X-Ray Fluorescence (XRF) Analysis of Major Oxide and Trace Element Concentrations for Rock Samples from AZ U:5:182 (ASM), Phoenix, Arizona

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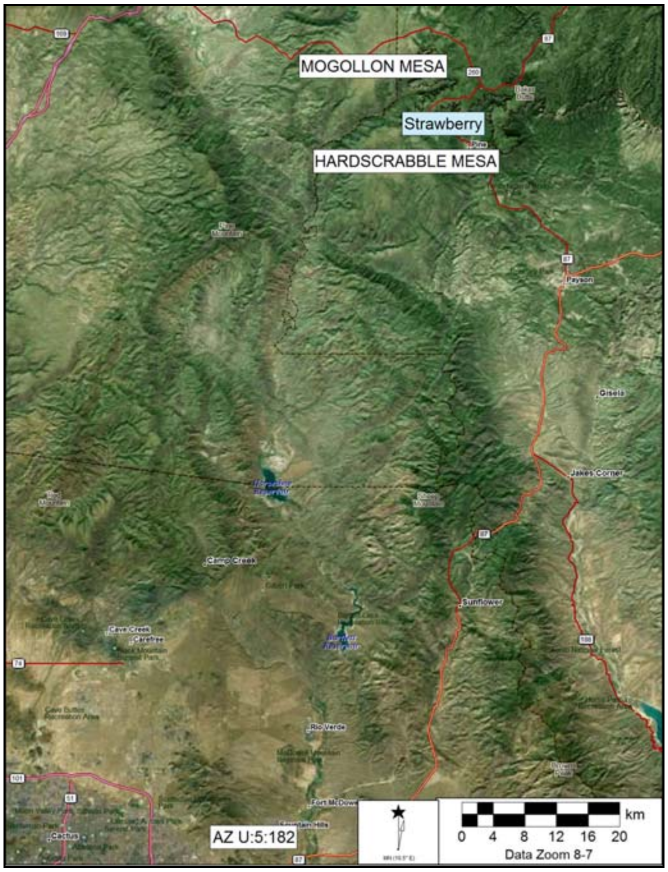

by

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INTRODUCTION

The trace element and oxide analysis here of rock samples from AZ U:5:182 (ASM) northwest of Phoenix, Arizona indicates that none of the artifacts match the source standards from the Mogollon or Hardscrabble Mesa dacite from near Strawberry, Arizona (Shackley 2013). Indeed the artifacts are produced from a large range of intermediate and mafic volcanic rocks from many sources, none of which have been chemically characterized and thus known.

Both the trace element and major oxide analyses indicate very different composition than the dacites on the southern edge of the Mogollon Rim in Arizona's Transition Zone. Based on this study, it seems that these Transition Zone dacites did not reach the Phoenix Basin, although there has been little research into these intermediate volcanic raw materials in the region (c.f. Shackley 2011b; see cover image here). Sample PD-1 does not match the trace element profile for the Strawberry dacites, but it could be a similar volcanic rock and possibly from a source nearby and related to the Strawberry dacites. (see Tables 1 and 2, and Figures 1 and 2).

LABORATORY SAMPLING, ANALYSIS AND INSTRUMENTATION

All archaeological 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 2011a).

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 least-squares or 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 linear (XML) for all elements but Fe where a derivative fitting is used to improve the fit for iron and thus for all the other 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 2011a). 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, K, 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 2011a). 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 software for statistical manipulation and the major oxides plotted on the TAS plot to determine rock type. In order to evaluate these quantitative determinations, machine data were compared to measurements of known standards during each run. AGV-1 a USGS andesite standard was analyzed during each sample run for obsidian artifacts to check machine calibration (Tables 1 and 2).

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Table 1. Trace element concentrations for the rock samples and USGS AGV-1.

Sample	Ti	Mn	Fe	Zn	Rb	Sr	Y	Zr	Nb	Ba	Pb	Th
PD1	2939	599	25392	147	49	524	16	188	36	1756	15	22
PD33	2833	589	24998	86	47	520	14	190	35	1647	17	19
PD35	5058	810	40417	107	41	921	20	155	32	1756	10	4
PD37	5230	832	38746	90	52	530	26	121	29	1259	20	4
PD67	2779	558	25732	82	44	549	19	201	36	1783	16	16
PD68	2700	560	23447	62	44	498	17	194	33	1662	13	19
XRF1[1]	4134	768	30602	325	57	541	19	124	37	1172	14	9
XRF2	2728	637	25623	285	46	510	14	187	37	1759	19	20
XRF3	11480	1114	70180	189	31	1041	21	208	31	3280	10	5
XRF4	3507	606	25337	87	57	443	20	131	35	1377	19	4
AGV-1	5634	648	42155	89	68	647	22	220	17	1102	29	4

[1] Unique numbers not identifiable. The XRF numbers are noted on the artifact bag.

Table 2. Major oxide concentrations for the archaeological samples and USGS AGV-1.

SAMPLE	Na2O %	MgO %	Al2O3 %	SiO2 %	K2O %	CaO %	TiO2 %	MnO %	Fe2O3 %	Σ
PD1	4.232	1.465	16.739	64.27	3.126	4.379	0.544	0.098	4.476	99.329
PD33	2.479	0.467	10.167	59.955	5.44	9.165	1.008	0.187	9.804	98.672
PD35	3.707	2.976	18.484	57.164	2.1	6.52	1.063	0.131	7.389	99.534
PD37	3.994	3.167	17.534	58.801	2.646	5.162	1.131	0.131	6.898	99.464
PD67	2.852	0.758	10.849	54.88	4.924	10.809	1.244	0.233	11.956	98.505
PD68	4.388	1.868	18.619	62.469	2.316	5.059	0.553	0.087	4.185	99.544
XRF1	5.077	0.913	9.502	52.385	5.634	9.492	1.878	0.297	12.519	97.697
XRF2	3.248	0.8	10.836	50.26	5.418	11.204	1.26	0.294	13.706	97.026
XRF3	3.689	4.371	17.674	49.869	1.859	8.153	2.021	0.16	11.129	98.925
XRF4	4.919	0.516	16.228	64.037	3.764	3.801	0.837	0.104	4.591	98.797
AGV-1	3.617	0.967	16.896	62.199	3	5.095	1.072	0.099	6.734	99.679

[1] Sum includes only relevant oxides, so does not sum to 100%.

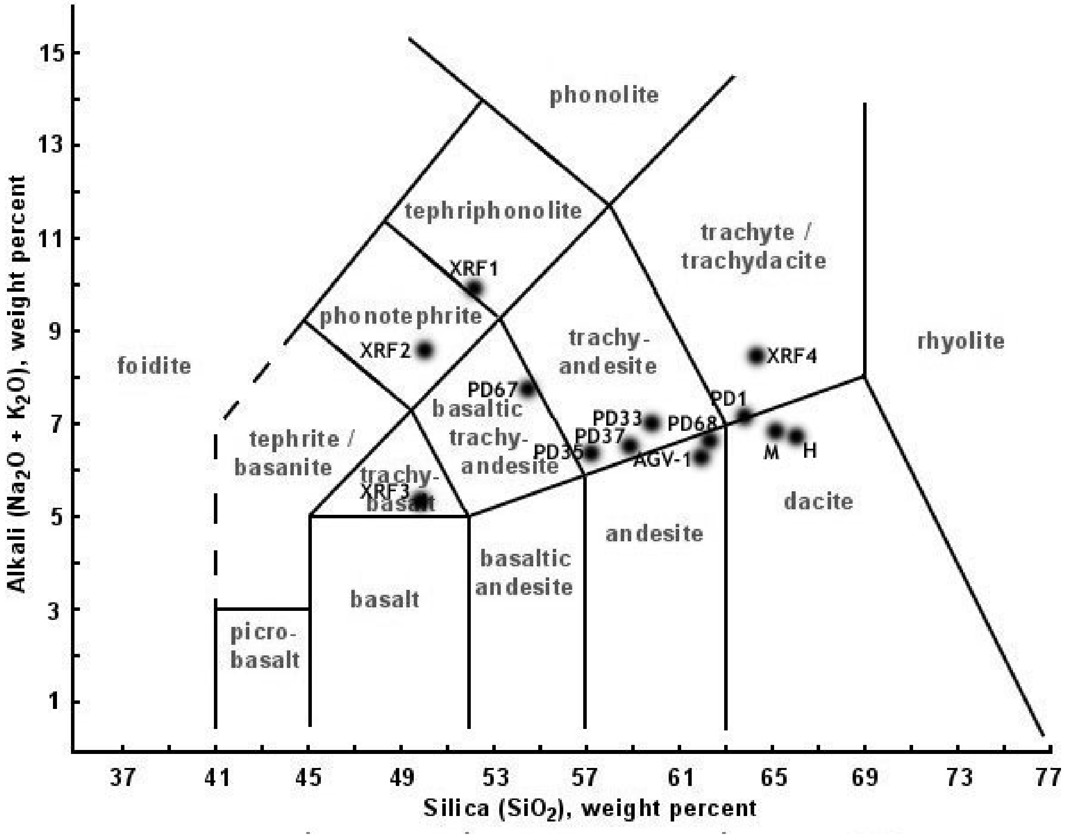

Figure 1. TAS plot of the archaeological samples, and two samples of "Strawberry dacite" (M=Mogollon Mesa; H=Hardscrabble Mesa) and USGS AGV-1 standard.

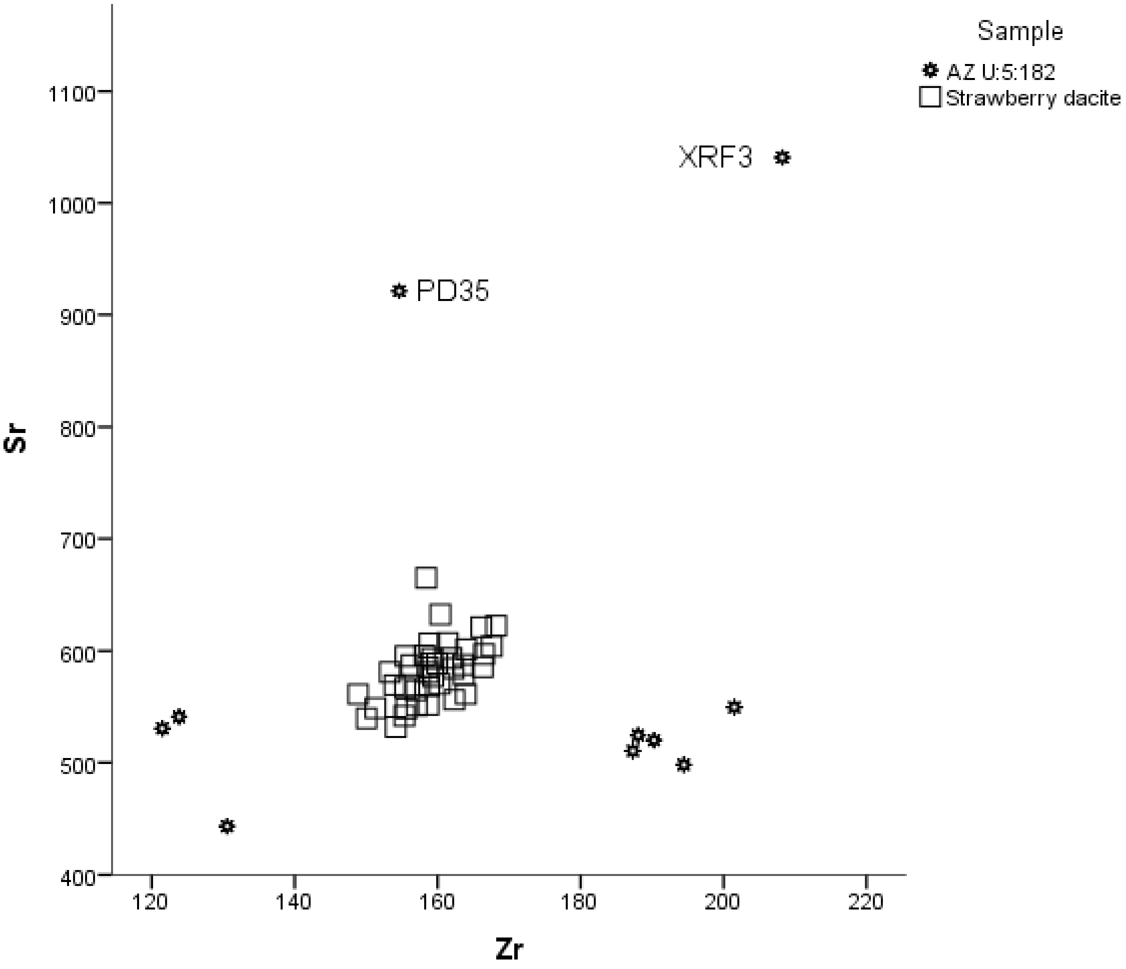

Figure 2. Zr versus Sr bivariate plot of archaeological samples and the Mogollon and Hardscrabble Mesa (Strawberry) dacite source rocks.