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Publication Date

2020-11-17

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ENERGY-DISPERSIVE X-RAY FLUORESCENCE (EDXRF) ANALYSIS OF MAJOR OXIDE AND TRACE ELEMENT CONCENTRATIONS FOR RHYOLITE AND DACITE PROJECTILE POINT FRAGMENTS FROM THE TULAROSA BASIN, SOUTHERN NEW MEXICO

by

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Report Prepared for

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17 November 2020

INTRODUCTION

The non-destructive whole rock analysis here of three projectile point fragments from unknown provenience in the Tularosa Basin of southern New Mexico indicates that one of the artifacts was likely produced from the Socorro hydrothermally altered rhyolite, and one possibly from the Mount San Antonio dacite source in northern New Mexico, hundreds of kilometers north of the basin (see discussion).

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).

The issue of accuracy using fundamental parameter calibrations of obsidian with EDXRF for whole rock non-destructive analyses has been discussed elsewhere (http://swxrflab.net/anlysis.htm). Variability can be as great as one to two percent, too great for source discrimination using non-destructive fundamental parameter analysis with EDXRF (see Brown and Nash 2014).

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, 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.

For the analysis of mid-Z condition elements the x-ray tube is operated at 30 kV, using a 0.05 mm (medium) Pd primary beam filter in an air path at 100 seconds livetime 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), and $L\alpha_1$-line data for lead (Pb), and thorium (Th). Not all these elements are reported since their values in many volcanic rocks are very low and often outside the detection limits. Trace element intensities were converted to concentration estimates by employing a linear 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. 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 and other volcanic rocks is available in Shackley (1988, 1995, 2005, 2011a; 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 (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 of Na, Mg, Al, Si, P. K, Ca, Ti, V, Mn, and Fe, is performed under the multiple conditions elucidated below. The fundamental parameter analysis (theoretical with standards), while not as accurate as destructive analyses (pressed powder and fusion disks) is usually within a portion of a percent of actual, based on the analysis of the 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 ten 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).

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 major oxide data from the WinTrace software were translated directly into Excel for Windows software for manipulation and on into IGPET petrological software for plotting. JMP 12.0.1 is used for trace element data analyses. In order to evaluate these quantitative determinations, machine data were compared to measurements of known standards during each run. RGM-1 a USGS obsidian standard is analyzed during each sample run for obsidian artifacts to check machine calibration (Tables 1 and 2).

DISCUSSION

The artifacts 827 and 855 are classified dacite or trachydacite based on the TAS plot of the alkalis and silica (Figure 1). Artifact 827 produced from a dacite was not produced from any known dacite sources in New Mexico. The projectile point 855 is possibly produced from the Mount San Antonio dacite shield volcano in the Taos Plateau Volcanic Field in northern New Mexico based on the TAS and trace element plots (Figures 1 and 2; see Shackley 2011b). This is a distance of at least 400 km from the basin. It is possible that Mt San Antonio dacite has entered the Rio Grande and available in Rio Grande Quaternary alluvium, but the only dacite thus far recovered from Rio Grande alluvium is Cerros del Rio dacite the primary source of which is located directly above the river and on Bandelier National Monument, much nearer the basin (Shackley 2011b). Projectile point 865 was most likely produced from the Black Canyon high silica rhyolite located west of Socorro New Mexico based on the TAS plot and two trace elements well within the within the range of the Black Canyon source (see Dello-Russo 2004; Shackley 2016; see also Figures 1 and 2).

While it seems likely that the artifacts assigned to source are indeed from those sources, the trachydacite specimen while appearing to be produced from Mount San Antonio could be from an as yet unknown source with similar elemental composition nearer the basin. Given that there are only three dacite sources recorded in New Mexico, and the great distance to the source, it will always be a possibility that the artifact was produced from an, as yet, unlocated source. This is not to say that it was not derived from the northern New Mexico source, but given the distance could be from another nearby source. The projectile point produced from the high silica rhyolite, called "Socorro jasper" in the vernacular is more likely from that source given the similar reddish color and similar chemistry, and the presence of this raw material in early archaeological contexts in New Mexico (see Dello-Russo 2004).

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Table 1. Major, minor oxides, and trace elemental concentrations for the artifacts, and the USGS RGM-1 rhyolite standard.

Sample	Na2O	MgO	Al2O3	SiO2	P2O5	K2O	CaO	TiO2	V2O5	MnO	Fe2O3	Σ			
	%	%	%	%	%	%	%	%	%	%	%				
2017.37.827	1.82	3.32	13.14	66.77	0.00	3.61	4.24	1.01	0.06	0.11	5.50	99.57			
2017.37.855	2.09	2.48	15.81	66.87	0.00	5.63	3.31	0.79	0.04	0.03	2.66	99.70			
2017.37.865	1.60	0.89	2.36	91.02	0.00	0.24	0.24	0.71	0.01	0.01	2.62	99.70			
RGM1-S4	4.05	0.00	13.05	73.76	0.00	4.93	1.41	0.30	0.02	0.04	2.21	99.77			
	Cl	Co	Ni	Cu	Zn	Ga	Rb	Sr	Y	Zr	Nb	Ba	Ce	Pb	Th
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
2017.37.827	1281	12	28	15	66	19	116	663	32	188	12	1210	48	27	17
2017.37.855	252	0	19	13	46	21	185	572	26	168	17	1615	24	21	8
2017.37.865	741	0	16	8	31	9	4	60	4	492	35	1128	13	313	6
RGM1-S4	495	0	15	12	41	18	155	105	23	223	10	793	25	22	20

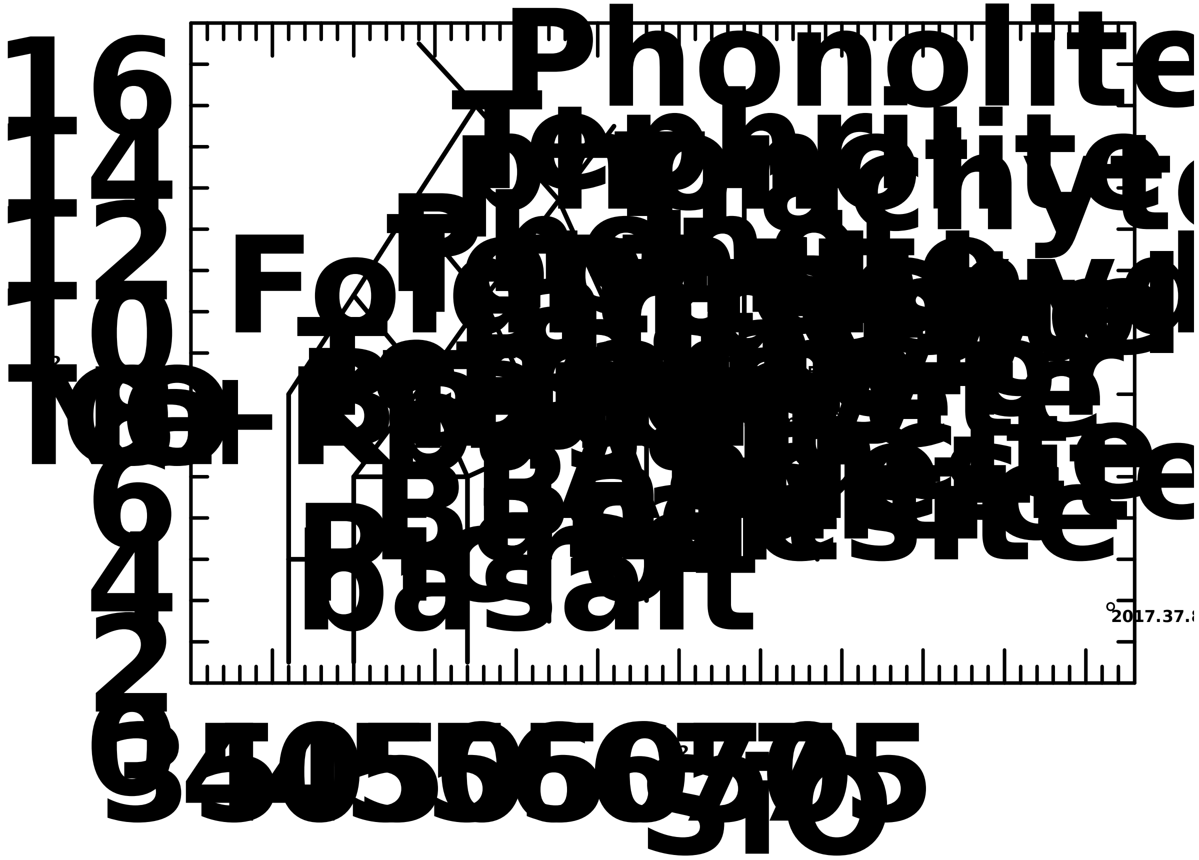

Figure 1. TAS plot of all samples (LeBas et al. 1986).

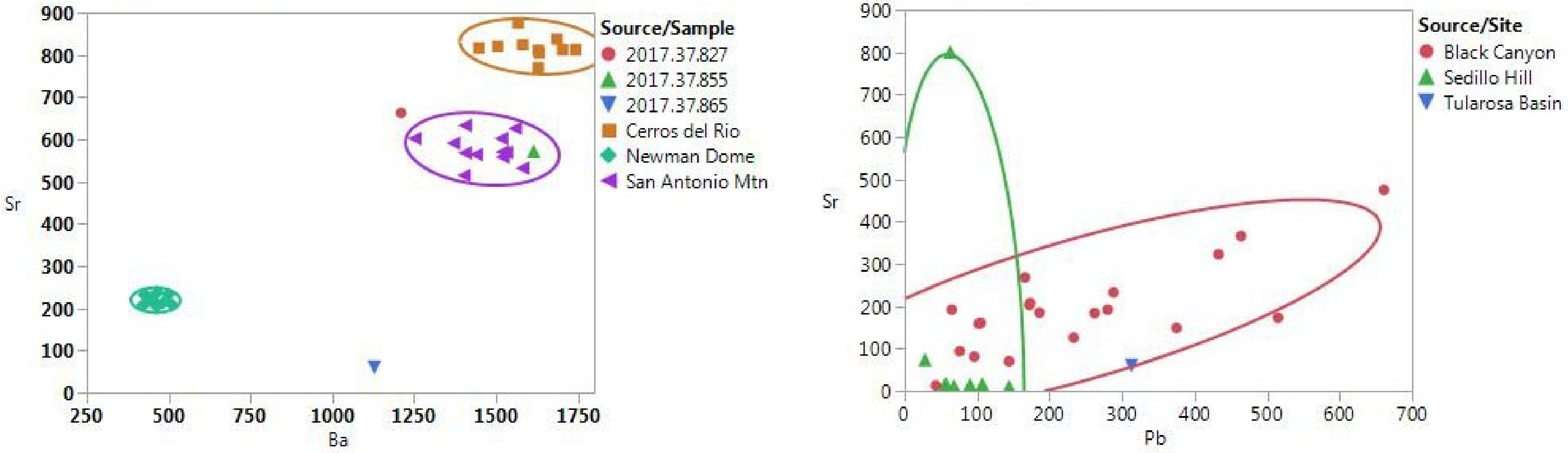

Figure 2. Ba/Sr bivariate plot (left) of the projectile points and the three documented dacite sources from northern New Mexico (from Shackley 2011b; confidence ellipses at 95%), and Pb/Sr bivariate plot (right) of Socorro high silica rhyolite source standards and projectile point 865 (see Figure 1). Confidence ellipses at 95%.