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**X-RAY FLUORESCENCE (XRF) ANALYSIS OF MAJOR, MINOR, AND TRACE
ELEMENTS FOR AN OBSIDIAN NODULE RECOVERED FROM GREEN
RIVER ALLUVIUM, GREEN RIVER, WYOMING**

by

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Report Prepared for

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INTRODUCTION

The results of the analysis here of one obsidian nodule from Green River alluvium near Green River, Wyoming does not match any of the 260+ sources or source groups in the Skinner/Shackley database for North America. It is certainly a rhyolite glass (obsidian) based on the TAS plot of silica and alkalis (Figure 1).

LABORATORY SAMPLING, ANALYSIS AND INSTRUMENTATION

The sample was 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).

All analyses for this study were conducted on a ThermoScientific *Quant'X* EDXRF spectrometer, located at 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 scandium (Sc). 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 100 seconds livetime generally using an 8.8 mm tube collimator to generate x-ray intensity Ka-line data for elements titanium (Ti), manganese (Mn), iron (as $\text{Fe}_2\text{O}_3^{\text{T}}$), 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 and below detection limits. 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) 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 volcanic rocks is available in Shackley (1995, 2005; also Mahood and Stimac 1990; 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 (hawaiiite), 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 Si, Al, Ca, Fe, K, Mg, Mn, Na, and Ti 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 or in this study the USGS AGV-1 andesite standard (see also Shackley 2011). The fundamental parameters (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). See Lundblad et al. (2011) for another set of conditions and methods for oxide analyses.

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 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 software for manipulation and on into IGPET for Windows for plotting. In order to evaluate these quantitative determinations, machine data were compared to measurements of known standards during each run. RGM-1 a USGS rhyolite (obsidian) standard was analyzed during each run of ≤ 20 samples. The USGS recommended values are included in Table 1. Trace element data exhibited in Table 1 is reported in parts per million (ppm), a quantitative measure by weight, and percent by weight as noted.

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Table 1. Elemental concentrations for the obsidian nodule, USGS RGM-1 rhyolite standard, and USGS recommended values. All measurements in parts per million (ppm) or weight percent as noted.

Sample	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	K ₂ O	CaO	TiO ₂	V ₂ O ₅	MnO	Fe ₂ O ₃	As ₂ O ₅	Σ
	%	%	%	%	%	%	%	%	%	%	%	%	
GREEN RIVER-1	3.47	0.512	13.143	72.341	0	3.539	2.808	0.32	0.025	0.102	3.179	0.001	99.44
RGM1-S4	4.044	0	13.055	73.836	0	4.91	1.383	0.3	0.002	0.044	2.192	0	99.766
RGM USGS Rec.	4.07	0.28	13.7	73.4	nr	4.3	1.15	0.27	nr	0.036	1.86	nr	
	Ni	Cu	Zn	Rb	Sr	Y	Zr	Nb	Ba	Pb	Th		
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm		
GREEN RIVER-1	16	18	61	81	211	18	178	13	1372	22	27		
RGM1-S4	16	11	43	147	110	25	222	9	848	24	10		
RGM USGS Rec.	nr	12	32	150	110	25	220	8.9	810	24	15		

¹ nr = not reported

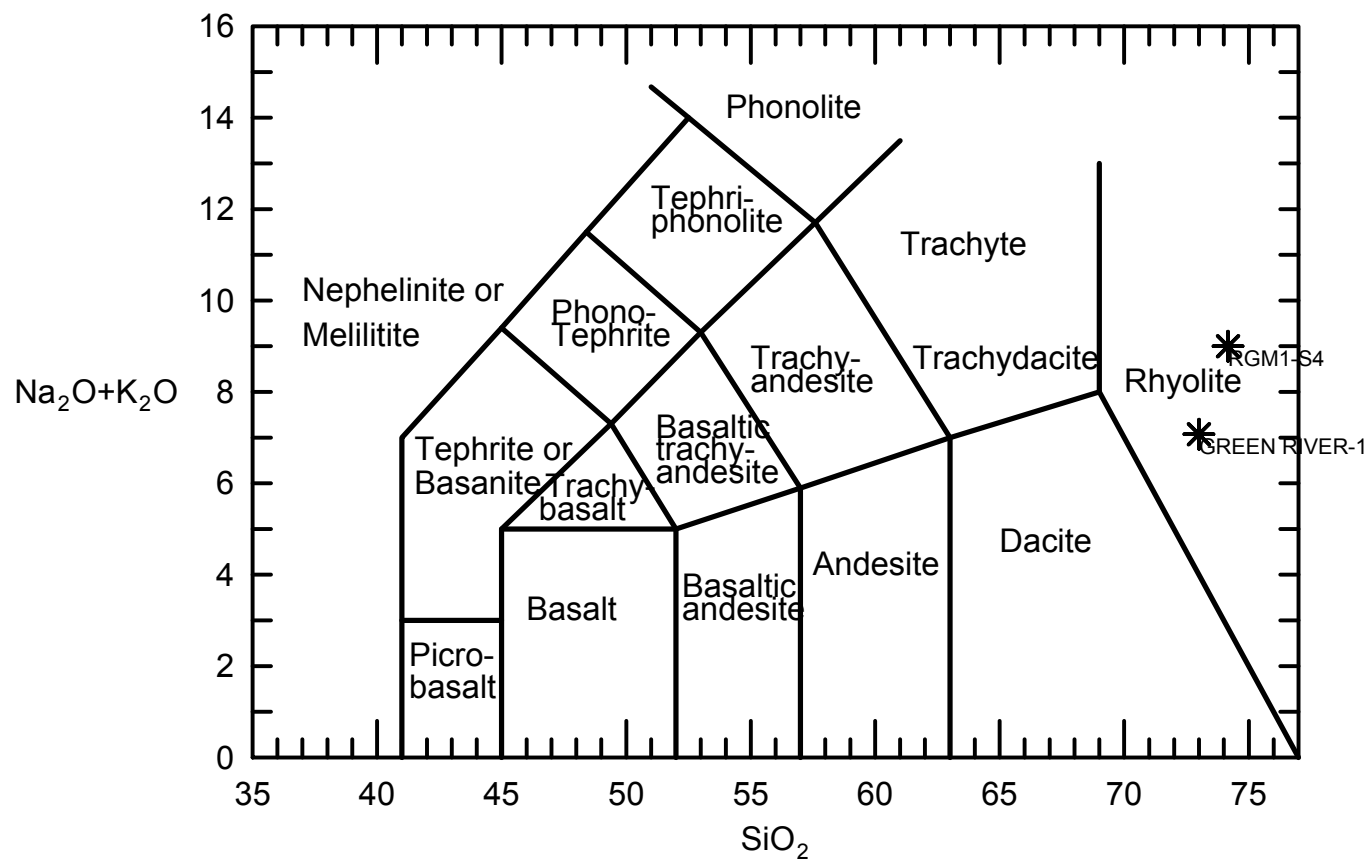


Figure 1. TAS plot of the obsidian nodule and USGS RGM-1 rhyolite standard (Le Maitre et al. 1989).