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Preliminary Results of X-Ray Fluorescence Analysis of
Archeological Materials from Southeastern Utah

by

David H. Snow*

H. J. Fullbright

*Guest Scientist, Museum of New Mexico, P.O. Box 2087, Santa Fe, NM 87501.

los alamos
scientific laboratory
of the University of California
LOS ALAMOS, NEW MEXICO 87545

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SAMAC ANALYTICAL NOTES II
PRELIMINARY RESULTS OF X-RAY FLUORESCENCE ANALYSIS OF
ARCHEOLOGICAL MATERIALS FROM SOUTHEASTERN UTAH

by

David H. Snow
and
H. J. Fullbright

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ABSTRACT

A series of prehistoric potsherds, local clay samples, and possible tempering materials from archeological excavations in southeastern Utah have been examined by x-ray fluorescence spectroscopy. The results obtained for this small sampling demonstrate the usefulness of the technique in characterizing the clays, the potsherd pastes, and the decorative pigments.

I. INTRODUCTION

Through the courtesy of the United States Department of Agriculture, Forest Service, Monticello District Office, and Ms. Marilyn Malone, District Archeologist, 59 prehistoric potsherds from archeological excavations and survey were submitted to the SAMAC* for analysis of elemental content by x-ray fluorescence spectroscopy.

*Southwest Archeological Materials Analysis Center, a cooperative research effort between the Los Alamos Scientific Laboratory of the University of California and the Museum of New Mexico.

In addition to the sherds, seven clay samples, two pieces of arkose, and two fragments of porphyritic rock were also submitted. The materials represent items, for the most part, from sites within the Monticello District of southeastern Utah, but include samples from sites as far away as Tsegi Canyon, Arizona, and Mesa Verde, Colorado, for comparative purposes. These are listed in Tables I, II, and III.

Qualitative x-ray fluorescence analysis was chosen as a quick and inexpensive method of attempting to characterize and discriminate among local and imported ceramic types from the Monticello District sites. Such chemical characterization provides the archeologist a means of grouping his material according to criteria not available from simple visual or microscopic examination and should provide data for discriminating between or among source materials from which the ceramics were made.

II. INSPECTION TECHNIQUE

Energy dispersive x-ray fluorescence analysis has become more common with the advent of high-resolution, lithium-drifted silicon detectors. Using such detectors, with radioactive isotopes or x-ray generators as the excitation source, the simultaneous measurement of many elements can be performed. The sample to be analyzed is placed in front of such an assembly and is irradiated by the source causing secondary x-ray emission characteristic of the elements contained in the sample. These x rays generate electrical pulses within the detector that are directly proportional to the energies of the x rays. The resultant signal is amplified, digitized, and processed into the memory of a multichannel pulse-height analyzer. Using such a system, with several different energy excitation sources, all of the elements above sodium can be detected and measured. With radioisotope source strengths on the order of 10 to 25 mCi, sufficient data for most purposes can be collected in a few minutes. This method is very sensitive to the surface elemental content of the sample, penetrating no more than a fraction of a millimeter for most samples. Very little sample preparation is required, in most instances, other than cleaning of the surface to be measured.

TABLE I
CERAMIC SAMPLES SUBMITTED FOR X-RAY FLUORESCENCE ANALYSIS

Type	Sample #	USDA #	XRF Target
Tusayan Polychrome	10	ML 1518	Paste and pigment
Mancos Corr. / Mancos N-b	11	ML 534	Paste and pigment
Sosi B/w	12	ML 534	Paste and pigment
Piedra B/w	13	ML 534	Paste and pigment
Mancos B/w	14	ML 534	Paste and pigment
Mancos Neck-banded	15	ML 534	Paste and pigment
Moccasin Neck-banded	16	ML 534	Paste and pigment
Bluff B/r	17	ML 534	Paste and pigment
Bluff B/r	18	ML 534	Paste and pigment
Piedra B/w	19	ML 534	Paste and pigment
Bluff B/r	20	ML 534	Paste and pigment
Bluff B/r	21	ML 534	Paste and pigment
Mancos B/w	22	ML 534	Paste and pigment
Mancos Corrugated	23	ML 534	Paste
Chapin Gray	24	ML 534	Paste
Mancos Corrugated	25	ML 534	Paste
Chapin Gray	26	ML 534	Paste
Moccasin Neck-banded	27	ML 534	Paste
Mancos Neck-banded	28	ML 534	Paste
Moccasin Neck-banded	29	ML 534	Paste
Moccasin Neck-banded	30	ML 534	Paste
Mesa Verde B/w	31	Mancos Canyon	Paste and pigment
Mancos B/w	32	/none/	Paste and pigment
Mancos Corrugated	33	/none/	Paste

TABLE I CONTINUED
CERAMIC SAMPLES SUBMITTED FOR X-RAY FLUORESCENCE ANALYSIS

Type	Sample #	USDA #	XRF Target
Betatakin Whiteware	34	FS 23/29	Paste and pigment
Kiet Siet Kayenta Polychrome	35	FS 144/11	Paste and pigment
Chapin Gray	36	425a971, B3b	Paste
Mesa Verde B/w	37	425a863-R12L1	Paste and pigment
Abajo R/o	38	425a971-B5	Paste and pigment
Abajo R/o	39	425a971-B3a	Paste and pigment
Early Mesa Verde Corrugated	41	ML 1147	Paste
Late Mesa Verde Corrugated	42	ML 1147	Paste
Early Mesa Verde B/w	43	ML 1147	Paste
Late Mesa Verde B/w	44	ML 1147	Paste and pigment
Unnamed Corrugated	45	ML 1147	Paste
Oxidized Corrugated	46	ML 1147	Paste
Mancos B/w	47	ML 1147	Paste
Mancos B/w	48	ML 1147	Paste and pigment
Abajo R/o	49	ML 1780	Paste and pigment
Mesa Verde B/w	50	ML 1147	Paste and pigment
Lino Gray	51	ML 1780	Paste
Chapin Gray	52	ML 1778	Paste
Chapin Gray	53	ML 1780	Paste
Mancos Neck-banded	54	ML 1782	Paste
Mesa Verde Corrugated	55	ML 153	Paste
Mancos Corrugated	56	ML 153	Paste
Mesa Verde B/w	57	ML 153	Paste
Mancos B/w	58	ML 153	Paste and pigment

TABLE I CONTINUED
CERAMIC SAMPLES SUBMITTED FOR X-RAY FLUORESCENCE ANALYSIS

<u>Type</u>	<u>Sample #</u>	<u>USDA #</u>	<u>XRF Target</u>
Mancos Corrugated	59	ML 153	Paste
Mesa Verde B/W	60	ML 153	Paste
Mesa Verde B/w	61	ML 153	Paste
Mesa Verde B/w	62	ML 153	Paste and pigment
Mancos B/w	63	ML 153	Paste and pigment
Jeddito Corrugated	64	ML 1146	Paste
Chapin Gray	65	ML 1146	Paste
Mesa Verde B/w	66	ML 1146	Paste
Mancos Corrugated	67	ML 1146	Paste
Moccasin Neck-banded	68	534 D-3	Paste
Chapin Gray	69	534 B-5	Paste

TABLE II
CLAY SAMPLES SUBMITTED FOR X-RAY FLUORESCENCE ANALYSIS

<u>Type</u>	<u>Sample #</u>	<u>Provenience</u>
Clay-Upper Chinle	1	South Cottonwood Road
Clay/Mudstone-Chinle	2	South Cottonwood Road
Clay-Upper Chinle	3	Bears Ears Outcrop
Clay-Mancos Shale	4	Monticello Lake Vicinity
Clay-Brushy Basin-Morrison	5	Recapture Road
Adobe	6	Lewis Lodge, ML 1146
Clay	7	ML 534

TABLE III
TEMPER MATERIALS SUBMITTED FOR X-RAY FLUORESCENCE ANALYSIS

<u>Type</u>	<u>Sample #</u>	<u>Provenience</u>
Porphyry Cobble	8	ML 534
Porphyry Axe Fragment	9	ML 555
Arkose Specimen	40	ML 1147
Arkose Specimen	54	ML 1147

For purposes of the study requested by the Monticello District Archeologist, which included characterization of paste, pigments, and temper agents, 95 individual spectra were obtained on the 70 samples submitted. The energy range employed for these measurements was from 0 to 20 keV using a 25-mCi cadmium-109 (^{109}Cd) excitation source. The inspection area was circular, 1 cm in diameter, with a data collection time of 10 minutes per sample. Analysis of these samples was based on comparison of the rubidium (Rb), strontium (Sr), and zirconium (Zr) patterns which characterize these materials. Our observations were based on the visual examination only of the patterns formed by these three elements relative to one another. For specific questions about pigments, particularly in the case where manganese (Mn) was suspected by the archeologist, the emission spectra for this and other elements were examined.

III. RATIONALE

We have noted elsewhere that "successful potters tend to return to traditional, proven clay sources to insure consistent results. Indeed, the use of traditional resources for the manufacture of pottery is a basic, but often untested hypothesis upon which many Southwestern ceramic classifications are established."¹ It follows from this, we believe, that the resources used by individuals or communities with established pottery traditions will cluster into characteristic patterns of elemental content which are discrete

from the output of other groups of potters. Clay sources, or pigments and other natural resources used in the manufacture of ceramics, can be fingerprinted, chemically, to reveal the elemental content of the materials used.

In the earlier study referred to above, we emphasized the apparent significance of Rb, Sr, and Zr content for distinguishing clays from different sources. Apache potsherds from three widely separated locales could be distinguished on the basis of the patterns of the K-alpha and K-beta characteristic x rays for these three elements present in each group of geographically distinct sherd complexes. Even more convincing, we believe, is the demonstration that Mayan ceramic wares from widely separated regions in the Yucatan peninsula can also be distinguished by observation of the patterns formed by the relative contents of these three elements.

The results of the present study of the Utah sherds and clays are in keeping with our previous findings. As was the case in those analyses, clays can be characterized as zirconium-rich or -poor depending on the relative Zr/Sr elemental ratios. Another diagnostic tool is the observation of the Rb/Sr ratio. It cannot be emphasized too strongly that our results are qualitative and subject to change when the data become quantitative, and the significance of our data must be tempered with the knowledge that quantification of these (and other) elemental contents may invalidate our tentative interpretations. It should also be made clear that, for the purposes of study presented here, the sample size is small, particularly for individual sites and pottery types, so that our data should only be considered suggestive of further x-ray fluorescence investigations of Utah materials.

IV. RESULTS

A. Pigments (13 samples)

Ceramic sherds containing three characteristic decorative media, represented in the sample by Tusayan Polychrome, Abajo Red/orange, Bluff Black/red, Piedra Black/white, Mancos Black/white, and Mesa

Verde Black/white, were grouped by the archeologist as follows: "iron paint" (Tusayan Polychrome, #10; Abajo R/o, #38, 39, 49), "carbon paint" (Mesa Verde B/w, #37, 62), and "iron-manganese" (Mesa Verde B/w, #50; Mancos B/w, #48; Bluff B/r, #17, 20, 21; Piedra B/w, #13). Of the 13 samples, 62% contain manganese and 43% of those sherds suspected of having manganese paint contained no detectable amount. All sherds contained iron (Fe), but there is an appreciable difference in iron content between the two suspected carbon-painted sherds, both of which are Mesa Verde B/w (one has high manganese and the other has none). Three of the four sherds classified as having only iron paint contain traces of manganese. Table IV provides a breakdown of the sherds identified according to the paint type and the relative proportions of the actual pigments present.

Specifically, the archeologist asked, "Do red paints (Tusayan Polychrome, #10) differ from black paints (#13, 17, 19, 20, and 21)?" and "Does the black paint contain more Mn than the red?" Table IV illustrates the qualitative differences in the Fe/Mn ratios among the pigment samples and it is evident that #10 differs in Mn content from the others. On the whole, "black paint" does contain more Mn than the others. Sample #13 (Piedra B/w) is very similar to Sample #37, carbon-painted Mesa Verde B/w.

B. Temper Materials (4 samples)

Although arkose was not specifically identified as a constituent tempering agent in any of the sherds submitted, presumably this was thought to have been the case. Both samples of this material (#40 and 54) were from the same site (ML 1147) and both are Zr-poor. Because individual grains of temper were not separated from the sherds, no direct comparison with or analysis of actual tempering agents present in the sherds was possible. The two samples of porphyry (#8 and 9) suspected of being temper were Zr-poor also but, as in the case of the arkose samples, porphyry was not specifically identified as temper in any of the sherd samples submitted nor are individual grains of porphyry temper from local sherds available for analysis.

TABLE IV
SUMMARY OF RELATIVE PAINT ELEMENT PEAK HEIGHTS (Fe, Mn)

<u>A) "iron paint"</u>		<u>Relative Peak Height Characterization</u>	
<u>Sample</u>		<u>Fe</u>	<u>Mn</u>
Tusayan Polychrome (1)		medium	trace
Abajo Red/orange (38)		high	none
Abajo Red/orange (39)		medium	trace
Abajo Red/orange (49)		high	trace
 <u>B) "carbon paint"</u>			
Mesa Verde Black/white (62)		high	high
Mesa Verde Black/white (37)		low	none
 <u>C) "iron-manganese"</u>			
Mesa Verde Black/white (50)		medium	none
Mancos Black/white (48)		medium	none
Bluff Black/red (17)		medium	high
Bluff Black/red (20)		medium	medium
Bluff Black/red (21)		low	high
Piedra Black/white (13)		low	none
Mancos Black/white (14)		medium	trace
Piedra Black/white (19)		high	trace

We were asked if the porphyry samples resemble locally tempered types. We cannot determine which of the sherds submitted are local types, thus it is not possible to make the comparison requested. Malone notes that Tusayan Polychrome #10 and Mancos Corrugated/Neck-banded #11 may have been locally made, presumably on the basis of temper. The former sherd is Zr-rich while the latter is Zr-poor.

Characterization of tempering agents in sherds by x-ray fluorescence will produce useful results only when the individual temper particles are separated from sherds and compared with suspected parent rocks obtained locally or from known sources.

C. Clays (7 samples)

Clay samples from different local sources within the Monticello District, including archeological samples, fall into the expected Zr-rich and-poor categories, as shown in Table V. Specifically, there exist no precise comparisons between individual clay and sherd spectra, as might be expected where a range of variation in elemental content can be anticipated, where the sample size is small, and where quantitative data are not available. The clays selected apparently have not been identified by other means as suspected potters' sources.

D. Sherds (59 samples)

Sherd samples were placed on edge in front of the detector in order to focus the excitation source on the paste for determining element content of the clay bodies. It was not possible to determine whether specific pottery types represented in the samples were locally made or were trade items. Nevertheless, and in spite of the small preliminary sample, some interesting observations can be made and are presented as suggestions for further research with pre-historic ceramics from southeastern Utah.

Of the black-on-white sherds, 90% are made from clay that is Zr-rich; only two sherds of Mesa Verde B/w (from sites ML 1146 and ML 1147) are poor, Tables VI and VII. Mesa Verde B/w usually is considered as a trade type where found outside Mesa Verde proper. By contrast, only 25% of the plain gray sherds (Chapin Gray and Lino Gray) are Zr-rich, and Chapin Gray, at least, might normally be considered as a trade ware from the Mesa Verde region as well. Certainly, different clays were selected for both B/w and plain gray wares, whether locally made or imported.

The utility types, corrugated and neck-banded, fall into two distinct groups according to their Zr content. All neck-banded,

TABLE V
ZIRCONIUM CHARACTERIZATION OF CLAY SAMPLES FROM MONTICELLO DISTRICT

<u>Sample</u>	<u>Zr-Rich</u>	<u>Zr-Poor</u>
1. South Cottonwood Road, Upper Chinle		X
2. South Cottonwood Road, Mudstone/Chinle	X	
3. Bear Ears Outcrop, Upper Chinle		X
4. Monticello Lake, Mancos Shale	X	
5. Recapture Road, Brushy Basin/Morrison		X
6. Lewis Lodge (ML 1146), Adobe	X	
7. ML 534	X	

TABLE VI
PERCENT OF ZR-RICH/POOR SHERDS BY CATEGORIES

<u>A) Black-on-white</u>	<u>Mesa Verde B/w(10)</u>	<u>Mancos B/w (7)</u>	<u>Piedra B/w (2)</u>	<u>Betatakin Whitesware-Sosi B/w (2)</u>
Zr-rich	80	100	100	100
Zr-poor	20			
<u>B) Polychrome</u>	<u>Tusayan Polychrome (1)</u>			<u>Kiet Siel/Kayenta Polychrome (1)</u>
Zr-rich	100			100
Zr-poor				
<u>C. Black/red, Red/orange</u>		<u>Abajo R/o (3)</u>		<u>Bluff B/r (4)</u>
Zr-rich		34		
Zr-poor		66		100
<u>D. Grayware</u>	<u>Lino Gray (1)</u>			<u>Chapin Gray (7)</u>
Zr-rich	100			14
Zr-poor				86

TABLE VI CONTINUED
PERCENT OF ZR-RICH/POOR SHERDS BY CATEGORIES

<u>E) Utility</u>	<u>Mancos Corr. (6)</u>	<u>Mesa Verde Corr. (3)</u>	<u>Mancos N-b (3)</u>	<u>Moccasin N-b (5)</u>	<u>Misc. Corr. (3)</u>
Zr-rich	66	100			66
Zr-poor	34		100	100	

TABLE VII
RELATIVE Zr CHARACTERIZATION OF 59 SHERDS BY SITE OR LOCALE

<u>A) Monticello District Sites</u>	<u>Zr-rich</u>	<u>Zr-poor</u>
ML 534: Mancos B/w	2	
Piedra B/w	2	
Sosi B/w	1	
Chapin Gray		3
Bluff B/r		4
Mancos Corrugated	2	
Mancos Corr/Moccasin N-b		1
Moccasin Neck-banded		5
Mancos Neck-banded	2	2
	<u>7 (32%)</u>	<u>15 (68%)</u>
ML 1147: Mancos B/w	2	
Mesa Verde B/w	2	
Mesa Verde Corrugated	2	1
Unnamed Corrugated	1	
Oxidized Corrugated	1	1
	<u>7 (77%)</u>	<u>2 (23%)</u>

TABLE VII CONTINUED

RELATIVE Zr CHARACTERIZATION OF 59 SHERDS BY SITE OR LOCALE

A) Monticello District Sites	Zr-rich	Zr-poor
ML 153: Mancos B/w	2	
Mesa Verde B/w	4	
Mancos Corrugated	1	1
Mesa Verde Corrugated	$\frac{1}{8}$ (88%)	$\frac{1}{1}$ (12%)
ML 1146: Mesa Verde B/w		1
Chapin Gray		1
Mancos Corrugated	1	
Jeddito Corrugated	$\frac{1}{2}$ (50%)	$\frac{2}{2}$ (50%)
ML 1780: Lino Gray	1	
Chapin Gray		
Abajo R/o	$\frac{1}{1}$ (34%)	$\frac{1}{2}$ (66%)
ML 1782: Mancos Neck-banded		1
ML 1778: Chapin Gray		1
ML 1518: Tusayan Polychrome	$\frac{1}{1}$ (34%)	$\frac{2}{2}$ (66%)
B) Non-Monticello District Sites		
425a971-Chapin Gray	1	
425a971-Abajo R/o	1	1
32-Mancos B/w	1	
Mancos Canyon-Mesa Verde B/w	1	

TABLE VII CONTINUED

RELATIVE Zr CHARACTERIZATION OF 59 SHERDS BY SITE OR LOCALE

<u>B) Non-Monticello District Sites</u>	<u>Zr-rich</u>	<u>Zr-poor</u>
37-Mesa Verde B/w	1	
FS 144-Kiet Siet/Kayenta Poly.	1	
FS 23-Betatakin whiteware	1	
33-Mancos Corrugated	$\frac{1}{8}$ (88%)	$\frac{1}{12}$ (12%)

sherds are Zr-poor, yet only three corrugated sherds fall into this category. Of the utility types, 43% are Zr-rich, all of them corrugated. Clearly there is some correlation between ceramic type and clay source demonstrated in this sample. Six (66%) of the nine redwares and polychromes are Zr-poor and, of these, Abajo R/o and Bluff B/r might be considered local types; 85% of these sherds (or 6 of 7) are Zr-poor. The four Bluff B/r sherds are the most homogeneous, in terms of visual inspection of their elemental spectra, of all samples submitted.

We were asked, "Are the following sherds local products: Tusayan Polychrome, Mancos Corrugated/Neck-banded, Sosi B/w, and Mancos Neck-banded (#15)?" We can only rephrase the question to read: does the paste of these sherds exhibit close similarities in elemental patterns to the clays submitted? Our qualitative answer is that there are no correspondences close enough to be certain that the clays and the pastes are the same, and such apparent similarities as might exist do not necessarily indicate local production of those types from the clay samples submitted.

The sherds listed more nearly resemble, in total elemental content, other sherd samples, although there are no two which match closely enough to suggest they were produced from the same clay source. Sample #11 (Mancos Corrugated/Neck-banded), for example, is virtually identical to Sample #26 (Chapin Gray) except for slightly lower Fe and K (potassium) in the former. Both are Zr-

poor, but beyond this comparison, we cannot determine local manufacture or import attribution.

V. CONCLUSIONS

In spite of the negative tone of the results presented above, in terms of the questions asked of the method, we suggest that research be continued and that it be directed toward answering the following questions.

a) What is the range of elemental variations in clay samples from a single source, such as the "Monticello Lake vicinity, Mancos shale"? More importantly, what are the elemental differences between samples from widely separated Mancos shale outcrops - say in the Mesa Verde and in the Monticello districts?, and

b) What, or how great, is the range of elemental content in statistically valid samples of sherd types from a single community and from a suspected source of imported types?

We close on a more programmatic approach by suggesting specifically valid samples of a single type of the predominant pottery type from small, chronologically tight sites be characterized to determine the range of elements present in the clay used and that groups of such studies be compared between widely separated communities using the same pottery types. From the samples examined here, we suggest that Mancos or Moccasin Neck-banded might serve as the starting point for such a project.

Similar studies should be attempted for groups of sherds representing suspected imports to southeastern Utah. For example, Mesa Verde area sites should be sampled to determine if the clay sources used are consistent for certain types that appear to have been exported to Utah.

REFERENCE

1. D. H. Snow and H. J. Fullbright, "Strontium/Rubidium Occurrence Patterns in Apachean Sherds (SAMAC Analytical Notes I)," Pottery Southwest 3, No. 2, pp. 3-6 (1976).