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GEOARCHAEOLOGICAL X-RAY FLUORESCENCE SPECTROMETRY LABORATORY

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**ENERGY-DISPERSIVE X-RAY FLOURESCENCE (EDXRF) ANALYSIS  
OF MAJOR, MINOR AND TRACE ELEMENTS FOR ONE TURQUOISE  
GLOBULAR BEAD AND ONE OBSIDIAN ARTIFACT FROM SITE  
SRPMICH-62, ON THE SALT RIVER PIMA-MARICOPA INDIAN  
COMMUNITY, CENTRAL ARIZONA**

by

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## INTRODUCTION

The analysis here of one obsidian flake and one turquoise bead indicates that the obsidian artifact was produced from the Vulture source west of the Phoenix Basin, commonly recovered in Preclassic Hohokam contexts in the Lower Salt River Valley (Shackley 2005, 2019; Table 1 herein). A short discussion of the turquoise bead is offered below as well.

## LABORATORY SAMPLING, ANALYSIS AND INSTRUMENTATION

All 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 comparative 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 spectrometer 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  $\mu\text{m}$  (3 mil) beryllium (Be) window (air cooled), that runs on a power supply operating from 4-50 kV/0.02-1.0 mA at 0.02 increments. The spectrometer is equipped with a 200  $\text{l min}^{-1}$  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 data from the WinTrace™ software were translated directly into Excel for Windows software for manipulation and on into IGPET ver. 2013 for plotting as required. 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 run of  $\leq 19$  samples. The USGS recommended values for G-2 are included in Table 1.

### **Trace Element Analysis**

In the analysis of mid Zb condition elements Ti-Nb, and high Zb 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 100 seconds livetime to generate x-ray intensity  $K\alpha_1$ -line data for elements manganese (Mn), cobalt (Co), nickel (Ni), copper, (Cu), zinc, (Zn), gallium (Ga), rubidium (Rb), strontium (Sr), yttrium (Y), zirconium (Zr), niobium (Nb), and  $L\alpha_1$  data for lead (Pb), and thorium (Th). 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) and cerium (Ce) 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, 2011; also Mahood and Stimac 1991; and Hughes and Smith 1993; Shackley et al. 2016, 2018). Nineteen specific pressed powder standards are used for the best fit regression calibration for elements Ti-Nb, Pb, Th, Ba, and Ce, and 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, Ti, V, 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  $\leq 1\%$  of actual, based on the analysis of the USGS RGM-1 rhyolite standard (Table 1). The fundamental parameter (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).

### **Conditions Of Fundamental Parameter Analysis<sup>1</sup>:**

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

Voltage	6 kV	Current	Auto <sup>2</sup>
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

<sup>1</sup> 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.

<sup>2</sup> Current is set automatically based on the mass absorption coefficient.

**DISCUSSION**

Chemical turquoise, a triclinic mineral that is a hydrous phosphate of copper and aluminum ( $\text{CuAl}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$ ), often a subsidiary copper ore occurring in botryoidal masses in the zone of alteration in aluminum rich volcanic rocks such as trachytes. The elemental concentration of copper is relatively high imbuing a green to blue color to the stone, in part, responsible for its popularity in world prehistory as a gemstone (Blake 1899; Harbottle and Weigand 1992; see also Mathien 1981). However, turquoise since it is relatively soft (Moh's scale around five) can weather over time and some elements can be depleted shifting the elemental

composition in prehistoric artifacts. While x-ray fluorescence spectrometry has been unsuccessful in confidently determining sources, given the elemental similarity among turquoise sources produced through precipitation at ambient temperatures, the composition of this bead with relatively high elemental copper, calcium, potassium, and categorizing it as an alumino-silicate suggests that it is indeed what can be called "cultural" turquoise (see Fertelmes and Loendorf 2012; Mathien and Olinger 1992; Shackley 2008; Table 2 herein). Cultural turquoise includes the turquoise group antlerite, azurite, chrysocolla, ferrian turquoise (i.e. Cerrillos turquoise), planerite, malachite, and some combinations with quartz ( $\text{SiO}_2$ , which this artifact could be a member) all containing some proportion of elemental copper (Béarat and Simon 2002; Kim et al. 2003; Sigleo 1975, Sinkankas 1966).

It is generally accepted that stable isotopic analyses using various instrumentation is the best method to determine source in copper based rocks and artifacts, however the isotopes best used in that endeavor are highly contested (Hull 2006; Hull et al. 2008; Thibodeau and Chelsey 2007; Young et al. 1994). Still there has been some success in both the Hull and Thibodeau studies, despite disagreements as to the most perspicacious method to use. I will not attempt to determine the source of the bead here, although the blue color is similar to Sleeping Beauty turquoise from the Clifton, Arizona area or Kingman from western Arizona mines, both mines and mine groups depleted and no longer available, but as noted above the color can shift over time, and given its small size it could also be from a number of other sources. I do not have samples from either locality, so no comparison can be made, and Fertelmes and Loendorf (2012) did not provide elemental source data from their study, so no comparison can be made with that study. I do have an ore sample I collected in 2006 from an adit in Cerrillos, northern New Mexico, the composition of which is shown in Table 2 along with this artifact. Cerrillos turquoise is typically megascopically more toward the green end and as can be seen in the analysis supported by the Cu

composition that is higher than this artifact's elemental concentration for copper, and the relatively high iron (nearly 7%) could put Cerrillos turquoise in the ferrian turquoise group (Table 2.). It is important to keep in mind that the variability within a single turquoise source is very high such that major, minor, and trace elements as acquired by XRF can rarely discriminate between turquoise sources (see Fertelmes and Loendorf 2012), thus the emphasis on stable isotope analysis that is not subject to the same variability as elements for source discrimination. Finally, most faked turquoise is stained howlite, a rock that is soft and generally white, but accepts staining well. Howlite is a calcium borosilicate hydroxide that contains almost no copper, so it is doubtful that the artifact here is a fake turquoise.

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Table 1. Elemental concentrations for the obsidian artifact, USGS G-2 granite standard and USGS recommended values. All measurements in parts per million (ppm).

Sample	Ti	Mn	Fe	Rb	Sr	Y	Zr	Nb	Ba	Pb	Th	Source
71235	1120	368	8611	134	45	20	133	26	435	18	6	Vulture, AZ standard
G-2	2619	300	16835	170	459	12	277	6	1637	24	22	
G-2 recommended	2878	232	18605	170	478	11	309	12	1880	30	25	

Table 2. Non-normalized major, minor and trace element values for the turquoise bead and Cerrillos turquoise ore from the source collected in 2006. All measurements in weight percent (%) or parts per million (ppm) as noted.

Sample	Na2O	MgO	Al2O3	SiO2	P2O5	K2O	CaO	TiO2	V2O5	Cr2O3	MnO	Fe2O3			
	%	%	%	%	%	%	%	%	%	%	%	%			
71285	5.59	0.63	1.14	42.68	1.17	5.29	15.64	0.21	0.03	0.03	0.20	0.65			
Cerrillos Ore	5.37	1.29	16.62	22.78	8.34	0.73	23.19	0.20	0.10	0.05	0.09	6.97			
	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
71285	11213	6	23	16114	268	8	20	64	4	87	1	3	26	81149	4
Cerrillos Ore	1720	34	26	59930	22	8	1	329	32	155	4	116	230	41	7