

UC Berkeley

Archaeological X-ray Fluorescence Reports

Title

ENERGY-DISPERSIVE X-RAY FLOURESCENCE (EDXRF) ANALYSIS OF MAJOR, MINOR AND TRACE ELEMENTS FOR VOLCANIC GLASS ROCKS FROM OAHU COUNTY, HAWAI'I

Permalink

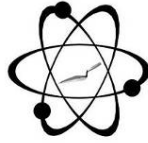
<https://escholarship.org/uc/item/7mw8s12w>

Author

Shackley, M. Steven

Publication Date

2020-07-28



GEOARCHAEOLOGICAL XRF LAB
A GREEN SOLAR FACILITY

GEOARCHAEOLOGICAL X-RAY FLUORESCENCE SPECTROMETRY LABORATORY
8100 Wyoming Blvd., Ste M4-158
USA

Albuquerque, NM 87113

**ENERGY-DISPERSIVE X-RAY FLOURESCENCE (EDXRF) ANALYSIS
OF MAJOR, MINOR AND TRACE ELEMENTS FOR VOLCANIC GLASS
ROCKS FROM OAHU COUNTY, HAWAI'I**

by

M. Steven Shackley, Ph.D., Director
Geoarchaeological XRF Laboratory
Albuquerque, New Mexico

Report Prepared for

Lizabeth Hauani'o
Keala Pono Archaeological Consulting
Pahoa, Hawai'i

28 July 2020

INTRODUCTION

The analysis here of six vitreous rock samples indicates trachy-andesite and basaltic trachy-andesite glasses according to an alkali/silica plot (Le Bas et al. 1986; Le Maitre et al. 1989; Table 1 and Figure 1 herein). Trachyte glass does occur in nature such as the Emuruangogolok volcano in Kenya, and a source in the Hawai'ian Islands, the former with SiO₂ values over 62% by weight (Steve Lundblad, personal communication; Weaver 1977). In order to quench to a natural glass in any volume however, SiO₂ needs cross the boundary between about 72 to 78 weight percent, slightly lower for peralkaline volcanic rocks (Borovec 1993; Cann 1983; Fink and Manley 1987; Lajcakova and Kraus 1993; Shackley 2005). Compositionally, the rocks are a trachy-andesite or basaltic trachy-andesite with SiO₂ values between 52.09 and 56.85 weight percent possibly lower than has ever been recorded in nature for glass nodules this size. Nevertheless, I removed two flakes easily and would expect that it would be a good media for stone tool production.

More specifically with regard to the major and minor oxides, there is some variability in Mg and Ca. Whether this is due to artificial production or natural processes is unknown. The remainder of the oxides and elements are relatively similar except for some variability in Cl and Ni, both of which are poorly measured in the method used in this analysis.

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 μm (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 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. In order to evaluate these quantitative determinations, machine data were compared to measurements of known standards during each run. RGM-1 a USGS rhyolite standard was analyzed during each run of ≤ 19 samples. The USGS recommended values for RGM-1 are included in Table 1. Trace element data exhibited in Table 1 are reported in weight percent and parts per million (ppm), a quantitative measure by weight as noted.

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 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.

References Cited

- Borovec, Z. 1993, The physico-chemical characteristics of natural glasses. In V. Bouška (Ed.) *Natural Glasses*, pp. 13-84. Prague: Czechoslovak Academy of Sciences.
- Cann, J.R. 1983, The petrology of obsidian artifacts. In Kempe, D.R.C. and Harvey, A.P. (Eds.) *The Petrology of Archaeological Artefacts*, pp. 227-255. Oxford: Clarendon Press.
- Davis, M.K., Jackson, T.L., Shackley, M.S., Teague, T., and Hampel J., [new introduction by M.S. Shackley], 2011, Factors affecting the energy-dispersive x-ray fluorescence (EDXRF) analysis of archaeological obsidian, In Shackley, M.S., (Ed.), *X-Ray Fluorescence Spectrometry (XRF) in Geoarchaeology*, pp. 45-64. New York: Springer Publishing.
- Fink, J.H., and Manley, C.R. 1987, Origin of pumiceous and glassy textures in rhyolite flows and domes. In Fink, J.H. (Ed.) *The Emplacement of Silicic Domes and Lava Flows*, pp. 77-88. Boulder, Colorado: Geological Society of America Special Paper 212.
- Govindaraju, K., 1994, Compilation of working values and sample description for 383 geostandards: *Geostandards Newsletter* v. 18 (special issue), 158 p.
- Hampel, J.H., 1984, Technical considerations in x-ray fluorescence analysis of obsidian; in R.E. Hughes ed., *Obsidian Studies in the Great Basin: Berkeley, Contributions of the University of California Archaeological Research Facility* 45, p. 21–25.
- Hildreth, W., 1981, Gradients in Silicic Magma Chambers: Implications for Lithospheric Magmatism. *Journal of Geophysical Research* 86:10153-10192.
- Hughes, R. E., and R. L. Smith, 1993, Archaeology, geology, and geochemistry in obsidian provenance studies. In J.K. Stein and A.R. Linse (Eds.), *Scale on Archaeological and Geoscientific Perspectives*, pp. 79-91. Geological Society of America Special Paper 283.
- Lajčáková A. and Kraus, I., 1993, Volcanic glasses. In V. Bouška (Ed.) *Natural Glasses*, pp. 85-121. Prague: Czechoslovak Academy of Sciences.
- Le Bas, M.J., Le Maitre, R.W., Streckeisen, A., and Zanettin, B., 1986, A chemical classification of volcanic rocks based on the total alkali silica diagram. *Journal of Petrology* 27:745-750.

- Le Maitre, R.W.; Bateman, P.; Dudek, A.; Keller, J.; Lameyre, J.; Le Bas, M.; Sabine, P.; Schmid, R.; Sorensen, H.; Streckeisen, A.; Woolley, A.; Zanettin, B. 1989, A classification of igneous rocks and glossary of terms. In Le Maitre, R.W. (Ed.) Recommendations of the International Union of Geological Sciences Subcommittee on the Systematics of igneous rocks. Oxford: Blackwell, 193 p.
- Mahood, Gail A., and James A. Stimac, 1990, Trace-element partitioning in pantellerites and trachytes. *Geochemica et Cosmochimica Acta* 54:2257-2276.
- McCarthy, J.J., and F.H. Schamber, 1981, Least-squares fit with digital filter: a status report. In K.F.J. Heinrich, D.E. Newbury, R.L. Myklebust, and C.E. Fiori (Eds.) *Energy Dispersive X-ray Spectrometry*, pp. 273-296. National Bureau of Standards Special Publication 604, Washington, D.C.
- Schamber, F.H., 1977, A modification of the linear least-squares fitting method which provides continuum suppression. In Dzuby, T.G. (Ed.) *X-ray Fluorescence Analysis of Environmental Samples*, pp. 241-257. Ann Arbor Science Publishers.
- Shackley, M.S., 1988, Sources of archaeological obsidian in the Southwest: an archaeological, petrological, and geochemical study. *American Antiquity* 53:752-772.
- Shackley, M. S., 1995, Sources of archaeological obsidian in the greater American Southwest: an update and quantitative analysis. *American Antiquity* 60(3):531-551.
- Shackley, M.S., 2005, *Obsidian: Geology and Archaeology in the North American Southwest*. University of Arizona Press, Tucson.
- Shackley, M.S., 2011, An introduction to x-ray fluorescence (XRF) analysis in archaeology. In M.S. Shackley (Ed.), *X-Ray Fluorescence Spectrometry (XRF) in Geoarchaeology*, pp. 7-44. Springer: New York.
- Weaver, S.D., 1977, The Quaternary caldera volcano Emuruangogolok, Kenya Rift, and the petrology of a bimodal ferrobasalt-pantellerite trachyte association. *Bulletin Volcanologique* 40:209-230.

Table 1. Non-normalized major, and minor elemental concentrations for the rock samples, USGS RGM-1 rhyolite standard, and USGS recommended mean values for RGM-1. All measurements in weight percent (%) or parts per million (ppm) as noted (see <http://swxrflab.net/anlysis.htm>).

Sample	Na2O %	MgO %	Al2O3 %	SiO2 %	P2O5 %	K2O %	CaO %	TiO2 %	V2O5 %	MnO %	Fe2O3 %	Σ					
1	8.77	0.36	21.16	55.98	0	0.48	1.53	1.19	3.30	0.03	7.02	99.83					
2	7.66	0.00	24.55	54.12	0	0.53	1.66	1.32	3.40	0.04	5.93	99.21					
3	8.67	0.44	21.26	56.85	0	0.47	1.66	1.08	2.92	0.02	6.41	99.78					
4	8.02	1.01	20.98	54.28	0	0.49	3.05	1.41	3.14	0.03	7.26	99.68					
5	6.35	2.20	20.23	56.81	0	0.52	1.95	1.05	3.69	0.03	6.94	99.77					
6	6.26	0.68	23.96	52.09	0	0.62	4.73	1.48	3.19	0.02	6.59	99.62					
RGM1-S4	4.06	0.00	12.91	73.89	0	4.93	1.42	0.27	0.03	0.04	2.21	99.76					
RGM1 recommended	4.07	0.28	13.70	73.40	nr	4.30	1.15	0.27	nr	0.04	1.86						
	Cl ppm	Co ppm	Ni ppm	Cu ppm	Zn ppm	Ga ppm	Rb ppm	Sr ppm	Y ppm	Zr ppm	Nb ppm	Ba ppm	Pb ppm	Th ppm			
1	0	145	1339	1	19	18	12	376	25	330	24	506	2	25			
2	0	164	4578	0	81	40	18	366	34	368	24	574	18	37			
3	148	119	1176	0	20	17	8	353	22	314	26	543	0	20			
4	910	106	451	0	18	17	10	373	28	340	22	481	0	14			
5	297	95	817	1	20	11	6	350	26	314	21	523	4	26			
6	394	134	2962	0	33	24	14	355	32	380	27	654	11	17			
RGM1-S4	480	0	18	9	37	14	148	111	25	220	10	790	18	16			
RGM1 recommended	510	2	nr	12	32	15	150	110	25	220	9	810	24	15			

nr = not reported

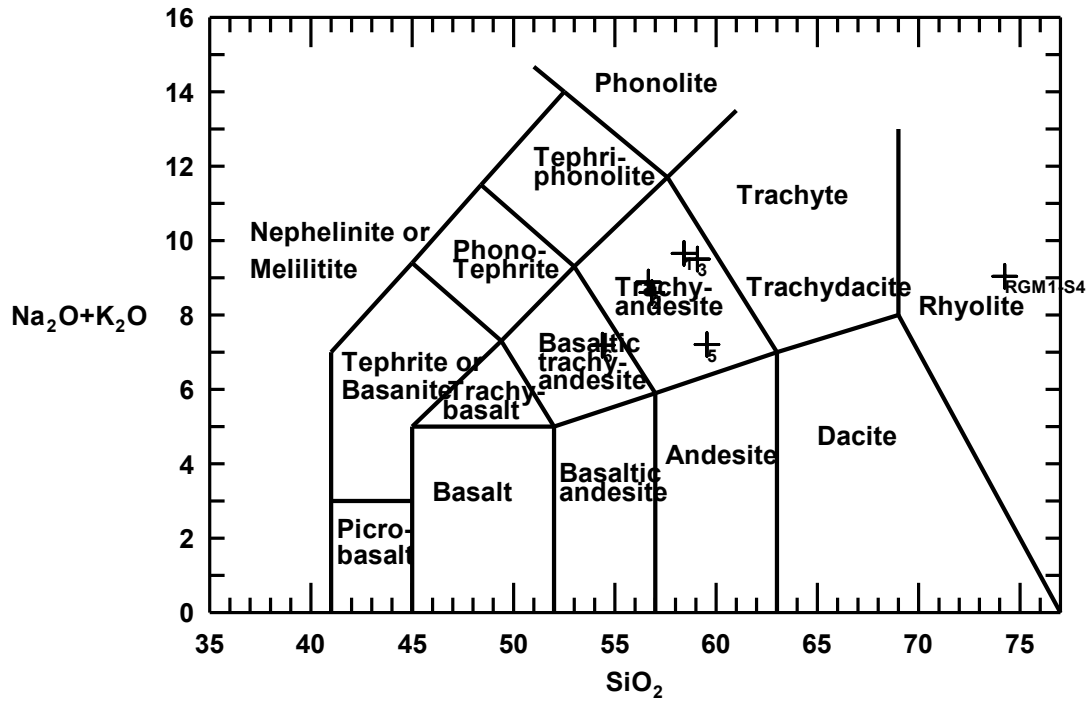


Figure 1. Non-normalized TAS plot of the rock samples and USGS RGM-1 (Le Maitre et al. 1989).