GEOARCHAEOLOGICAL XRF LAB

GEOARCHAEOLOGICAL X-RAY FLUORESCENCE SPECTROMETRY LABORATORY
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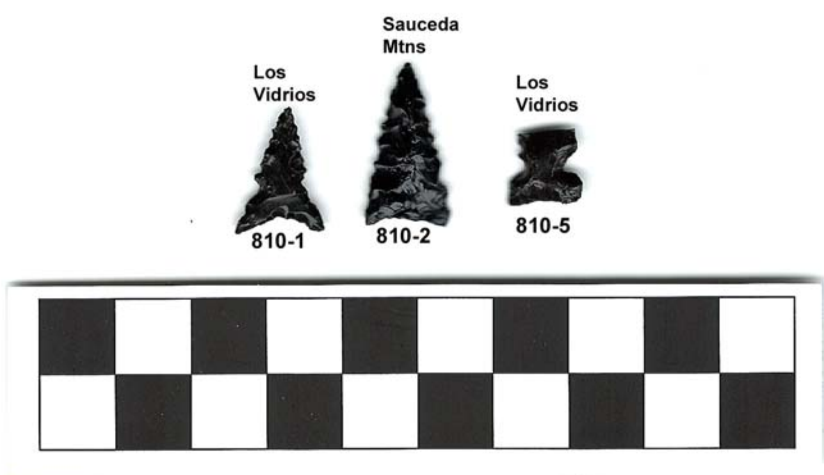
X-RAY FLUORESCENCE (XRF) ANALYSIS OF OBSIDIAN ARTIFACTS AND PLUTONIC ROCK SOURCE STANDARDS FROM THE CABEZA PRIETA NATIONAL WILDLIFE REFUGE, SOUTHWESTERN ARIZONA



Obsidian projectile points and source provenance from Jose Juan (AZ Y:16:510)

by

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INTRODUCTION

The 63 obsidian artifacts from Cabeza Prieta were produced from diverse sources in the Sonoran Desert both north and south of the international border, all but one of which could be considered local (Sauceda Mountains, 36.5%; Los Vidrios, 44.4%; Los Sitios del Agua, 17.5%). One sample was produced from the Bull Creek source north near Bagdad, Yavapai County, Arizona (see Shackley 2005; Table 1 here). While the assemblage suggests that the local environment was important, connections to the north and south are apparent.

An analysis of two plutonic rock samples from AZ Y:15:1&2, and AZ Y:16:510 indicate two different rock types, alkalic granite, and a quartz diorite. The trace element composition is also distinctive.

LABORATORY SAMPLING, ANALYSIS AND INSTRUMENTATION

All archaeological and source samples are 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).

Trace Element Analyses

All analyses for this study were conducted on a ThermoScientific *Quant'X* EDXRF spectrometer, located in the Geoarchaeological XRF Laboratory, Albuquerque, New Mexico. It 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 titanium (Ti). 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 to generate x-ray intensity Ka-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. Trace element intensities were converted to concentration estimates by employing a quadratic 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 quadratic (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 obsidians is available in Shackley (1988, 1995, 2005; also Mahood and Stimac 1991; 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 (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), NOD-A-1 and NOD-P-1 (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 of Na, Mg, Al, Si, K, Ca, V, Cr, Mn, and Fe 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 standard (see also Shackley 2011). The fundamental parameters (theoretical) method is run under conditions commensurate with the elements of interest and calibrated with four USGS standards (RGM-1, rhyolite; AGV-2, andesite; BHVO-1, hawaiite; BIR-1, basalt), and one Japanese Geological Survey rhyolite standard (JR-1).

Conditions of Fundamental Parameter Analysis[1]

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)

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, K, Ca)

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 and SPSS (ver. 21) software for statistical manipulation. In order to evaluate these quantitative determinations, machine data were compared to measurements of known standards during each run. G-2 a USGS granite standard was analyzed during each sample run for plutonic rock samples to check machine calibration (Tables 1 and 2). Two of the latter seven samples analyzed exhibited considerable caliche or other material on the surface. This served to increase the Sr values significantly, but the remainder of the elemental concentrations were well within the Los Vidrios source standard ranges. This has been seen to be a problem elsewhere (Shackley and Dillian 2002).

DISCUSSION

As noted above, the vast majority of obsidian artifacts were produced from sources in the local area, within a radius of 70 km or less. The direction of the sources, Los Sitios del Agua and Los Vidrios, Sonora to the south, and Sauceda Mountains and Bull Creek to the north, indicates considerable movement over 100s of km north and south (Tables 1 and 3, Figure 1). All of these obsidian sources are generally equal media for tool production in quality and nodule size, although Los Vidrios can be very brittle in hard hammer percussion, but equal to the other for pressure work (Martynec et al. 2011; Shackley 2005).

The two analyzed plutonic rock samples indicate very different composition both in the oxides and trace elements (Table 2). One of the samples is an alkalic granite, and the other a quartz diorite (see Frost et al. 2001). The trace element composition suggests that these two can be useful in source provenance studies assuming that they represent homogeneous elemental chemistry at the sources.

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Table 1. Elemental concentrations for the artifacts and USGS RGM-1.

Sample	Ti	Mn	Fe	Zn	Rb	Sr	Y	Zr	Nb	Source
510-1	745	263	13718	106	263	12	75	238	34	Los Vidrios
510-2	652	194	11200	91	237	12	66	218	26	Los Vidrios
716-1	1607	300	10787	96	170	106	27	180	21	Sauceda Mtns
716-2	1216	477	26253	184	143	12	80	726	48	Los Sitios del Agua
768-1	1671	378	10208	87	170	78	36	202	23	Sauceda Mtns
768-2	1446	361	9641	74	154	70	34	187	19	Sauceda Mtns
770	1527	284	10406	68	166	101	30	190	18	Sauceda Mtns
91	669	241	11454	105	225	51	71	213	32	Los Vidrios
92	767	212	10811	119	216	208	67	217	28	Los Vidrios?
93	787	222	11990	111	248	13	70	223	29	Los Vidrios
94	750	235	12022	118	240	31	68	222	32	Los Vidrios
95	737	225	11522	135	239	18	64	218	29	Los Vidrios
97	840	259	12457	133	240	43	70	226	30	Los Vidrios
103	982	260	11334	109	213	139	68	221	34	Los Vidrios?
800-1	1235	424	25957	207	142	9	74	711	40	Los Sitios del Agua
800-2	1621	375	10569	132	164	73	31	193	19	Sauceda Mtns
801-1	460	396	7226	40	204	21	34	73	26	Bull Creek
801-2	640	227	12173	118	245	12	69	225	27	Los Vidrios
803-1	1486	401	10249	46	174	74	36	209	25	Sauceda Mtns
803-2	694	246	12981	143	261	11	72	226	29	Los Vidrios
803-3-1	1704	372	10023	138	156	70	32	185	20	Sauceda Mtns
803-3-2	950	201	12310	140	242	13	60	223	28	Los Vidrios
803-3-3	774	228	12030	134	250	12	69	222	29	Los Vidrios
803-4-1	1728	321	11260	93	170	106	29	190	17	Sauceda Mtns
803-4-2	966	203	11196	133	230	10	65	211	25	Los Vidrios
804-1	1512	286	10192	42	164	107	30	192	17	Sauceda Mtns
804-2	1257	465	27521	152	146	11	87	741	46	Los Sitios del Agua
808-1	1766	315	11878	73	179	108	26	186	18	Sauceda Mtns
808-2	1530	293	10582	54	160	99	27	183	18	Sauceda Mtns
809-1	681	210	11741	121	237	11	65	220	29	Los Vidrios
809-2	702	244	12474	117	249	13	68	224	31	Los Vidrios
810-1	790	196	11168	118	236	9	64	215	27	Los Vidrios

Sample	Ti	Mn	Fe	Zn	Rb	Sr	Y	Zr	Nb	Source
810-2	1561	363	9943	67	167	76	32	205	25	Sauceda Mtns
810-3	1565	286	10299	72	169	108	27	186	18	Sauceda Mtns
810-4	727	246	12002	97	240	10	65	220	26	Los Vidrios
810-5	711	225	12153	128	253	10	66	220	31	Los Vidrios
812	1459	282	9939	44	158	107	30	191	20	Sauceda Mtns
816	1235	498	26737	156	150	11	85	753	49	Los Sitios del Agua
819-1	1054	478	25239	146	147	12	83	732	45	Los Sitios del Agua
819-2	1194	278	13806	99	129	73	34	234	20	Sauceda Mtns
819-3	1739	300	11268	53	176	110	31	196	22	Sauceda Mtns
819-4	735	222	11470	93	238	7	64	221	28	Los Vidrios
820-1	1184	508	27988	170	151	8	81	751	49	Los Sitios del Agua
820-2	1409	373	10093	73	164	76	36	202	21	Sauceda Mtns
821-1	1309	550	29573	165	151	12	87	747	50	Los Sitios del Agua
821-2	719	236	12918	99	246	11	69	227	29	Los Vidrios
821-3	1770	392	10600	54	174	78	35	202	19	Sauceda Mtns
824-1	719	213	11791	119	242	12	69	211	26	Los Vidrios
824-2	727	241	11930	132	245	12	66	219	27	Los Vidrios
825	1146	466	27240	161	148	8	85	744	45	Los Sitios del Agua
827-1	1544	399	10553	76	167	75	37	203	25	Sauceda Mtns
827-2	1667	413	10697	61	172	74	34	205	25	Sauceda Mtns
827-3	1181	400	21331	142	126	12	77	673	45	Los Sitios del Agua
830-1	1574	299	10574	50	164	106	25	185	18	Sauceda Mtns
830-2	1332	272	9362	45	155	103	31	184	19	Sauceda Mtns
834	1296	499	28905	180	154	7	87	752	44	Los Sitios del Agua
I128	701	216	12417	106	251	12	66	221	27	Los Vidrios
I75	747	242	12819	144	257	11	69	224	29	Los Vidrios
JJV-1	696	222	12197	93	251	10	64	229	26	Los Vidrios
JJV-2	693	197	11591	92	235	8	64	218	27	Los Vidrios
JJV-3	709	219	11664	98	251	11	67	222	28	Los Vidrios
JJV-4	1393	494	28355	185	152	10	84	758	49	Los Sitios del Agua
JJV-5	1131	264	13367	75	136	78	31	240	21	Sauceda Mtns
RGM1-S4	1572	270	13302	39	154	109	24	224	15	standard
RGM1-S4	1562	270	13247	41	149	104	26	224	9	standard

RGM1-S4	1612	270	13305	40	151	107	28	224	10	standard
RGM1-S4	1509	296	13110	40	150	106	27	221	8	standard

Table 2. Major oxide and trace element concentrations for two plutonic rock samples, and USGS G-2.

Sample	Na2O %	MgO %	Al2O3 %	SiO2 %	Cl %	K2O %	CaO %	TiO2 %	V2O5 %	Cr2O3 %	MnO %	Fe2O3 %	Rock type
Y-15-1&2-1	0.933	5.795	11.531	75.594	0	4.04	0.287	0.186	0.01	0	0.028	1.543	alkali granite
Y-16-510-1	2.846	2.632	9.48	63.762	0	11.388	2.648	0.662	0.081	0.002	0.135	5.973	Qtz diorite
G-2	3.701	0.797	14.203	70.417	0	5.067	2.317	0.443	0.032	0	0.037	2.726	granite standard

Sample	Ti ppm	Mn ppm	Fe ppm	Zn ppm	Rb ppm	Sr ppm	Y ppm	Zr ppm	Nb ppm	Ba ppm	Pb ppm	Th ppm
Y-15-1&2-1	1059	226	10467	26	190	8	18	113	13	129	12	14
Y-16-510-1	1180	248	12170	44	283	13	18	111	10	279	12	37
G-2	3007	255	18493	90	173	482	13	293	14	1866	27	25

Table 3. Frequency distribution of the obsidian sources in the assemblage.

		Frequency	Percent
Source	Bull Creek	1	1.6
	Los Sitios del Agua	11	17.5
	Los Vidrios	28	44.4
	Sauceda Mtns	23	36.5
	Total	63	100.0

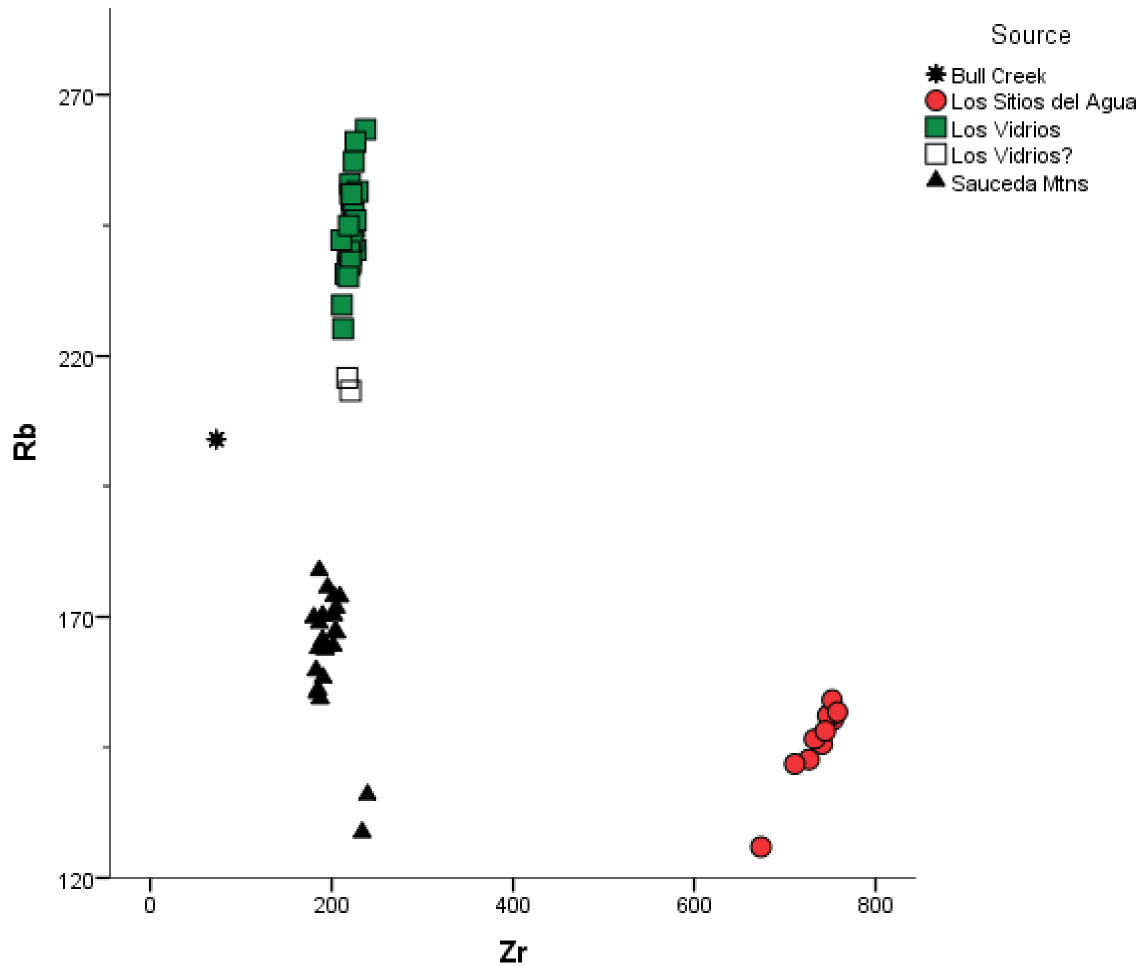

Figure 1. Zr versus Rb bivariate plot of the archaeological obsidian specimens. Note the bimodal distribution of Sauceda Mountains samples (see Shackley 2005).