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ENERGY DISPERSIVE X-RAY FLUORESCENCE (EDXRF) ANALYSIS OF MAJOR OXIDE, MINOR OXIDE AND TRACE ELEMENT CONCENTRATIONS FOR A POSSIBLE HOHOKAM BALL



by

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Report Prepared for

Dr. Sandra Lynch Sharlot Hall Museum Prescott, Arizona

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INTRODUCTION

The major and minor oxide and trace element analysis here of the possible Hohokam ball indicates that less than 50% of the composition can be acquired by XRF (x-ray fluorescence spectrometry) [see Table 1]. This does suggest that the ball is predominantly hydrocarbon, but cannot be verified by XRF (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 2011).

Trace Element Analyses

Trace element analyses were conducted to aid in the determination of rock type. 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 μ m (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.

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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 Kα-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 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 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 Cu-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, P, Cl, K, Ca, Ti, V, Cr, Mn, Fe, and As 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 few percent of actual, based on the analysis of SARM-69 Ceramic-1 standard (see also Shackley 2011). The fundamental parameters (theoretical) method is run under conditions commensurate with the elements of interest and calibrated with tem 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 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 En	ergy 10 keV	Count Rate	Low		
Mid Zb (K, Ca,	Гi, V, Cr, Mn, Fe)				
Voltage	32 kV	Current	Auto		
Livetime	100 seconds	Counts Limit	0		
Filter	Pd (0.06 mm)	Atmosphere	Vacuum		
Maximum En	ergy 40 keV	Count Rate	Medium		

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

Low Zb (S, Cl, K, Ca)									
	Maximum Energy	y 40 keV	Count Rate	High					
	Filter	Cu (0.559 mm)	Atmosphere	Vacuum					
	Livetime	100 seconds	Counts Limit	0					
	Voltage	50 kV	Current	Auto					

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 if necessary. Given that the ball had to be placed near the target and detector openings, no standard could be analyzed, and the results are likely not up to specifications, but close to target data.

DISCUSSION

Natural rubber is a latex polyisoprene compound, essentially a hydrocarbon (Greve 2000;

see Figure 1 here). From Hosler et al. (1999:1988):

The raw material for most Mesoamerican rubber balls and for other

Mesoamerican rubber artifacts is a latex acquired from the Castilla elastica tree

(5). The tree is indigenous to tropical lowland Mexico and Central America.

Castilla latex is a sticky white liquid that when dried is too brittle to retain its

shape. Sixteenth century Spaniards relate that ancient Mesoamerican peoples

processed the raw material by mixing *C. elastica* latex with juice from *Ipomoea alba* (6) (a species of morning glory vine)...

It was used to produce rubber balls for the ballgame since at least 1600 BC (Hosler et al. 1999). The use of rubber balls was witnessed by the Spanish in the 16th century in Central American ballgames. I won't investigate the Hohokam ballgame here. It has been extensively investigated by archaeologists in the North American Southwest for a century, and literature reflects that (see Hosler et al. 1999). It does appear that the ballgame was discontinued sometime during the Hohokam Late Sacaton (Sedentary) Period, perhaps as early as the Middle Sedentary (sometime in the 11th century), at least as far as the evidence from Las Colinas in the Lower Salt River Valley of central Arizona is concerned (Fertelmes et al. 2012).

There are few non-destructive methods for analyzing elements below about Z=11 (Na). While chromatography and mass spectrometry could detail the composition, they are generally destructive. What is interesting here is that over 45% of the composition of the ball is inorganic compounds. Iron comprises over 20% of the composition, certainly not an element in latex (see Figure 1 and Table 1). This is likely due to the method of production prehistorically, or post-depositional contamination (i.e. buried contexts). There is little in the literature concerning the production of these balls in Mesoamerica, so it's difficult to elucidate. I suggest contacting Dorothy Hosler at MIT (hosler@mit.edu). Dorothy will have a better idea whether there is a non-destructive method for analyzing this object.

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SAMPLE	SUM	Na2O	MgO	Al2O3	SiO2	P2O5	CI	K2O	CaO	TiO2	V2O5	MnO	Fe2O3	CoO	CuO	ZnO	As2O5	Ag2O	SnO2	Sb2O5
		%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
BALL	45.528	<0.001	0.233	0.194	0.414	0.103	0.051	0.046	0.439	<0.001	1.895	5.96	20.89	11.588	0.979	0.918	<0.001	0.212	1.024	0.582
		Ti	Co	Ni	Cu	Zn	Ga	Rb	Sr	Y	Zr	Nb	Ва	Pb	Th					
		ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm					
BALL		663.977	<1	14.438	2.836	4.257	10.98	4.773	43.344	0.881	20.391	0.395	<1	<1	3.046					

Table 1. Oxide and trace element composition of the rubber ball. Weight percent or parts per million (ppm) concentrations as noted.



Figure 1. Simplified scheme showing synthesis of natural rubber (from Greve 2000).