



GEOARCHAEOLOGICAL XRF LAB
A GREEN SOLAR FACILITY

GEOARCHAEOLOGICAL X-RAY FLUORESCENCE SPECTROMETRY LABORATORY
8100 Wyoming Blvd., Ste M4-158

Albuquerque, NM 87113 USA

SOURCE PROVENANCE OF AN OBSIDIAN POLYHEDRAL BLADE AND TWO FRAGMENTS FROM LA 169 (OTOWI), LA 54147 AND LA 80000, NEW MEXICO



The polyhedral blade and fragments from central and northern New Mexico

by

M. Steven Shackley, Ph.D., Director
Geoarchaeological XRF Laboratory
Albuquerque, New Mexico

Report Prepared for

Dr. Sean Dolan
Santa Fe, New Mexico

11 November 2018

Introduction

The major, minor, and trace element x-ray fluorescence (XRF) analysis of three samples of decidedly green obsidian from three sites in central and northern New Mexico indicate a provenance from the Pachuca 1 source in the Sierra de Pachuca, in Hidalgo State, Mexico, as defined by a Pachuca 1 sample in this laboratory and Glascock (2011; see also Argote-Espino et al. 2012; Ponomarenko 2004; see cover image).

Laboratory Sampling, Analysis and Instrumentation

The solid samples were analyzed whole. The results presented here are quantitative in that they are derived from "filtered" intensity values ratioed 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). Or more essentially, these data through the analysis of international rock standards, allow for inter-instrument comparison with a predictable degree of certainty (Hampel 1984; Shackley 2011).

All analyses for this study were conducted on a ThermoScientific *Quant'X* EDXRF spectrometer, located at the Geoarchaeological XRF Laboratory, Albuquerque, New Mexico. The instrument is equipped with a thermoelectrically Peltier cooled solid-state Si(Li) X-ray detector, with a 50 kV, 50 W, ultra-high-flux end window bremsstrahlung Rh target X-ray tube and a 76 μm (3 mil) beryllium (Be) window (air cooled), that runs on a power supply operating 4-50 kV/0.02-1.0 mA at 0.02 increments. The spectrometer is equipped with a 200 l min⁻¹ Edwards vacuum pump, allowing for the analysis of lower-atomic-weight elements between sodium (Na) and scandium (Sc). Data acquisition is accomplished with a pulse processor and an analogue-to-digital converter. Elemental composition is identified with digital filter background removal,

least squares empirical peak deconvolution, gross peak intensities and net peak intensities above background.

The analysis for mid Zb condition elements Ti-Nb, Pb, Th, the x-ray tube is operated at 30 kV, using a 0.05 mm (medium) Pd primary beam filter in an air path at 200 seconds livetime generally using an 8.8 mm tube collimator to generate x-ray intensity $K\alpha_1$ -line data for elements titanium (Ti), manganese (Mn), iron (as Fe_2O_3^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). Not all these elements are reported since their values in many volcanic rocks are very low and below detection limits. Trace element intensities were converted to concentration estimates by employing a linear calibration line ratioed to the Compton scatter 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. When barium (Ba) is analyzed in the High Zb condition, the Rh tube is operated at 50 kV and up to 1.0 mA, ratioed to the bremsstrahlung region (see Davis 2011; Shackley 2011). Further details concerning the petrological choice of these elements in Southwest volcanic rocks is available in Shackley (1995, 2005; also Mahood and Stimac 1990; and Hughes and Smith 1993). Nineteen specific pressed powder standards are used for the best fit regression calibration for elements Ti-Nb, Pb, Th, and Ba, include G-2 (basalt), AGV-2 (andesite), GSP-2 (granodiorite), SY-2 (syenite), BHVO-2 (hawaiiite), 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), NOD-A-1 and NOD-P-1 (oceanic manganese) all US Geological Survey standards, NIST-278 (obsidian), U.S. National Institute of Standards and Technology, BE-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).

Major and Minor Oxide Analysis

Analysis of the major oxides is performed under the multiple conditions elucidated below. This fundamental parameter analysis (theoretical with standards), while not as accurate as destructive analyses (pressed powder and fusion disks) is usually within a few percent of actual, based on the analysis of USGS RGM-1 obsidian or in this study the USGS SCO-1 shale standard (see also Shackley 2011). The fundamental parameters (theoretical) method is run under conditions commensurate with the elements of interest and calibrated with 11 USGS standards (RGM-1, rhyolite; AGV-2, andesite; BHVO-1, hawaiite; BIR-1, basalt; G-2, granite; GSP-2, granodiorite; BCR-2, basalt; W-2, diabase; QLO-1, quartz latite; STM-1, syenite), and one Japanese Geological Survey rhyolite standard (JR-1). See Lundblad et al. (2011) for another set of conditions and methods for oxide analyses.

Conditions Of Fundamental Parameter Analysis¹:

Low Za (Na, Mg, Al, Si, P)

Voltage	6 kV	Current	Auto ²
Livetime	100 seconds	Counts Limit	0
Filter	No Filter	Atmosphere	Vacuum
Maximum Energy	10 keV	Count Rate	Low

Mid Zb (K, Ca, Ti, V, Cr, Mn, Fe, Co, Cu, Zn, Rb, Sr, Y, Zr, Nb, Pb, Th, Bi, As, Ba)

Voltage	32 kV	Current	Auto
Livetime	100 seconds	Counts Limit	0
Filter	Pd (0.06 mm)	Atmosphere	Vacuum
Maximum Energy	40 keV	Count Rate	Medium

High Zb (Sn, Sb, Ba, Ag, Cd)

Voltage	50 kV	Current	Auto
Livetime	100 seconds	Counts Limit	0
Filter	Cu (0.559 mm)	Atmosphere	Vacuum
Maximum Energy	40 keV	Count Rate	High

Low Zb (S, Cl, Si, P, K, Ca, Pb)

Voltage	8 kV	Current	Auto
Livetime	100 seconds	Counts Limit	0
Filter	Cellulose (0.06 mm)	Atmosphere	Vacuum
Maximum Energy	10 keV	Count Rate	Low

¹ Multiple conditions designed to ameliorate peak overlap identified with digital filter background removal, least squares empirical peak deconvolution, gross peak intensities and net peak intensities above background.

² Current is set automatically based on the mass absorption coefficient.

The data from the WinTrace™ software were translated directly into Excel for Windows software and then into JMP 12.0.1 for statistical analysis. RGM-1 a USGS rhyolite standard was analyzed during each run of ≤ 20 samples. Elemental data exhibited in Table 1 are reported in parts per million (ppm), a quantitative measure by weight, and percent by weight as noted.

Discussion

Various studies of the Pachuca source have indicated at least three chemical groups in the Sierra de Pachuca and Sierra Las Navajas, in the state of Hidalgo, Mexico. These are some of the most widely distributed sources in North and Central America (Argote-Espino et al. 2012; Barker et al. 2002; Ponomarenko 2004; Tenorio et al. 1998). The chemical group called Pachuca 1 by Glascock (2011), and Cruz del Milagro by Argote-Espino et al. (2012) appear to be the most utilized source, and the most likely source for the three samples here (see Table 1 and Figures 1

and 2). This mildly peralkaline peraluminous obsidian is elementally and morphologically distinctive with its decidedly translucent green cast and high Fe and Zr. While Pachuca is not the only green peralkaline obsidian in North America (i.e. Antelope Wells/El Berrendo in southern New Mexico and northern Chihuahua), it is generally unusual to be recovered in archaeological contexts in the North American Southwest.

References Cited

- Argote-Espino, D., J. Solé, P. López-García, and O. Sterpone
2012 Obsidian Subsource Identification in the Sierra de Pachuca and Otumba Volcanic Regions, Central Mexico, but ICP-MS and DBSCAN Statistical Analysis. *Geoarchaeology* 27:48-62.
- Barker, A.W., C. Skinner, M.S. Shackley, M.D. Glascock, and J.D. Rogers
2002 Mesoamerican Origin for an Obsidian Scraper from the Precolumbian Southeastern United States. *American Antiquity* 67(1):103-108.
- Davis, M.K., T.L. Jackson, M.S. Shackley, T. Teague, and J. Hampel
2011 Factors Affecting the Energy-Dispersive X-Ray Fluorescence (EDXRF) Analysis of Archaeological Obsidian. In *X-Ray Fluorescence Spectrometry (XRF) in Geoarchaeology*, edited by M.S. Shackley, pp. 45-64. Springer, New York.
- Glascock, M.D.
2011 Comparison and Contrast Between XRF and NAA: Used for Characterization of Obsidian Sources in Central Mexico. In *X-Ray Fluorescence Spectrometry (XRF) in Geoarchaeology*, edited by M.S. Shackley, pp. 161-192. Springer, New York.
- Govindaraju, K.
1994 1994 Compilation of Working Values and Sample Description for 383 Geostandards. *Geostandards Newsletter* 18 (special issue).
- Hampel, Joachim H.
1984 Technical Considerations in X-ray Fluorescence Analysis of Obsidian. In *Obsidian Studies in the Great Basin*, edited by R.E. Hughes, pp. 21-25. Contributions of the University of California Archaeological Research Facility 45. Berkeley.
- Hildreth, W.
1981 Gradients in Silicic Magma Chambers: Implications for Lithospheric Magmatism. *Journal of Geophysical Research* 86:10153-10192.
- Hughes, Richard E., and Robert L. Smith
1993 Archaeology, Geology, and Geochemistry in Obsidian Provenance Studies. In *Scale on Archaeological and Geoscientific Perspectives*, edited by J.K. Stein and A.R. Linse, pp. 79-91. Geological Society of America Special Paper 283.

- Lundblad, S.P., P.R. Mills, A. Drake-Raue, and S.K. Kikiloi
 2011 Non-Destructive EDXRF Analyses of Archaeological Basalts. In *X-Ray Fluorescence Spectrometry (XRF) in Geoarchaeology*, edited by M.S. Shackley, pp. 65-80. Springer, New York.
- Mahood, Gail A., and James A. Stimac
 1990 Trace-Element Partitioning in Pantellerites and Trachytes. *Geochemica et Cosmochimica Acta* 54:2257-2276.
- McCarthy, J.J., and F.H. Schamber
 1981 Least-Squares Fit with Digital Filter: A Status Report. In *Energy Dispersive X-ray Spectrometry*, edited by K.F.J. Heinrich, D.E. Newbury, R.L. Myklebust, and C.E. Fiori, pp. 273-296. National Bureau of Standards Special Publication 604, Washington, D.C.
- Ponomarenko, A. L.
 2004 The Pachuca Obsidian Source, Hidalgo, Mexico: A Geoarchaeological Perspective. *Geoarchaeology* 19:71-91.
- Schamber, F.H.
 1977 A Modification of the Linear Least-Squares Fitting Method which Provides Continuum Suppression. In *X-ray Fluorescence Analysis of Environmental Samples*, edited by T.G. Dzubay, pp. 241-257. Ann Arbor Science Publishers.
- Shackley, M. Steven
 1995 Sources of Archaeological Obsidian in the Greater American Southwest: An Update and Quantitative Analysis. *American Antiquity* 60(3):531-551.
- 2005 *Obsidian: Geology and Archaeology in the North American Southwest*. University of Arizona Press, Tucson.
- 2011 An Introduction to X-Ray Fluorescence (XRF) Analysis in Archaeology. In *X-Ray Fluorescence Spectrometry (XRF) in Geoarchaeology*, edited by M.S. Shackley, pp. 7-44. Springer, New York.
- Tenorio, D., A. Cabral, P. Bosch, M. Jimenez-Reyes, and S. Bulbulian
 1998 Differences in Coloured Obsidians from Sierra del Pachuca, Mexico. *Journal of Archaeological Science* 25:229-234.

Table 1. Elemental concentrations for the samples, USGS RGM-1 rhyolite standard, the Pachuca 1 source sample in this laboratory, and Glascock (2011) NAA and XRF values combined for Pachuca 1. All measurements in parts per million (ppm) or weight percent as noted.

Sample	Site	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	K ₂ O	CaO	V ₂ O ₅	Fe ₂ O ₃	Σ			
		%	%	%	%	%	%	%	%	%	%			
6918	LA 54147	3.666	0	6.429	71.555	0	9.066	0.987	0.014	6.307	98.024			
55	LA 80000	3.581	0	6.445	71.237	0.02	9.347	1.186	0.023	6.294	98.133			
1598	LA 169 (Otowí)	4.78	0	10.577	77.08	0	4.435	0.1137	0.0068	2.284	98.976			
Pachuca- 1		4.708	0	10.519	77.416	0	4.263	0.118	0	2.266	99.29			
RGM1-S4		4.18	0	12.988	73.77	0	4.875	1.429	0.0007	2.213	99.4557			
		Cl	Ti	Mn	Zn	Rb	Sr	Y	Zr	Nb	Ba	Pb	Th	
		ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	
6918	LA 54147	5042	1165	883	263	204	11	101	918	94	<1	28	17	
55	LA 80000	4496	1328	928	305	214	14	106	923	90	<1	32	17	
1598	LA 169 (Otowí)	1909	1120	789	216	199	10	104	906	93	<1	22	23	
PACHUCA-1		1888	1170	773	212	201	13	102	903	95	<1	25	11	
RGM1-S4		486	1548	306	41	150	108	28	220	8	815	19	17	
Glascock 2011		nr	801-1089 ¹	733-1148	188-226	186-195	6-14	89-128	848-1019	76-92	19-43	nr	18	

¹ The data from Glascock are the range of mean values for both the NAA and XRF analyses reported in that study (2011:180). Generally, the analysis of the Geoarchaeological XRF Laboratory's Pachuca standard and the archaeological samples is closest due to inter-instrument variability (see Glascock 2011; Shackley 2011).

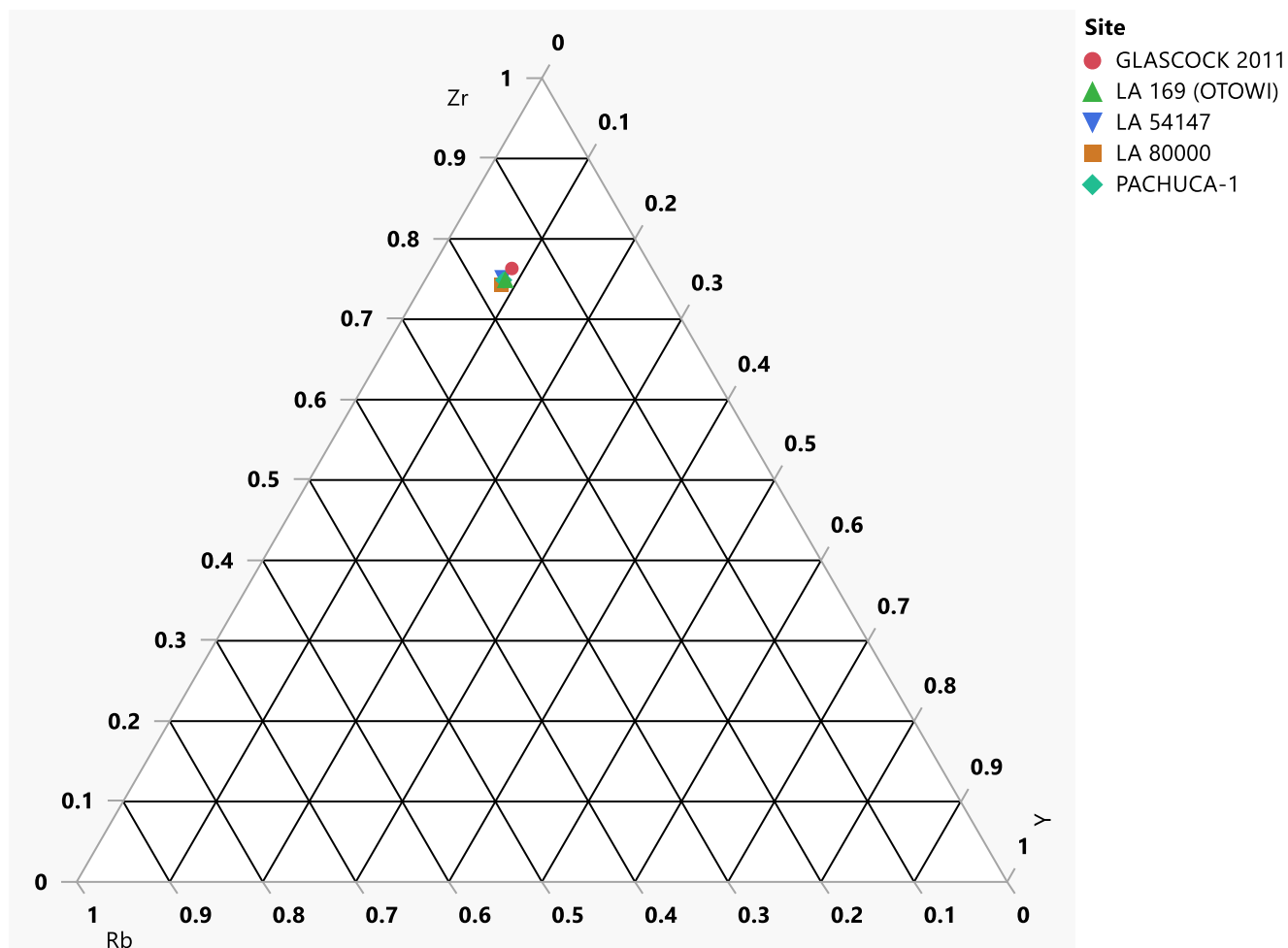


Figure 1. Ternary plot of Rb/Y/Zr elements of the archaeological samples, the Pachuca-1 laboratory source standard, and Glascock (2011) data for Pachuca 1 source standards (see Table 1). All measurements in parts per million (ppm).

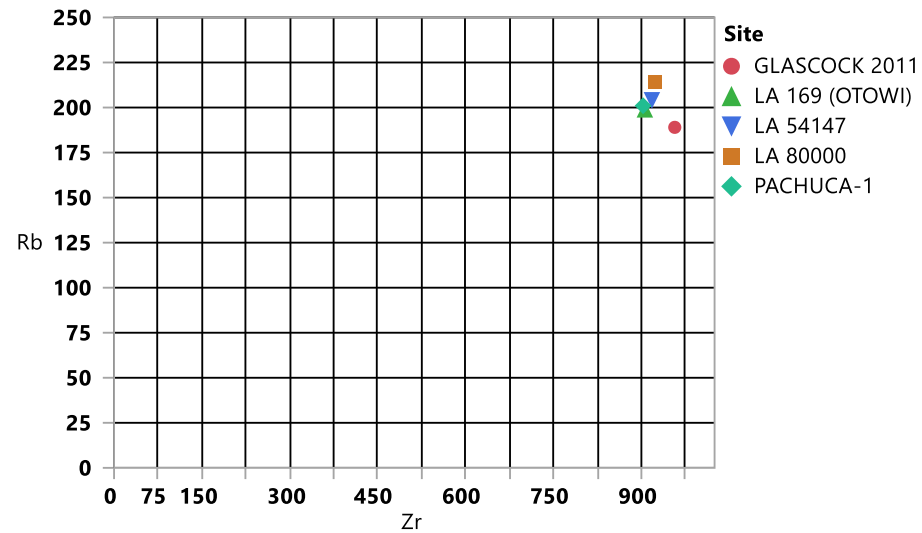
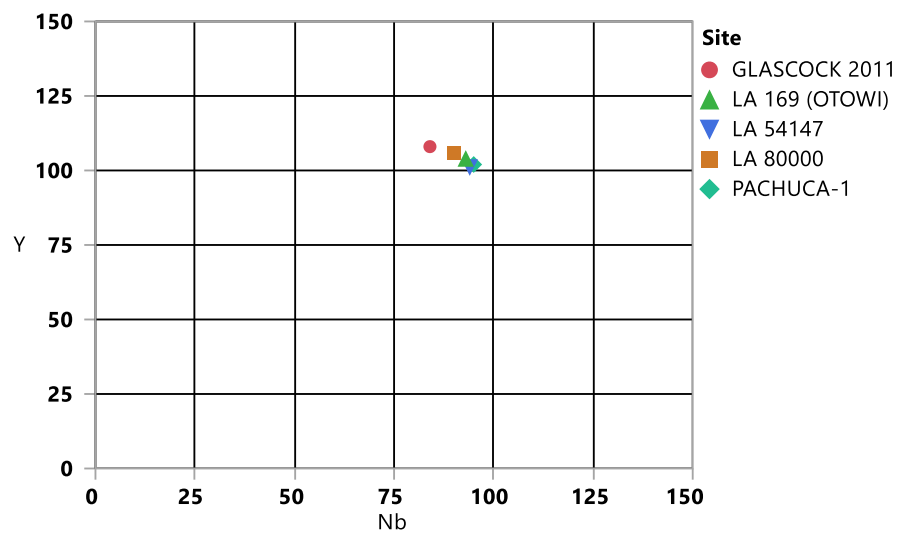


Figure 2. Nb/Y and Zr/Rb bivariate plots (set at 0-n) of the archaeological samples, the Pachuca-1 laboratory source sample, and Glascock (2011) mean data for Pachuca-1 source standards (see Table 1).