	657	6360	39	234	47	17	84	26	Chivay
107	953	648	5833	40	230	44	14	77	20	Chivay
137	905	706	6423	44	249	48	18	84	25	Chivay
167	891	734	6539	44	245	41	15	88	10	Chivay
171	1199	566	8488	53	147	194	8	153	12	Alca-2
176	995	713	6781	48	251	52	20	75	26	Chivay
199	848	644	6334	35	239	50	17	82	19	Chivay
237	936	631	6099	39	234	45	19	89	25	Chivay
246	968	685	6215	38	243	51	19	77	24	Chivay
248	872	628	6178	42	242	47	22	86	12	Chivay
276	1003	644	6532	41	251	42	19	87	23	Chivay
277	944	663	6419	34	246	43	25	85	17	Chivay
300	916	686	6645	37	259	46	19	87	20	Chivay
309	942	632	5985	39	214	50	21	75	19	Chivay
343	855	646	5985	35	226	45	23	82	24	Chivay
347	680	460	5339	29	200	42	17	68	17	Chivay
363	882	777	6824	42	255	42	18	76	20	Chivay
367	1001	668	6199	42	224	43	18	83	21	Chivay
394	993	699	6547	36	245	48	15	83	33	Chivay
396	986	687	6454	39	246	47	17	83	24	Chivay
399	915	652	6393	45	240	45	18	77	18	Chivay
436	949	700	6140	43	234	45	19	83	23	Chivay
462	921	625	6195	35	238	42	22	81	20	Chivay
465	828	686	6245	37	237	45	18	84	22	Chivay
485	926	715	6695	43	254	50	16	87	11	Chivay
487	953	660	6428	40	244	43	15	81	24	Chivay
494	1014	682	6295	38	236	50	19	86	21	Chivay
499	993	752	6716	40	267	49	14	86	20	Chivay
526	891	689	6360	41	248	46	17	79	21	Chivay
544	905	725	6801	48	249	50	17	92	20	Chivay
591	914	650	6066	39	235	46	15	79	18	Chivay
607	934	744	6761	41	257	50	19	83	28	Chivay
622	1029	742	6514	39	255	45	20	81	24	Chivay
625	883	615	5929	45	223	43	12	82	19	Chivay
630	896	652	6292	43	236	46	10	84	27	Chivay
634	900	653	6209	39	234	41	18	74	25	Chivay
645	945	727	6794	37	262	48	14	89	16	Chivay
646	958	750	6701	39	253	50	18	80	21	Chivay
662	772	668	6045	42	226	47	23	89	11	Chivay
664	978	773	6726	42	256	50	21	83	23	Chivay
665	906	738	6528	36	252	49	17	86	10	Chivay
671	927	698	6519	39	247	43	26	83	22	Chivay
676	872	664	6410	41	248	48	21	86	21	Chivay
681	841	730	6571	39	239	45	20	75	19	Chivay
686	939	656	6511	40	239	45	16	77	31	Chivay
687	1073	680	6287	35	230	38	22	86	18	Chivay
694	951	719	6519	44	251	44	19	84	22	Chivay
695	882	555	6068	48	131	178	18	65	5	Alca-2?
723	891	608	5948	29	225	44	17	79	18	Chivay
725	855	723	6418	40	247	51	16	86	22	Chivay
745	857	712	6170	42	243	43	16	86	22	Chivay
751	926	737	6352	42	246	49	19	80	13	Chivay
752	1008	705	6469	42	240	45	15	88	26	Chivay
766	878	624	6189	43	223	39	15	80	17	Chivay
767	959	668	6534	39	241	48	20	82	18	Chivay
773	906	707	6518	38	247	47	16	80	25	Chivay
783	1076	857	6921	43	253	48	23	74	22	Chivay
786	1092	684	6512	57	249	49	15	74	27	Chivay
793	814	644	6290	43	250	42	23	78	20	Chivay
841	912	585	5946	36	216	41	16	83	10	Chivay
846	964	582	6222	42	222	43	15	81	22	Chivay
853	873	613	5903	36	236	44	20	75	28	Chivay
858	963	706	6412	36	232	50	26	76	25	Chivay
860	920	662	6388	38	243	42	20	83	12	Chivay
899	939	786	6845	48	261	49	17	90	14	Chivay

Table 3
Elemental concentrations for the archaeological obsidian samples characterized by PXRF

ID	Sr	Rb	Zr	Zn	Fe	Mn	Source
14	49	248	126	37	4865	674	Chivay
33	48	259	128	34	4869	661	Chivay
83	68	253	78	29	4900	671	Chivay
104	56	240	80	30	4932	661	Chivay
107	36	260	121	33	4882	668	Chivay
137	60	225	98	34	4908	675	Chivay
167	53	249	98	32	4886	681	Chivay
171	155	117	161	25	5130	412	Unknown
176	49	264	125	33	4852	677	Chivay
199	52	280	132	27	4832	677	Chivay
237	61	261	121	31	4865	661	Chivay
246	74	271	118	31	4802	704	Chivay
248	49	242	91	38	4901	678	Chivay
276	85	275	101	34	4797	709	Chivay
277	95	273	106	33	4771	722	Chivay
300	50	310	119	35	4831	655	Chivay
309	41	245	108	32	4904	671	Chivay
343	67	249	121	34	4843	686	Chivay
347	58	300	172	35	4779	656	Chivay
363	55	228	116	35	4841	725	Chivay
367	93	241	131	32	4826	678	Chivay
394	55	224	109	27	4950	635	Chivay
396	58	247	119	32	4873	670	Chivay
399	77	265	147	30	4821	660	Chivay
436	96	272	131	33	4805	662	Chivay
462	68	253	79	35	4897	667	Chivay
465	82	267	121	32	4816	683	Chivay
485	38	233	131	29	4906	662	Chivay
487	63	250	139	34	4833	681	Chivay
494	71	270	129	35	4827	668	Chivay
499	72	282	70	36	4838	701	Chivay
526	81	286	85	32	4855	660	Chivay
544	77	258	83	32	4873	676	Chivay
591	72	282	70	36	4838	701	Chivay
607	79	254	98	29	4856	684	Chivay
622	65	268	88	35	4834	710	Chivay
625	72	250	101	39	4874	664	Chivay
630	36	246	94	29	4903	692	Chivay
634	62	275	95	33	4849	686	Chivay
645	51	240	85	31	4901	692	Chivay
646	46	225	94	29	4949	657	Chivay
662	79	264	112	31	4821	694	Chivay
664	87	302	122	32	4786	671	Chivay
665	58	252	122	30	4861	677	Chivay
671	87	302	122	32	4786	671	Chivay
676	64	250	91	36	4856	703	Chivay
681	63	262	124	32	4826	693	Chivay
686	39	240	150	30	4883	658	Chivay
687	48	244	100	39	4904	665	Chivay
694	90	282	181	30	4733	684	Chivay
695	238	173	130	27	4864	568	Unknown
723	69	265	106	37	4840	684	Chivay
725	76	267	107	32	4858	660	Chivay
745	51	246	77	28	4890	708	Chivay
751	62	243	99	29	4927	640	Chivay
752	74	270	126	32	4854	644	Chivay
766	44	268	126	34	4852	675	Chivay
767	48	208	98	31	4951	664	Chivay
773	64	244	118	29	4871	674	Chivay
783	57	239	169	33	4822	681	Chivay
786	48	280	131	36	4823	682	Chivay
793	41	229	108	34	4901	687	Chivay
841	78	262	126	39	4825	670	Chivay

Table 3 (continued)

ID	Sr	Rb	Zr	Zn	Fe	Mn	Source
846	68	240	104	34	4862	692	Chivay
853	63	247	82	34	4917	656	Chivay
858	49	234	115	35	4897	670	Chivay
860	53	238	135	32	4879	662	Chivay
899	67	224	64	31	4923	692	Chivay

differ significantly. These differences are not surprising given: variation in the quantitative methods implemented in the two software packages, use of different obsidian standards by each laboratory, differences in excitation sources, and differences in the Compton and coherent scatter (background) between the two systems. However, when the measured elements are aggregated correlations are high. This suggests that the two instruments are generally comparable, but individual element readings are only weakly correlated.

5. Conclusions

Laboratory XRF and PXRF instruments both indicate that the residents of Jiskairumoko were obtaining obsidian from Chivay which is a distant non-local source. The Aconcagua source contains obsidian of suitable quality and is located

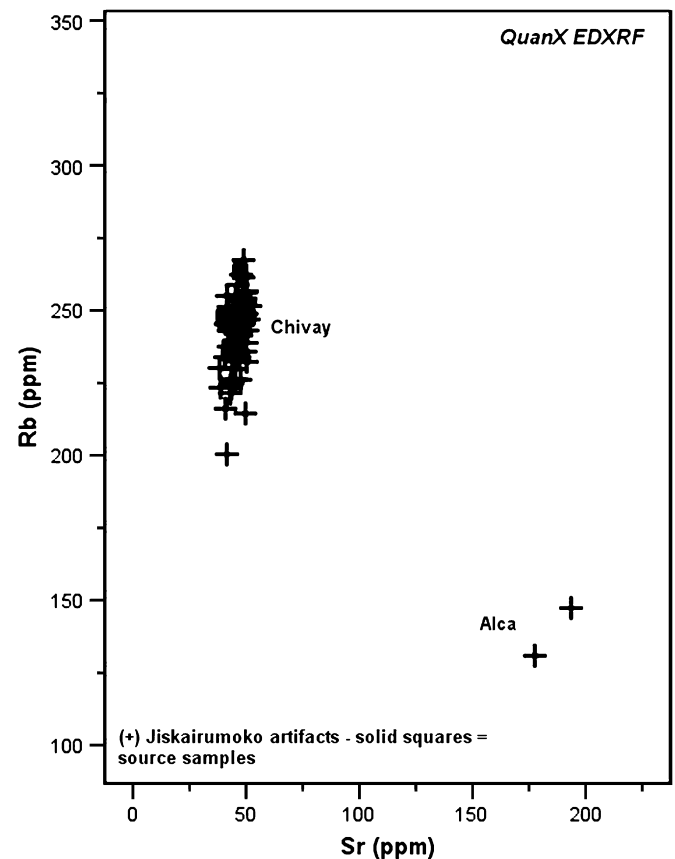


Fig. 2. Sr versus Rb bivariate plot of the obsidian archaeological specimens and Chivay source standards submitted by Tripcevich. Greater dispersion of the artifacts due to sample size limits of EDXRF.

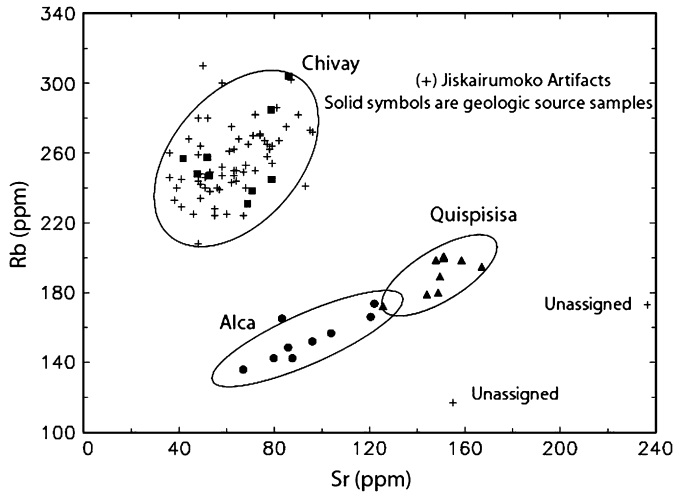


Fig. 3. Sr versus Rb bivariate plot of the obsidian archaeological specimens and Chivay source standards submitted by Tripcevich. Greater dispersion of artifacts due to sample size limits of PXRf.

close to Jiskairumoko, but the more distant Chivay source is much more heavily represented. This consistent patterning of use suggests the formation of regular trade articulations between the Titicaca Basin and the Chivay source in the Colca Canyon near Arequipa.

Temporally sensitive projectile points (Klink and Aldenderfer, 2005) recovered from surface survey (Klink, 2005) and

radiocarbon dated excavation in the Ilave (Craig, 2005) and the Island of the Sun (Stanish et al., 2002) show that more regular use of Chivay obsidian emerged in the Titicaca Basin during the end of the Late Archaic and intensified during the Terminal Archaic.

This trend appears to develop contemporaneous with the earliest evidence for corralling in the region (Aldenderfer, 2002: 394; Aldenderfer, 1998: 131, 266; Dransart, 1991, 2002; Hesse, 1982; Nuñez, 1982: 150; Wheeler, 1999) and likely serves as initial indication of the development of regional camelid caravan networks (Craig and Aldenderfer, in press). Pastoralism and caravan systems leave ephemeral archaeological remains (Kuznar, 1995, 2001). Particularly during early periods of development, the study of long distance caravan systems is more readily addressed by a systematic robust materials analysis program applied to a broad range of sources and final products. These results are only preliminary, but the potential to use portable equipment should significantly foster the growth of chemical sourcing studies, which is necessary to rigorously evaluate the development Andean caravan networks. Additional comparative and exploratory research in the region is necessary to address these questions in a rigorous manner.

Experimental comparison of XRF and PXRf characterization of Andean obsidian demonstrates that archaeologically consistent results were obtained using both instrumental methods. Despite differences in five of six individual elemental raw concentration values, results are easily normalized by

Table 4

Comparison of mean and Std Dev determined by INAA for Chivay, Alca-1, Alca-2, Alca-3, sample 695, sample 171, and artifact KOWA02 from Khonko Wankane, Bolivia

Element	Chivay (n = 21) s.d.	Alca-1 (n = 36) s.d.	Alca-2 (n = 2) s.d.	Alca-3 (n = 2) s.d.	#171	#695	KOWA02
Ba (ppm)	163 ± 15	995 ± 25	952 ± 10	1018 ± 3	894	1209	1195
La (ppm)	19.0 ± 0.3	28.8 ± 0.8	43.5 ± 0.4	36.2 ± 0.1	38.2	21.5	21.9
Lu (ppm)	0.32 ± 0.02	0.19 ± 0.01	0.21 ± 0.01	0.22 ± 0.02	0.26	0.26	0.21
Nd (ppm)	21.3 ± 4.2	21.8 ± 4.7	31.0 ± 0.9	19.1 ± 0.3	21.2	18.0	16.6
Sm (ppm)	4.15 ± 0.10	3.50 ± 0.13	4.20 ± 0.07	3.81 ± 0.34	3.95	3.53	3.53
U (ppm)	7.86 ± 0.70	3.39 ± 0.27	3.80 ± 0.66	2.76 ± 0.60	2.89	4.23	3.90
Yb (ppm)	1.61 ± 0.10	1.02 ± 0.04	1.07 ± 0.02	1.29 ± 0.04	1.12	1.11	1.06
Ce (ppm)	41.0 ± 0.4	57.6 ± 1.5	80.0 ± 0.2	69.2 ± 0.1	66.9	41.8	42.7
Co (ppm)	0.34 ± 0.05	0.23 ± 0.01	0.44 ± 0.03	n.d.	0.30	0.12	0.13
Cs (ppm)	9.91 ± 0.11	2.83 ± 0.08	2.71 ± 0.10	3.00 ± 0.10	4.69	5.12	5.23
Eu (ppm)	0.28 ± 0.01	0.56 ± 0.18	0.65 ± 0.01	1.00 ± 0.01	0.70	0.71	0.72
Fe (ppm)	4880 ± 83	5422 ± 101	7580 ± 182	8050 ± 59	6692	4588	4757
Hf (ppm)	3.73 ± 0.07	3.60 ± 0.10	4.76 ± 0.12	4.58 ± 0.03	4.48	2.82	2.83
Rb (ppm)	244 ± 4	136 ± 2	141 ± 1	125 ± 1	140	124	128
Sb (ppm)	0.89 ± 0.05	0.17 ± 0.02	0.12 ± 0.00	0.27 ± 0.01	0.25	0.44	0.42
Sc (ppm)	3.08 ± 0.05	1.77 ± 0.03	1.94 ± 0.00	1.85 ± 0.01	2.25	1.61	1.62
Sr (ppm)	49 ± 10	113 ± 21	242 ± 13	320 ± 7	174	194	269
Ta (ppm)	1.75 ± 0.02	0.94 ± 0.01	0.95 ± 0.01	0.90 ± 0.01	0.84	1.05	1.03
Tb (ppm)	0.47 ± 0.06	0.34 ± 0.03	0.33 ± 0.02	0.39 ± 0.02	0.41	0.41	0.38
Th (ppm)	23.2 ± 0.3	13.7 ± 0.2	16.0 ± 0.1	14.0 ± 0.1	14.5	9.9	10.0
Zn (ppm)	35 ± 6	43 ± 5	50 ± 1	48 ± 1	41	46	58
Zr (ppm)	132 ± 9	116 ± 8	166 ± 3	160 ± 9	165	92	111
Al (%)	6.81 ± 0.29	6.92 ± 0.26	7.34 ± 0.03	7.28 ± 0.07	7.65	7.38	7.20
Cl (ppm)	396 ± 106	678 ± 97	653 ± 96	706 ± 40	642	398	597
Dy (ppm)	2.66 ± 0.31	1.93 ± 0.39	1.80 ± 1.01	2.00 ± 0.24	1.78	2.32	1.91
K (%)	3.69 ± 0.19	3.69 ± 0.18	3.60 ± 0.05	3.42 ± 0.05	3.74	4.06	3.91
Mn (ppm)	710 ± 12	476 ± 5	459 ± 1	564 ± 5	562	575	560
Na (%)	3.06 ± 0.05	3.16 ± 0.06	3.34 ± 0.03	3.31 ± 0.02	3.13	3.14	3.10

Table 5
Principal components eigenvalues for laboratory XRF results

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	2.636	43.937	43.937	2.636	43.937	43.937	1.717	28.624	28.624
2	2.038	33.973	77.910	2.038	33.973	77.910	1.492	24.867	53.490
3	.744	12.395	90.306	.744	12.395	90.306	1.246	20.773	74.263
4	.397	6.611	96.916	.397	6.611	96.916	1.097	18.278	92.541
5	.132	2.205	99.121	.132	2.205	99.121	.395	6.580	99.121
6	.053	.879	100.000						

Table 6
Principal components eigenvectors for laboratory XRF results

	Component				
	1	2	3	4	5
Mn (XRF)	-.167	.904	.106	.318	-.204
Fe (XRF)	.686	.654	-.183	.111	.213
Zn (XRF)	.596	.356	.654	-.299	-.017
Rb (XRF)	-.618	.741	-.096	-.151	.133
Sr (XRF)	.900	-.255	.090	.306	.039
Zr (XRF)	.768	.229	-.504	-.278	-.160

Table 7
Varimax factor rotation of laboratory XRF principal components

	Component				
	1	2	3	4	5
Mn (XRF)	-.316	.042	.934	.131	.088
Fe (XRF)	.133	.652	.406	.282	.550
Zn (XRF)	.153	.158	.117	.965	.078
Rb (XRF)	-.874	-.060	.435	-.045	.148
Sr (XRF)	.882	.299	-.070	.229	.234
Zr (XRF)	.188	.973	-.032	.117	.044

Rotation converged in 6 iterations.

Table 8
Principal components eigenvalues for PXRF results

Component	Initial Eigenvalues		
	Total	% of Variance	Cumulative %
1	2.799	46.658	46.658
2	1.421	23.688	70.346
3	.772	12.874	83.220
4	.713	11.876	95.096
5	.294	4.903	99.999
6	4.450E-05	.001	100.000

Table 9
Principal components eigenvectors for PXRF results

	Component				
	1	2	3	4	5
Sr (PXRF)	-.506	.544	.667	.025	.045
Rb (PXRF)	.873	.237	.017	-.159	-.396
Zr (PXRF)	-.149	.809	-.531	.174	.104
Mn (PXRF)	.611	-.130	.138	.768	.010
Fe (PXRF)	-.776	-.593	-.153	.112	-.101
Mn (PXRF)	.885	-.216	.046	-.232	.338

Table 10
Varimax factor rotation of PXRF principal components

	Component				
	1	2	3	4	5
Sr (PXRF)	-.081	.977	.080	-.118	-.137
Rb (PXRF)	.953	-.209	-.035	.163	.143
Zr (PXRF)	.061	.078	.989	-.064	-.090
Mn (PXRF)	.186	-.122	-.066	.966	.119
Fe (PXRF)	-.779	-.168	-.272	-.172	-.511
Mn (PXRF)	.422	-.353	-.256	.176	.775

Rotation converged in 5 iterations.

Table 11
XRF-PXRF paired element sample correlations

Pairing	Cor	Sig
Mn (XRF) & Mn (PXRF)	.332	.006
Fe (XRF) & Fe (PXRF)	.452	.000
Zn (XRF) & Zn (PXRF)	-.211	.084
Rb (XRF) & Rb (PXRF)	.515	.000
Sr (XRF) & Sr (PXRF)	.780	.000
Zr (XRF) & Zr (PXRF)	.037	.763

ratios. Furthermore, the presence of significant differences in five of the six element concentration values has no bearing on consistency in obsidian source determination. Sourcing studies are based on a comparison between geologic standards from known sources to archaeological samples from undetermined sources. Raw 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.

Although the PXRF used in this study measures fewer elements than a conventional laboratory-based unit,² there is now solid empirical evidence demonstrating the adequacy of portable instrumentation for obsidian source discrimination in the central Andes. As a result, portable instruments can

² Since generating the PXRF data in Perú in 2005, MURR has acquired a second PXRF system. The newer system, an ElvaX (a miniature bench top instrument), permits quantification of the same range of elements as those that were generated at Berkeley. The ElvaX also has comparable detection limits. In addition to the wider range of elements, the ElvaX instrument comes with software that permits data transformation using a best fit regression calibration rather than a fundamental parameters model.

Table 12
XRF-PXRF paired samples *t*-test results

	Paired Differences				<i>t</i>	df	Sig. (2-tailed)	
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
				Lower				Upper
Mn (XRF) – Mn (PXRF)	7.34	60.703	7.361	–7.36	22.03	.997	67	.322
Fe (XRF) – Fe (PXRF)	1542.66	364.155	44.160	1454.52	1630.81	34.933	67	.000
Zn (XRF) – Zn (PXRF)	7.91	5.999	.728	6.46	9.36	10.875	67	.000
Rb (XRF) – Rb (PXRF)	–14.68	25.205	3.057	–20.78	–8.58	–4.802	67	.000
Sr (XRF) – Sr (PXRF)	–16.74	17.766	2.154	–21.04	–12.44	–7.768	67	.000
Zr (XRF) – Zr (PXRF)	–29.84	26.065	3.161	–36.15	–23.53	–9.440	67	.000

Table 13
XRF-PXRF Z-score results

	Zr XRF	Zr PXRF	Sr XRF	Sr PXRF	Rb XRF	Rb PXRF	Zn XRF	Zn PXRF	Fe XRF	Fe PXRF	Mn XRF	Mn PXRF
Mean	82.076	111.712	45.909	62.833	241.455	256.394	40.121	32.712	6379.864	4859.576	682.061	676.6364
Known Variance	4.750	23.950	3.260	15.240	12.400	20.790	4.270	2.840	290.420	45.430	58.520	18.25
Observations	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1
Hypothesized Mean Difference	0.000		0.000		0.000		0.000		0.000		0.000	
<i>z</i>	–5.532		–3.935		–2.593		2.779		82.957		0.619	
<i>p</i> (<i>Z</i> ≤ <i>z</i>) one-tail	0.000		0.000		0.005		0.003		0.000		0.268	
<i>z</i> Critical one-tail	1.645		1.645		1.645		1.645		1.645		1.645	
<i>p</i> (<i>Z</i> ≤ <i>z</i>) two-tail	0.000		0.000		0.010		0.005		0.000		0.536	
<i>z</i> Critical two-tail	1.960		1.960		1.960		1.960		1.960		1.960	
Result	<i>z</i> > <i>z</i> critical		<i>z</i> > <i>z</i> critical		<i>z</i> > <i>z</i> critical		<i>z</i> > <i>z</i> critical		<i>z</i> > <i>z</i> critical		<i>z</i> < <i>z</i> critical means equal	
	Means different		Means different		Means different		Means different		Means different			
	<i>p</i> (<i>Z</i> ≤ <i>z</i>) <.05		<i>p</i> (<i>Z</i> ≤ <i>z</i>) <.05-		<i>p</i> (<i>Z</i> ≤ <i>z</i>) <.05		<i>p</i> (<i>Z</i> ≤ <i>z</i>) <.05		<i>p</i> (<i>z</i> ≤ <i>Z</i>) <.05		<i>P</i> (<i>Z</i> ≤ <i>z</i>) two tail >.05	
	Methods different		Methods different		Methods different		Methods different		Methods different		Methods same	

be taken to artifact curation facilities. In many research contexts obtaining permission to export artifacts for analysis is either difficult or impossible. Except in special cases, central Andean obsidian artifacts no longer need to be exported for source identification. If source identification cannot be made by PXRF, then another technique like INAA is required. PXRF can be used to examine large collections to determine which artifacts require more sensitive characterization methods.

The ability to analyze artifacts non-destructively, either in the field or in museums, is an obvious advantage of PXRF. Many North American museums are custodians of Native American artifacts that have been, or are in the process of being, repatriated. Special permission from the museum and consultation with most likely descendant Native Americans is often required for analytical projects.

Non-destructive analyses performed on-site are more conducive to obtaining permission to carry out research. Museum curators and governmental agencies responsible for collections stewardship will not have to be concerned about collections being lost or damaged during transit. Mobile analytical instruments improve opportunities for most likely descendent Native Americans, museum curators, and government officials to observe and participate in analyses. Elemental analysis of artifacts in the field using portable instruments facilitates integration into archaeological field research and training programs. PXRF can eliminate these logistical complications and provide high-resolution data at a low analytical cost and short time-frame.

Acknowledgement

We wish to thank Nico Tripcevic for collecting additional source specimens and providing them to both the Archaeological XRF Laboratory at the University of California Berkeley and the Archaeometry Laboratory at the University of Missouri Research Reactor.

Fieldwork at Jiskairumoko in was supported by National Science Foundation grant SBR-9816313 in 1998, and a supplement for fieldwork in 2002; National Science Foundation Equipment Grant SBR-9978006; and a John H. Heinz II Charitable Trust in 1997 and 2002. All fieldwork grants were awarded to Aldenderfer.

MURR analyses were supported in part by National Science Foundation grant (0405042) which made the purchase of the PXRF instrument possible and a laboratory support grant (0504015) which facilitated the INAA.

Popelka-Filcoff was supported by a National Science Foundation Graduate Fellowship.

The Archaeological XRF Laboratory at UC Berkeley is supported, in part, by funding from the Stahl Endowment for Archaeological Research, UC Berkeley, and the Departments of Anthropology and Earth and Planetary Sciences, UC, Berkeley.

References

Adan-Bayewitz, D., Asaro, F., Giaque, R.D., 1999. Determining pottery provenance: application of a new high-precision X-ray fluorescence method

- and comparison with instrumental neutron activation analysis. *Archaeometry* 41, 1–24.
- Aldenderfer, M.S., 1998. *Montane Foragers Asana and the South-Central Andean Archaic*. University of Iowa Press, Iowa City.
- Aldenderfer, M.S., 1999. Cronología y conexiones: evidencias precerámicas de asana. In: Kaulicke, P. (Ed.), *Boletín de Arqueología pucp*. Pontificia Universidad Católica del Perú, Lima, pp. 375–392.
- Aldenderfer, M.S., 2002. Explaining changes in settlement dynamics across transformations of modes of production: from hunting to herding in the south-central Andes. In: Fitzhugh, B., Habu, J. (Eds.), *Beyond Foraging and Collecting: Evolutionary Change in Hunter-Gatherer Settlement Systems*. Kluwer Academic Publishers, New York, pp. 387–412.
- Bachofer, S.J., 2004. Field sampling with a fp-xrf: a real-world lab experience. *Spectroscopy Letters* 37, 115–128.
- Bernick, M.B., Campagna, P.R., 1995. Application of field-portable X-ray fluorescence spectrometers for field-screening air monitoring filters for metals. *Journal of Hazardous Materials* 43, 91–99.
- Burger, R.L., Asaro, F., 1977. Trace Element Analysis of Obsidian Artifacts from the Andes: New Perspectives on Pre-Hispanic Economic Interaction in Peru and Bolivia. Lawrence Berkeley Laboratory. University of California at Berkeley, Berkeley, pp. 1–93.
- Burger, R.L., Asaro, F., 1978. Obsidian distribution and provenience in the central highlands and coast of Peru during the preceramic period. *Contributions of the University of California Archaeology Research Facility* 36, 61–83.
- Burger, R.L., Asaro, F., 1993. La distribución y procedencia de artefactos de obsidiana durante el periodo inicial y horizonte temprano. In: Burger, R.L. (Ed.), *Emergencia de la Civilización en los Andes: Ensayos de Interpretación*. Universidad Nacional Mayor de San Marcos, Lima, pp. 189–264.
- Burger, R.L., Asaro, F., Michel, H.V., Stross, F., Ernesto, S., 1994. An initial consideration of obsidian procurement and exchange in prehispanic Ecuador. *Latin American Antiquity* 5, 228–255.
- Burger, R.L., Asaro, F., Michel, H.V., 1998. The sources of obsidian for artifacts from Chobshi cave. Ecuador. *Andean Past* 2, 33–37.
- Burger, R.L., Chávez, K.L., Chávez, S., 2000. Through the glass darkly: prehispanic obsidian procurement and exchange in southern Perú and northern Bolivia. *Journal of World Prehistory* 14, 267–362.
- Cann, J.R., Renfrew, C., 1964. The characterization of obsidian and its application to the Mediterranean region. *Proceedings of the American Philosophical Society* 30, 111–133.
- Carter, G.F., 1971. Compositions of some copper-based coins of augustus and tiberius. In: Brill, R.H. (Ed.), *Science and Archaeology*. MIT Press, Cambridge, pp. 114–130.
- Clark, S., Menrath, W., Chen, M., Roda, S., Succop, P., 1998. Use of a Field Portable X-ray Fluorescence Analyzer to Determine the Concentration of Lead and Other Metals in Soil and Dust Samples. Warsaw'98, International Symposium and Exhibition on Environmental Contamination in Central and Eastern Europe, Symposium Proceedings, 4th, Warsaw, Sept. 15–17, 1998, pp. 1313–1319.
- Cobean, R.H., Coe, M.D., Perry Jr., E.A., Turekian, K.K., Kharkar, D.P., 1971. Obsidian trade at San Lorenzo Tenochtitlan, Mexico. *Science* 174, 141–146.
- Craig, N., 2005. The Formation of Early Settled Villages and the Emergence of Leadership: a Test of Three Theoretical Models in the Rio Ilave, Lake Titicaca Basin, Southern Perú, Anthropology. University of California at Santa Barbara, Santa Barbara, pp. 995.
- Craig, N., Aldenderfer, M., in press. Trends in early non-local obsidian artifacts from the rio ilave viewed from surface survey and late archaic excavations. In: Klarich, E.A., Stanish, C. (Eds.), *Advances in Titicaca Basin Archaeology II*, University of California, Los Angeles, Cotsen Institute of Archaeology, Los Angeles.
- Culbert, T.P., Schwalbe, L.A., 1987. X-ray fluorescence survey of Tikal ceramics. *Journal of Archaeological Science* 14, 635–657.
- Dransart, P., 1991. Llamas, herders and the exploitation of raw materials in the atacama desert. *World Archaeology* 22, 304–319.
- Dransart, P., 2002. *Earth, Water, Fleece, and Fabric: An Ethnography and Archaeology of Andean Camelid Herding*. Routledge, New York.
- Eisenraut, P.J., 1998. Macrobotanical Remains from Southern Peru: A Comparison of Late Archaic- Early Formative Period Sites from the Puna and

- Suni Zones of the Western Titicaca Basin. Department of Anthropology, University of California, Santa Barbara, pp. 1–299.
- Frye, K.L., Aldenderfer, M., Glascock, M.D., 1998. The Aconchagua Obsidian Source and its Relation to South Central Andean Exchange Systems. 38th Annual Andean Meeting, Berkeley, CA.
- García-Heras, M., Fernández-Ruiz, R., Tornero, J.D., 1997. Analysis of archaeological ceramics by txrf and contrasted with naa. *Journal of Archaeological Science* 24, 1003–1014.
- Giesso, M., 2000. Stone Tool Production in the Tiwanaku Heartland: The Impact of State Emergence and Expansion on Local Households, Anthropology. University of Chicago, Chicago, p. 426.
- Glascock, M.D., Neff, H., Stryker, K.S., Johnson, T.N., 1994. Sourcing archaeological obsidian by an abbreviated naa procedure. *Journal of Radioanalytical and Nuclear Chemistry* 180, 29–35.
- Glascock, M.D., Braswell, G.E., Cobean, R.H., 1998. A systematic approach to obsidian source characterization. In: Shackley, M.S. (Ed.), *Archaeological Obsidian Studies: Method and Theory*. Plenum Press, New York and London, pp. 15–65.
- Glascock, M.D., Kunselman, R., Wolfman, D., 1999. Intrasource chemical differentiation of obsidian in the Jemez mountains and Taos plateau, New Mexico. *Journal of Archaeological Science* 26, 861–868.
- Govindaraju, K., 1994. Compilation of working values and sample descriptions for 383 geostandards. *Geostandards Newsletter* 18 (special issue), 1–158.
- Hampel, J.H., 1984. Technical considerations in X-ray fluorescence analysis of obsidian. In: Hughes, R.E. (Ed.), *Obsidian Studies in the Great Basin*. Contributions of the University of California Archaeological Research Facility no 45.
- Hedges, R.E.M., Moorey, P.R.S., 1975. Pre-Islamic ceramic glazes at Kish and Nineveh in Iraq. *Archaeometry* 17, 25–43.
- Heizer, R.F., Williams, H., Graham, J., 1965. Notes on Mesoamerican obsidians and their significance in archaeological studies. Contributions of the University of California Archaeological Research Facility 1, 94–103.
- Hesse, B., 1982. Animal domestication and oscillating climates. *Journal of Ethnobiology* 2, 1–15.
- Hovers, E., Ilani, S., Bar-Yosef, O., Vandermeersch, B., 2003. An early case of color symbolism. *Current Anthropology* 44, 491–522.
- Hughes, R.E., Smith, R.L., 1993. Archaeology, geology, and geochemistry in obsidian provenance studies. In: Stein, J.K., Linse, A.R. (Eds.), *Scale on Archaeological Geoscientific Perspectives*. Geological Society of America Special Paper 283, Boulder, pp. 79–91.
- Jack, R.N., Heizer, R.F., 1968. 'Finger-printing' of some Mesoamerican obsidian artifacts. Contributions of the University of California Archaeological Research Facility 5, 81–100.
- Jennings, J., Glascock, M.D., 2002. Description and method of exploitation of the Alca obsidian source, Perú. *Latin American Antiquity* 13, 107–117.
- Kalnicky, D.J., Singhvi, R., 2001. Field portable xrf analysis of environmental samples. *Journal of Hazardous Materials* 83, 93–122.
- Klink, C., 2005. Archaic period research in the Rio Huenque valley, Perú. In: Stanish, C., Cohen, A.B., Aldenderfer, M.S. (Eds.), *Advances in Titicaca Basin Archaeology*. Costen Institute of Archaeology, Los Angeles, pp. 13–24.
- Klink, C., Aldenderfer, M.S., 2005. A projectile point chronology for the south-central Andean highlands. In: Stanish, C., Cohen, A.B., Aldenderfer, M.S. (Eds.), *Advances in Titicaca Basin Archaeology*. Costen Institute of Archaeology, Los Angeles, pp. 25–54.
- Kuhn, R.D., 1987. Trade and exchange among the Mohawk-Iroquois: a trace element analysis of ceramic smoking pipes. *North American Archaeologist* 8, 305–315.
- Kuznar, L.A., 1995. *Awatimarka: The Ethnology of an Andean Herding Community*. Harcourt Brace, Orlando.
- Kuznar, L.A. (Ed.), 2001. *Ethnoarchaeology of Andean South America*. International Monographs in Prehistory, Ann Arbor.
- Mahood, G., Stimac, J.A., 1990. Trace-element partitioning in pantellerites and trachytes. *Geochimica et Cosmochimica Acta* 54, 2257–2276.
- McCarthy, J.J., Schamber, F.H., 1981. Least-squares fit with digital filter: a status report. In: Heinrich, K.F.J., Newbury, D.E., Myklebust, R.L., Fiori, E. (Eds.), *Energy Dispersive X-ray Spectrometry*. National Bureau of Standards Special Publication 604, Washington D.C., pp. 273–296.
- Morgenstein, M., Redmont, C.A., 2005. Using portable energy dispersive X-ray fluorescence (edxf) analysis for on-site study of ceramic sherds at El Hibeh, Egypt. *Journal of Archaeological Science* 32, 1613–1623.
- Murray, A.P., 2005. Indicators of Domestication Among an Assemblage of Chenopodium Quinoa Seeds from Southern Perú, 70th Annual Meeting of the Society for American Archaeology, Salt Lake City, Utah.
- Nissenbaum, J., Holzer, A., Roth, M., Schieber, M., 1981. X-ray fluorescence analysis of high z materials with mercuric iodide room temperature detectors. *Advances in X-Ray Analysis* 24, 303–309.
- Núñez, L., 1982. Temprana emergencia de sedentarismo en el desierto chileno: Proyecto caserones. *Chungará* 9, 80–122.
- Ogburn, D.E., 2004. Evidence for long-distance transportation of building stones in the inka empire, from Cuzco, Peru to Saraguro, Ecuador. *Latin American Antiquity* 15, 419–439.
- Padilla, R., Van Espen, P., Godo Torres, P.P., 2006. The suitability of xrf analysis for compositional classification of archaeological ceramic fabric: a comparison with a previous naa study. *Analytica Chimica Acta* 558, 283–289.
- Pandey, H.D., Prasad, M.S., Ramaswamy, V., 1983. Rapid nondestructive coke-ash determination using a portable xrf analyzer. *Steel India* 6, 41–44.
- Parks, G.A., Tieh, T.T., 1966. Identifying the geographical source of artefact obsidian. *Nature* 211, 289–290.
- Poole, A.B., Finch, L.R., 1972. The utilization of trace chemical composition to correlate British post-medieval pottery with European kiln site materials. *Archaeometry* 14, 79–91.
- Potts, P.J., Webb, P.C., Williams-Thorpe, O., Kilworth, R., 1995. Analysis of silicate rocks using field-portable X-ray fluorescence instrumentation incorporating a mercury (ii) iodide detector: a preliminary assessment of analytical performance. *Analyst (Cambridge, United Kingdom)* 120, 1273–1278.
- Potts, P.J., Williams-Thorpe, O., Webb, P.C., 1997. The bulk analysis of silicate rocks by portable X-ray fluorescence: effect of sample mineralogy in relation to the size of the excited volume. *Geostandards Newsletter* 21, 29–41.
- Rhodes, J.R., Rautala, P., 1983. Application of a microprocessor-based portable xrf analyzer in minerals analysis. *International Journal of Applied Radiation and Isotopes* 34, 333–343.
- Romano, F.P., Calvi, G., Furia, E., Garraffo, S., Marchetta, C., Pappalardo, G., Pappalardo, L., Rizzo, F., Rovelli, A., 2005. A new portable xrf spectrometer with beam stability control. *X-Ray Spectrometry* 34, 135–139.
- Schamber, F.H., 1977. A modification of the linear least-squares fitting method which provides continuum suppression. In: Dzubay, T.G. (Ed.), *X-ray Fluorescence Analysis of Environmental Samples*. Ann Arbor Science Publishers, Ann Arbor, pp. 241–257.
- Shackley, M.S., 1988. Sources of archaeological obsidian in the southwest: an archaeological, petrological, and geochemical study. *American Antiquity* 53, 752–772.
- Shackley, M.S., 1990. Early Hunter-Gatherer Procurement Ranges in the Southwest: Evidence from Obsidian Geochemistry and Lithic Technology (volumes i and ii). Department of Anthropology, Arizona State University, Tempe, AZ.
- Shackley, M.S., 1991. Tank mountains obsidian: a newly discovered archaeological obsidian source in east-central Yuma county, Arizona. *The Kiva* 57, 17–25.
- Shackley, M.S., 1992. The upper Gila River gravels as an archaeological obsidian source region: implications for models of exchange and interaction. *Geoarchaeology* 7, 315–326.
- Shackley, M.S., 1994. Intersource and intrasource geochemical variability in two newly discovered archaeological obsidian sources in the southern great basin. *Journal of California and Great Basin Anthropology* 16, 118–129.
- Shackley, M.S., 1995. Sources of archaeological obsidian in the greater American Southwest: an update and quantitative analysis. *American Antiquity* 60, 531–551.
- Shackley, M.S., 1998. Geochemical differentiation and prehistoric procurement of obsidian in the mount Taylor volcanic field, northwest New Mexico. *Journal of Archaeological Science* 25, 1073–1082.
- Shackley, M.S., 2002a. More than exchange: pre-ceramic through ceramic period obsidian studies in the greater North American southwest.

- In: Glascock, M.D. (Ed.), *Geochemical Evidence for Long-Distance Exchange*. Bergin and Garvey, Westport, CT-London, pp. 53–87.
- Shackley, M.S., 2002b. Precision versus accuracy in the xrf analysis of archaeological obsidian: some lessons for archaeometry and archaeology. In: Jerem E., Biro K.T. (Eds.), *Archaeometry 98, Proceedings of the 31st International Symposium on Archaeometry, BAR International Series 1043 (2)*, Budapest, Hungary, pp. 805–809.
- Shackley, M.S., 2004. Obsidian in the North American Southwest: Geology, Archaeology, and History. University of Arizona Press, Tucson.
- Shackley, M.S., Tucker, D.B., 2001. Limited prehistoric procurement of sand tank obsidian, southwestern Arizona. *The Kiva* 66, 345–374.
- Shackley, M.S., Hyland, J.R., del la Luz Gutierrez M, M., 1996. Mass production and procurement at Valle del Azufre: a unique archaeological obsidian source in Baja California Sur. *American Antiquity* 61, 718–731.
- Shackley, S.M., Eklund, E., Ogasawara, C., 2004. Source Provenance of Obsidian Artifacts Jiskairumoko (189). University of California Berkeley Archaeological XRF Laboratory, Department of Anthropology, Peru, p. 10.
- Stanish, C., Burger, R.L., Cipolla, L.M., Glascock, M.D., Quelima, E., 2002. Evidence for early long-distance obsidian exchange and watercraft use from the southern Lake Titicaca Basin of Bolivia and Perú. *Latin American Antiquity* 13, 444–454.
- Thomsen, V., Schatzlein, D., 2002. Advances in field-portable xrf. *Spectroscopy* (Duluth, MN, United States), 14–21.
- Trigger, B.G., Yaffe, L., Diksic, M., Galinier, J.L., Marshall, H., Pendergast, J.F., 1980. Trace-element analysis of Iroquoian pottery. *Canadian Journal of Archaeology* 4, 119–145.
- Wager, E.C.W., Jenkins, D.A., Owen, A.W., Ottaway, B.S., 2002. Portable X-ray fluorescence analysis as a tool for the identification of copper ore processing sites on the Great Orme, north Wales, UK. In: Jerem E., Biro K.T. (Eds.), *Archaeometry 98, Proceedings of the 31st International Symposium on Archaeometry, BAR International Series 1043 (2)*, Budapest, Hungary, pp. 491–496.
- Westgard, J.O., 1998. Use and interpretation of common statistical tests in method-comparison studies. *Clinical Chemistry* 44, 2240–2242.
- Westgard, J.O., Hunt, M.R., 1973. Use and interpretation of common statistical tests in method-comparison studies. *Clinical Chemistry* 19, 49–57.
- Wheeler, J.C., 1999. Patrones prehistóricos de utilización de los camélidos sudamericanos. In: Kaulicke, P. (Ed.), *Boletín de Arqueología PUCP*. Pontificia Universidad Católica del Perú, Lima, pp. 297–306.
- Williams-Thorpe, O., Webb, P.C., Jones, M.C., 2003. Non-destructive geochemical and magnetic characterization of group xviii dolerite stone axes and shaft-hole implements from England. *Journal of Archaeological Science* 30, 1237–1267.