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Publication Date
2015-02-12

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ENERGY DISPERSIVE X-RAY FLUORESCENCE (EDXRF) ANALYSIS OF MAJOR AND MINOR OXIDE AND TRACE ELEMENT CONCENTRATIONS FOR HISTORIC CHOCTAW CERAMICS FROM MISSISSIPPI AND OKLAHOMA

by

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12 February 2015

INTRODUCTION

The major and minor oxide and trace element analysis here of 24 ceramic sherds from sites in western Mississippi and eastern Oklahoma indicates some variability in oxides and trace elements (Table 1). Whether these are due to source clay, temper, or a combination of both is unknown. Further investigation should shed light on the subject.

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 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 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 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 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 SPSS software for statistical manipulation when required. In order to evaluate these quantitative determinations, machine data were compared to measurements of known standards during each run. SARM-69 (Ceramic-1) an Iron Age potsherd standard from the Orange Free State, Republic of South Africa was analyzed during each sample run to check machine calibration (Table 1; http://www.mintek.co.za/technical-divisions/analytical-services-asd/sarm/sarm-certificates/).

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Table 1. Elemental concentrations for the artifacts and SARM-69 by site. Measurements in parts per million (ppm) or percent by weight as noted.

SAMPLE	Na_2O %	MgO %	Al_2O_3 %	SiO_2 %	P_2O_5 %	Cl %	K_2O %	CaO %	TiO_2 %	V_2O_5 %	Cr_2O_3 %	MnO %	Fe_2O_3 %	As_2O_5 %
22KE501-1	2.614	0.228	13.847	60.02	0.124	0	3.534	0.997	2.371	0.101	0.043	0.209	15.355	0.009
22KE525-1	0.857	0.515	22.428	66.855	0	0	2.311	0.457	1.239	0.041	0.026	0.045	5.02	0.001
22KE525-2	1.273	0.629	17.532	70.302	0	0.044	2.21	2.035	1.097	0.055	0.015	0.06	4.316	0.001
22KE554-1	1.089	0.512	20.794	68.142	0	0	2.441	0.474	1.037	0.062	0.009	0.155	5.072	0.001
22KE554-2	0.84	0.176	20.058	69.627	0	0	2.245	0.463	1.411	0.083	0.02	0.086	4.794	0.002
22KE554-3	1.182	0.94	20.358	68.761	0	0	2.124	0.433	1.136	0.075	0.015	0.244	4.477	0.001
22KE555-1	1.07	1.313	19.343	68.455	0	0	2.033	0.929	1.133	0.048	0.023	0.092	5.367	0.001
22KE556-1	1.102	0.78	18.874	68.702	0	0	2.222	1.066	1.246	0.06	0.01	0.115	5.616	0.002
22KE556-2	1.091	0.285	18.724	71.41	0	0	1.985	0.348	1.454	0.082	0.019	0.031	4.383	0.001
22KE567-1	1.06	1.04	21.612	63.677	0	0	2.266	0.326	1.259	0.062	0.03	0.109	8.331	0.002
22KE569-1	1.081	0.568	24.694	62.172	0	0.017	1.893	0.391	1.46	0.078	0.034	0.217	7.118	0.004
22KE569-2	1.024	1.031	19.612	65.364	0	0	2.616	0.297	1.231	0.083	0.009	0.074	8.464	0.009
34MC399-1	2.687	0	11.07	53.748	0.178	0.229	2.678	5.36	5.205	0.266	0.06	0.285	17.335	0.005
34MC399-1	2.687	0	11.07	53.748	0.178	0.229	2.678	5.36	5.205	0.266	0.06	0.285	17.335	0.005
34MC399-2	1.297	0.554	16.768	65.027	0	0.024	1.15	3.768	2.695	0.082	0.021	0.176	8.135	0.001
34MC399-2	1.297	0.554	16.768	65.027	0	0.024	1.15	3.768	2.695	0.082	0.021	0.176	8.135	0.001
34MC399-3	0.873	1.043	20.633	60.644	0	0.035	1.469	4.593	1.096	0.066	0.022	0.238	8.854	0.002
34MC399-4	2.553	0.416	10.484	43.819	0.374	0.153	4.217	11.494	5.909	0.295	0.085	0.211	18.924	0.003
34MC399-4	2.553	0.416	10.484	43.819	0.374	0.153	4.217	11.494	5.909	0.295	0.085	0.211	18.924	0.003
34MC399-5	1.367	1.182	19.771	58.278	0.043	0.089	2.172	4.208	3.13	0.157	0.046	0.119	9.049	0
34MC399-5	1.367	1.182	19.771	58.278	0.043	0.089	2.172	4.208	3.13	0.157	0.046	0.119	9.049	0
34MC399-6	1.508	2.136	16.81	65.934	0	0.008	2.274	2.565	0.768	0.025	0.036	0.141	7.659	0.001
34MC399-6	1.508	2.136	16.81	65.934	0	0.008	2.274	2.565	0.768	0.025	0.036	0.141	7.659	0.001

34MC544-1	1.187	0.893	13.545	70.989	0	0.043	1.826	3.119	0.92	0.047	0.012	0.097	7.079	0.001
34MC544-2	1.239	0.536	18.402	69.697	0	0	1.827	0.311	1.143	0.048	0.015	0.055	6.573	0.001
34MC544-3	1.263	0.785	14.418	68.566	0.028	0.065	2.108	3.5	0.994	0.068	0.014	0.041	7.915	0.002
34MC544-4	1.195	0.467	20.563	59.658	0.708	0	1.152	4.587	2.877	0.122	0.038	0.13	8.17	0.003
34MC544-5	1.109	0.704	14.537	73.415	0	0	0.946	1.522	1.259	0.057	0.012	0.135	6.139	0.002
34MC974-1	1.061	0.317	14.559	76.685	0	0	0.792	2.063	1.21	0.051	0.008	0.214	2.767	0.001
SARM-69	1.416	2.116	16.937	65.845	0	0	2.267	2.561	0.81	0.05	0.037	0.137	7.687	0

	Cu ppm	Zn ppm	Ga ppm	Rb ppm	Sr ppm	Y ppm	Zr ppm	Nb ppm	Ba ppm	Pb ppm	Th ppm
22KE501-1	25	90	21	95	69	29	236	19	1124	53	15
22KE525-1	31	105	22	81	87	26	289	19	923	26	9
22KE525-2	48	97	16	79	157	26	356	18	2541	30	17
22KE554-1	26	113	20	98	97	22	220	14	1108	34	8
22KE554-2	33	94	21	75	79	35	316	17	778	40	6
22KE554-3	37	110	21	84	78	30	271	15	1379	26	9
22KE555-1	11	123	22	90	118	29	223	18	971	32	14
22KE556-1	17	108	20	80	97	22	295	16	908	38	8
22KE556-2	34	91	21	81	94	26	278	15	784	27	11
22KE567-1	36	124	21	84	74	65	327	16	1008	27	18
22KE569-1	28	128	21	52	54	36	265	18	848	51	14
22KE569-2	23	126	19	99	90	28	278	19	849	100	20
34MC399-1	41	123	20	71	264	38	591	166	1236	24	23
34MC399-2	45	106	19	71	229	38	557	156	1091	21	29
34MC399-3	18	153	22	99	232	36	225	17	2406	34	17
34MC399-4	63	111	22	78	425	38	491	128	1360	21	14
34MC399-5	68	140	21	72	535	39	522	137	1254	28	19

34MC399-6	36	101	21	78	217	32	570	161	532	24	31
34MC544-1	40	94	17	97	155	31	353	12	1229	21	10
34MC544-2	28	122	20	87	68	45	318	21	499	26	11
34MC544-3	19	78	20	97	173	33	267	16	1206	29	14
34MC544-4	66	153	25	55	315	46	534	146	1089	37	26
34MC544-5	34	68	18	87	76	38	327	13	572	33	17
34MC974-1	33	50	17	41	75	34	486	21	1251	32	10
SARM-69	42	62	20	69	115	32	263	8	530	15	4