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**AN ENERGY-DISPERSIVE X-RAY FLUORESCENCE (EDXRF) ANALYSIS OF
MAJOR, MINOR, AND TRACE ELEMENTS FOR GROUNDSTONE
FRAGMENTS, AND SOURCE PLUTONIC ROCKS FROM SITES ON FORT
BLISS, NEW MEXICO**

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INTRODUCTION

The analysis here of 11 groundstone artifacts and ten source rocks, plus the six from the previous study exhibit an unclear relationship between the source rocks and the artifacts. The source assignments here are based on multivariate statistical analyses and three-dimensional plotting. Major oxide analyses of a sample of the source rocks from both the Organ and Elephant Mountains indicates intermediate through silicic plutonic rocks from diorite to granodiorite to granite. The oxide analysis indicates the difficulty of using elemental analysis for source characterization for these large crystalline plutonic rocks.

ANALYSIS AND INSTRUMENTATION

All archaeological samples are analyzed whole, and due to size were analyzed individually in the instrument chamber. 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).

The trace element analyses were performed in the NSF Geoarchaeological XRF Laboratory, Department of Anthropology, University of California, Berkeley, using a Thermo Scientific *Quant'X* energy dispersive x-ray fluorescence spectrometer. The spectrometer is equipped with a ultra-high flux peltier air cooled Rh x-ray target with a 125 micron beryllium (Be) window, an x-ray generator that operates from 4-50 kV/0.02-1.0 mA at 0.02 increments, using an IBM PC based microprocessor and WinTrace™ 4.1 reduction software. The spectrometer is equipped with a 2001 min⁻¹ Edwards vacuum pump for the analysis of elements below titanium (Ti). Data is acquired through a pulse processor and analog to digital converter. This is a significant improvement in analytical speed and efficiency beyond the former Spectrace 5000 and *QuanX* analog systems (see Davis et al. 1998; Shackley 2005).

For Ti-Nb, Pb, Th elements the mid-Zb condition is used operating the x-ray tube 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 $K\alpha_1$ -line data for elements titanium (Ti), manganese (Mn), iron (as Fe^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 is 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 but Fe where a derivative fitting is used to improve the fit for iron and thus for all the other elements. When barium (Ba) is acquired, the Rh tube is operated at 50 kV and 0.5 mA in an air path at 200 seconds livetime to generate x-ray intensity $K\alpha_1$ -line data, through a 0.630 mm Cu (thick) filter ratioed to the bremsstrahlung region (see Davis et al. 1998). Further details concerning the petrological choice of these elements in North American obsidians is available in Shackley (1988, 1990, 1995, 2005; also Mahood and Stimac 1991; and Hughes and Smith 1993). A suite of 17 specific standards used for the best fit regression calibration for elements Ti- Nb, Pb, and Th, 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), BCR-2 (basalt), TLM-1 (tonalite), SCO-1 (shale), all US Geological Survey standards, NBS-278 (obsidian) from the National Institute of Standards and Technology, BR-1 (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).

The oxide analysis is a developing experimental method on the Quant'X. The oxides for silica, aluminum, calcium, iron, potassium, magnesium, manganese, sodium, and titanium, as well as others not reported here are acquired using a theoretical fundamental parameters method with four separate conditions from low Z_a to high Z_a all under vacuum. All other instrumental conditions are the same as for the traces discussed above. The USGS G-2 granite standard was run with these samples and exhibited fair agreement with USGS reported analyses (Table 1). Trace element concentrations for all the submitted source standards is exhibited in Table 2.

The data from the WinTrace software were translated directly into Excel for Windows and into SPSS for statistical manipulation (Table 3 for trace elements). In order to evaluate these quantitative determinations, machine data were compared to measurements of known standards during each run (Table 1 and 3). For the source rock, USGS G-2 granite standard was run. The data from nine of the acquired trace elements were subjected to hierarchical cluster and three-dimensional plotting to determine chemical groups (Figures 1 through 3).

DISCUSSION

It is axiomatic in statistics and science in general, as the sample size increases, the variability increases. This is the case here. By increasing the sample size of these large crystalline plutonic rocks, the variability decreases exponentially. It is obvious that an elemental analysis will not solve the issue here. A destructive isotopic study (Nd, Pb, Sr) would probably be indicated, or LA-ICP-MS or microprobe analyses of selected minerals. Nevertheless, there are some patterns discernable, but these are essentially outliers in the data. Source samples Organ Mountain 1 and 7 clearly cluster together and in the three most prominent elements are quite different (Figures 1 and 2). The rest of the data are not well clustered. While the cluster analysis does see some differences, they mix the various rock types base on the trace elements (Figure 3). While the ability to assign these plutonic rock artifacts to source is difficult, the experiment was useful if for no other reason than to point to more parsimonious studies.

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Table 1. Oxide analysis for a sample of the Elephant and Organ Mountain source rocks. All analyses in percent by weight.

Source/Sample	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	K ₂ O	MgO	MnO	Na ₂ O	TiO ₂	Rock type
Elephant Mnt2	57.45	9.472	8.381	9.436	7.582	0.781	0.72	2.763	0.866	diorite
Elephant Mnt5	64.16	14.55	3.269	4.931	5.632	1.933	0.106	4.093	0.732	granodiorite
Elephant Mnt7	70.74	10.57	7.195	3.608	1.557	0.484	0.094	3.639	1.209	granite
Organ Mtns8	69.63	11.37	3.433	6.343	2.419	3.264	0.091	2.041	1.04	granodiorite
Organ Mtns9	60.15	10.28	6.884	7.735	9.275	0.595	0.14	2.795	1.346	diorite
G2-standard	70.48	14.11	2.35	2.71	5.162	0.833	0.04	3.566	0.48	granite (standard)

Table 2. Elemental concentrations for Elephant and Organ Mountains source standards (GRn) and previous source standard analyses from Shackley (2009). All measurements in parts per million (ppm).

Sample	Provenience	Ti	Mn	Fe	Zn	Rb	Sr	Y	Zr	Nb	Ba
GR1	Elephant Mtn1	1742	275	1089	16	2	306	21	166	9	12
GR2	Elephant Mtn2	3761	583	2579	45	70	1156	24	159	10	1884
GR3	Elephant Mtn3	2801	554	2034	37	65	534	19	160	7	1769
GR4	Elephant Mtn4	2502	465	2047	35	104	954	21	160	16	2230
GR5	Elephant Mtn5	3870	522	2320	42	79	931	22	162	8	3599
GR6	Elephant Mtn6	3122	400	2683	35	84	696	24	176	10	2499
GR7	Elephant Mtn7	1763	204	9825	53	10	383	26	170	10	591
GR8	Organ Mtn8	4682	424	2931	71	146	505	30	123	23	800
GR9	Organ Mtn9	4668	426	2250	50	162	454	14	101	9	1455
GR10	Organ Mtn10	2480	260	1181	32	110	542	8	76	1	773
1		4783	867	3427	63	139	398	23	133	12	673
2		3980	1881	3451	74	124	1018	15	127	9	1820
3		3066	390	1996	94	72	714	9	155	7	1495
4		3636	373	2806	29	92	919	25	199	8	2102
5		4613	452	2500	45	130	391	21	127	17	905
6		1705	261	2519	17	147	27	115	393	44	234

Table 3. Elemental concentrations for the archaeological specimens and the USGS RGM-1 and G-2 standard. All measurements in parts per million (ppm).

Sample	Ti	Mn	Fe	Zn	Rb	Sr	Y	Zr	Nb
492	4983	439	22428	67	234	139	61	258	18
495	2808	412	12518	58	143	245	19	113	15
496	1392	216	12402	57	297	91	30	118	4
1610	3866	183	4318	221	7	4	2	22	0
1610	15583	685	12370	68	23	37	11	59	7
1636	4203	731	25633	59	129	987	29	198	11
1643	4776	220	15737	35	240	426	43	267	37
1665	2927	449	23017	31	119	980	26	181	13
2758	2804	278	8510	66	149	478	25	153	12
5070	3832	701	28585	55	97	744	22	179	12
XRF1	3540	582	21180	48	66	842	24	163	13
G2	3096	260	17514	92	179	489	13	279	12

Dendrogram using Average Linkage (Within Group)

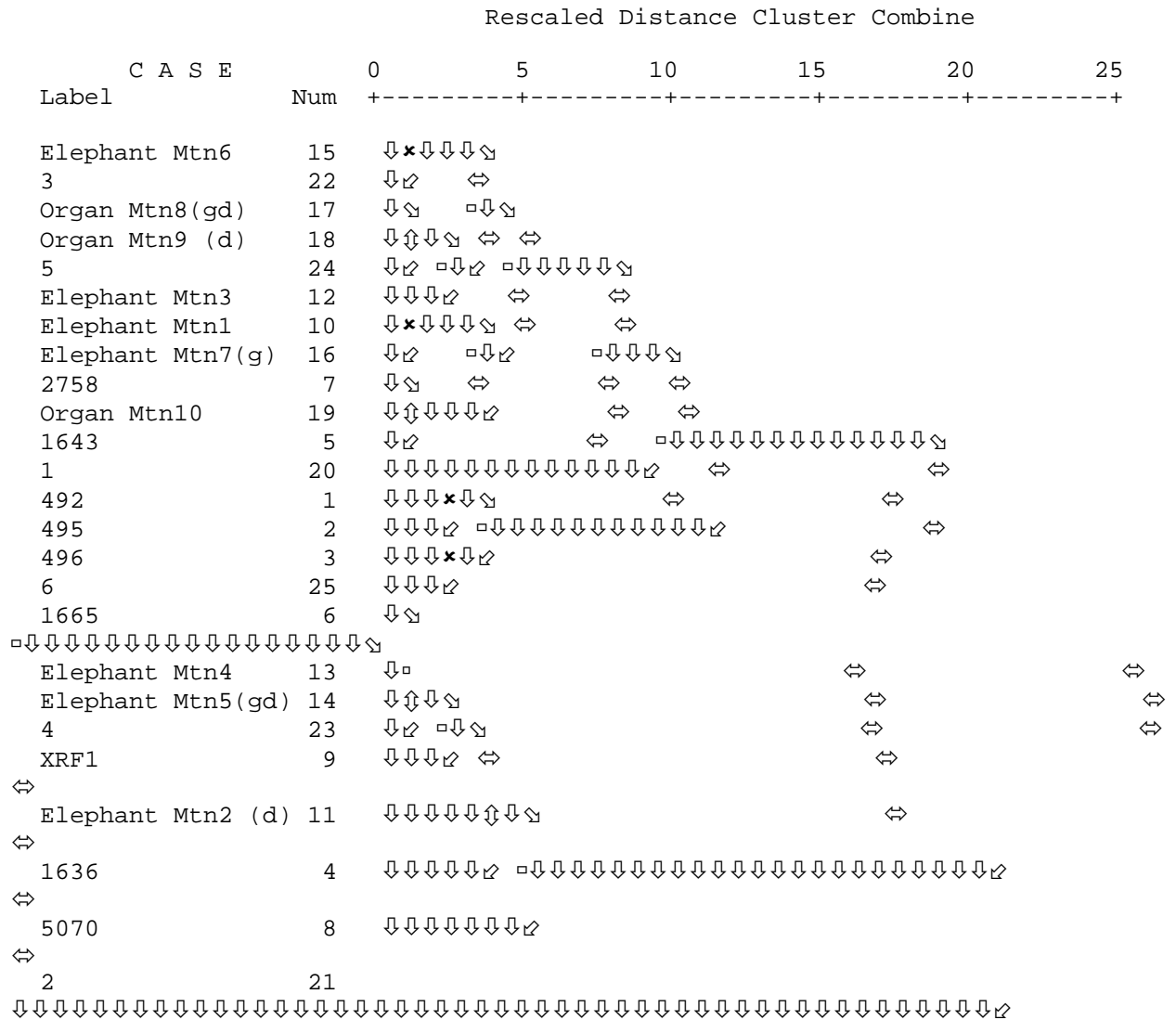


Figure 1. Average linking method/squared Euclidean distance cluster dendrogram for Rb, Sr, Mn elements for source rock (single digit numbers, Elephant and Organ Mtn) and artifacts. Rock type designations: d = diorite; g = granite; gd = granodiorite.

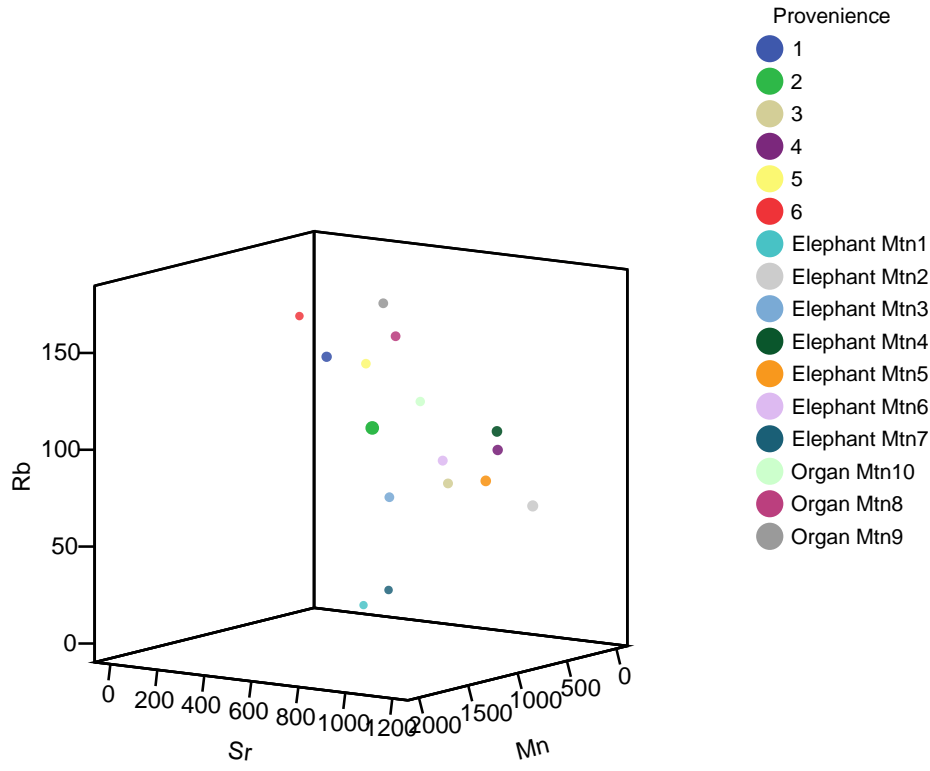


Figure 2. Rb, Sr, Mn three-dimensional plot of the source standards.

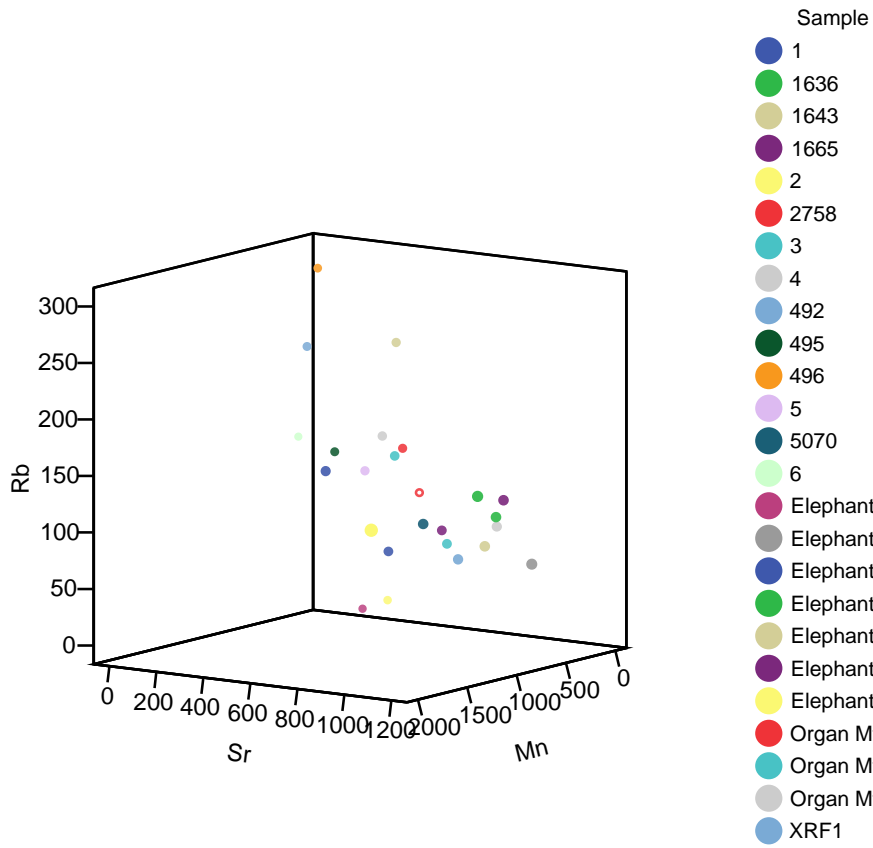


Figure 3. Rb, Sr, and Mn three dimensional plot of the artifacts and source standards.