Title

ENERGY-DISPERSIVE X-RAY FLOURESCENCE (EDXRF) WHOLE ROCK ANALYSIS OF MAJOR, MINOR AND TRACE ELEMENTS FOR SEVENPOWDERED LIMESTONE AND PLUTONICROCK SAMPLES

Author

Shackley, M. Steven

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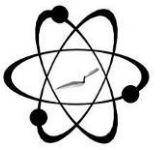

GEOARCHAEOLOGICAL X-RAY FLUORESCENCE SPECTROMETRY LABORATORY
8100 Wyoming Blvd., Ste M4-158 Albuquerque, NM 87113
USA

ENERGY-DISPERSIVE X-RAY FLOURESCENCE (EDXRF) WHOLE ROCK ANALYSIS OF MAJOR, MINOR AND TRACE ELEMENTS FOR SEVEN POWDERED LIMESTONE AND PLUTONIC ROCK SAMPLES

by

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

Report Prepared for

Kelsey Spain
Department of Geosciences
Fort Hays State University
Hays, Kansas

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INTRODUCTION

The analysis here of seven powdered samples indicates a variable composition (Table 1). The plutonic rocks vary from mafic to silicic (Table 1).

LABORATORY SAMPLING, ANALYSIS AND INSTRUMENTATION

All samples are analyzed whole without further sample preparation. The powdered samples were placed in closed-end sample cups with 6 μm mylar polyester thin film for presentation to the x-ray beam. The results 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 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.

Trace Element Analysis

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 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. 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 (1988, 1995, 2005, 2021; Shackley et al. 2016, 2018; 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, 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, P, 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 a few percent of actual, based on the analysis of USGS RGM-1 obsidian or 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).

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 data from the WinTrace software were translated directly into Excel for Windows and into SPSS ver. 27 or JMP 12.0.1 for statistical manipulation as appropriate. The USGS RGM-1 rhyolite standard is analyzed during each sample run of ≤ 19 samples to evaluate machine calibration (Table 1).

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Table 1. Major , minor and trace element results of the seven samples and the USGS RGM-1 rhyolite standard. Measurements in weight percent (%) or parts per million (ppm) as noted.

Sample	Na2O	MgO	Al2O3	SiO2	P2O5	K2O	CaO	TiO2	V2O5	MnO	Fe2O3	∑	rock type
	%	%	%	%	%	%	%	%	%	%	%		
DRLS	2.77	11.62	0.21	39.14	1.54	0.00	40.91	0.15	0.00	0.22	3.33	99.89	limestone
LSC1	2.78	4.73	8.67	34.01	0.12	1.85	1.94	2.31	0.26	0.16	42.84	99.66	plutonic
LSC2	2.85	5.18	9.01	37.09	0.20	2.12	1.94	2.50	0.20	0.15	38.42	99.65	plutonic
LSC5	3.40	1.23	11.27	62.47	0.00	5.53	1.93	1.14	0.05	0.21	12.05	99.28	plutonic
MCLS	3.71	0.78	0.35	1.77	2.53	0.00	89.90	0.04	0.03	0.05	0.64	99.79	limestone
RS1	2.76	2.69	7.88	40.41	0.73	0.74	9.49	2.08	0.13	0.57	31.77	99.22	plutonic
RS2	3.09	2.02	8.68	36.88	0.56	3.32	9.95	2.99	0.30	0.54	31.05	99.38	plutonic
RGM1-S4	3.95	0.00	13.30	73.69	0.00	4.87	1.41	0.29	0.01	0.04	2.20	99.76	standard
RGM-1 recommended	4.07	0.28	13.70	73.40	nr[1]	4.30	1.15	0.27	nr	0.04	1.86		

	Cl	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
DRLS	0	18	14	129	10	0	67	15	19	1	15	17	3	8
LSC1	0	22	114	170	20	19	17	23	125	3	376	0	0	4
LSC2	0	20	93	146	20	24	14	28	119	4	422	33	3	4
LSC5	0	17	25	232	18	51	138	23	193	4	1363	19	2	9
MCLS	517	15	0	23	9	0	503	10	23	8	59	10	2	7
RS1	0	20	783	118	19	10	372	37	188	1	163	34	8	4
RS2	0	19	373	135	21	41	367	32	148	1	643	19	0	7
RGM1-S4	521	17	13	47	16	145	104	28	220	7	813	40	18	16
RGM-1 recommended	510	nr	12	32	15	150	110	25	220	9	810	47	24	15

[1] = not reported