Geochemical Characterization of Prehistoric Gray Ware Ceramics from the Upper Basin Region of the Grand Canyon, Northern Arizona

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INTRODUCTION

Chemical characterization of archaeological ceramics is a useful way to constrain models regarding variation in pottery manufacturing techniques, including identifying the sources of raw materials. In the American Southwest, ceramic compositional studies have become commonplace over the last 40 years. Most studies have focused on issues of provenance or documentation of intra-assemblage variability in source materials for ceramics.

Two recent petrographic and strontium isotope studies (Carter and Sullivan 2007; Carter et al. 2011) have focused on identifying the mineral and chemical composition of prehistoric utilitarian gray ware ceramics that were manufactured between AD 700 and 1300 in the Upper Basin of the Grand Canyon, Northern Arizona. Specifically, these studies proposed that two ceramic gray ware types - San Francisco Mountain Gray Ware (SFMGW) and Tusayan Gray Ware (TGW) - are compositionally distinct. Results also suggest that SFMGW ceramics were produced from a narrow range of non-local materials, whereas TGW ceramics were manufactured from a wide range of materials. These initial findings challenge traditional theories of ceramic production and transportation that posited a local material source for Upper Basin gray ware ceramics (e.g., Colton 1946).

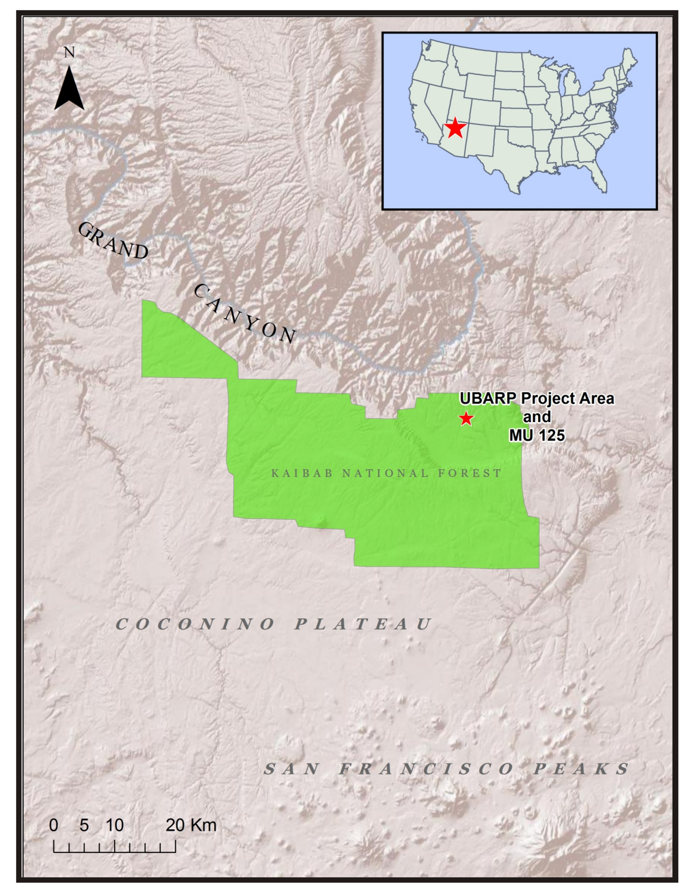
To test these inferences, X-ray fluorescence (XRF) is used to chemically determine major and minor element compositions of 33 TGW and 32 SFMGW sherds from site MU 125 in the Upper Basin which has been dated to ca. AD 1080. The purpose of this study is to determine if earlier results of the petrographic and strontium isotope analyses can be corroborated through a comprehensive study of the chemical composition of ceramic artifacts.

METHODS

Ceramic samples were powdered by hand until a particle size of between 5 and 10 microns was reached. Powdered material then was pressed into pellets using a Spex 35-ton X-Press laboratory press. Pellets were analyzed using a Rigaku 3070 X-ray Fluorescence spectrometer. XRF was used to record the concentrations of 26 major and minor (or trace) elements.

Major elements (represented here as oxides) include silicon (SiO_2), titanium (TiO_2), aluminum (Al_2O_3), iron (Fe_2O_3), manganese (MnO), magnesium (MgO), calcium (CaO), sodium (Na_2O), potassium (K_2O), and phosphorous (P_2O_5). Minor elements include barium (Ba), cobalt (Co), chromium (Cr), copper (Cu), molybdenum (Mo), niobium (Nb), nickel (Ni), lead (Pb), rubidium (Rb), strontium (Sr), thorium (Th), uranium (U), vanadium (V), yttrium (Y), zinc (Zn), and zirconium (Zr).LOI was measured to provide bulk measurements on water, carbon (C) and sulfur (S) content.

Elemental concentrations were converted to weight percent (wt%) for major elements and parts per million (ppm) for minor elements. Elemental concentrations were analyzed with Principal Component Analysis (PCA) to determine if sherds assigned to each type (TGW and SFMGW) could be distinguished chemically.



Location of Upper Basin and Site MU 125

View of the Upper Basin of the Grand Canyon

SFMGW Rim Sherd from Site MU 125

Site MU 125 during Archaeological Excavation

RESULTS

The results of this study show a significant ($F = 23.344$; $p < 0.001$) chemical distinction between TGW and SFMGW samples. Major elements identified as accounting for substantial portions of the inter-type variation through PCA analysis include K_2O (Axis 1), Na_2O (Axis 2), and MgO (Axis 3). Potassium especially is a significant source of variation as it is over twice as abundant (on average) in SFMGW sherds than TGW ceramics. Of the major elements, TiO_2 and P_2O_5 also appear to play a significant role in the differentiation of the two ceramic types

When the PCA loadings are plotted (Axis 1 to Axis 3), a clear distinction between TGW and SFMGW samples is found with only minimal overlap represented by outliers.

Overall, SFMGW sherds have minimal variability in K_2O (2.24-4.72 wt%), Na_2O (0.21-0.62 wt%), and MgO (0.82-1.52 wt%) concentrations while TGW sherds have greater chemical variability: K_2O (0.70-2.55 wt%), Na_2O (0.10-0.81 wt%), and MgO (0.88-1.71 wt%).

Average and standard deviation of major and minor elements*

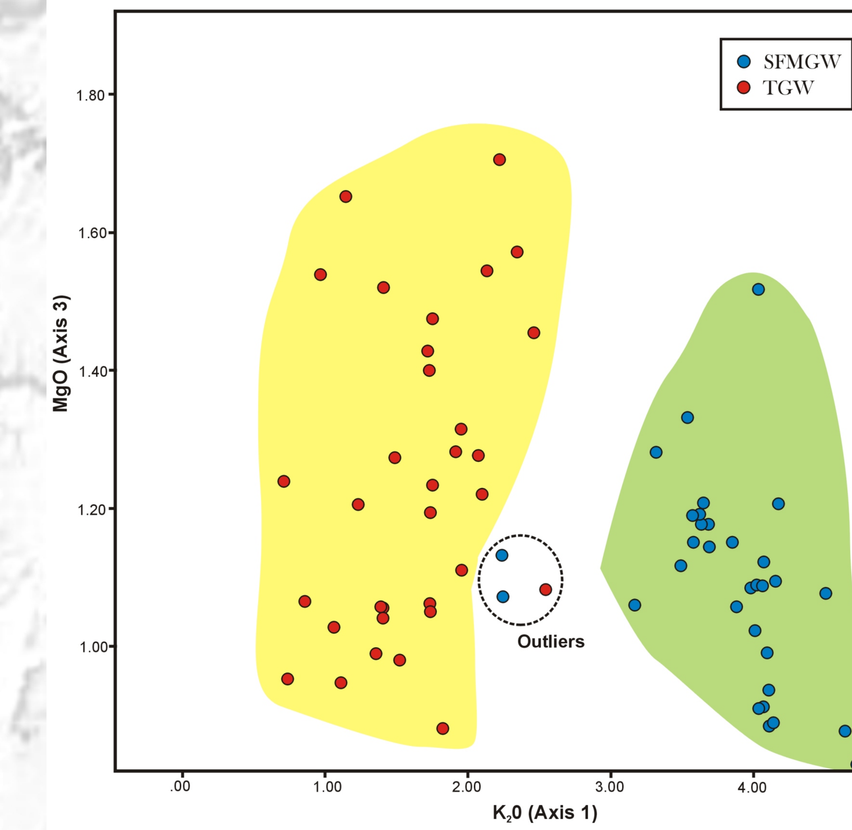
	SFMGW		TGW	
Elements	Average	Std.	Average	Std.
SiO_2	65.87	1.99	67.58	3.04
TiO_2	0.56	0.12	0.98	0.16
Al_2O_3	18.67	1.32	21.19	2.69
Fe_2O_3	4.62	0.90	3.15	0.86
MgO	1.09	0.15	1.24	0.23
CaO	2.33	0.75	1.74	0.74
Na_2O	0.30	0.10	0.37	0.14
K_2O	3.81	0.54	1.62	0.48
P_2O_5	0.16	0.07	0.12	0.06
Ba	697.66	89.94	498.63	170.16
Cr	68.64	6.23	122.90	32.42
Cu	15.92	9.54	51.94	23.15
Ni	43.04	1.89	42.69	4.22
Rb	164.47	18.71	89.41	25.46
Sr	142.51	27.12	209.54	66.47
Th	10.73	2.07	19.86	7.36
U	1.27	2.11	8.26	4.99
V	66.75	18.67	125.25	21.65
Y	65.06	4.478	63.79	14.42
Zn	129.11	44.94	87.13	25.54
Zr	145.58	31.6	203.01	34.65

*data from SiO_2 to P_2O_5 in wt%; others in ppm. Co, MnO, Mo, Nb, and Pb are excluded from this table as measurements were negligible or below detection.

Rotated component loading matrix from PCA*

Element	Axis 1	Axis 2	Axis 3
SiO_2	0.176	-0.055	-0.069
TiO_2	0.904	0.282	-0.164
Al_2O_3	0.655	-0.087	-0.137
Fe_2O_3	-0.478	-0.111	-0.100
MgO	0.335	0.008	0.843
CaO	-0.400	0.137	0.381
Na_2O	0.142	0.764	0.136
K_2O	-0.929	-0.145	-0.008
P_2O_5	-0.335	0.104	0.842
Ba	-0.746	0.347	-0.092
Cr	0.778	-0.255	0.097
Cu	0.798	0.311	-0.119
Ni	0.032	-0.026	-0.014
Rb	-0.854	-0.325	0.108
Sr	0.512	0.483	0.320
Th	0.814	0.027	0.037
U	0.816	-0.015	0.073
V	0.896	0.160	-0.017
Y	0.111	-0.044	-0.043
Zn	-0.547	-0.155	0.112
Zr	0.767	0.206	0.266
Eigenvalues	41.7%	7.7%	7.3%

*Co, MnO, Mo, Nb, and Pb are excluded from this table as measurements were negligible or below detection.



PCA Loadings Plotted by Axis 1 and Axis 3

CONCLUSIONS

In conclusion, the XRF analysis conducted on Upper Basin TGW and SFMGW sherds supports previous petrographic and strontium isotope findings in two ways.

First, TGW and SFMGW sherds clearly were produced from distinct material sources. Based on petrography and isotope analysis, at least some ceramic vessels were produced from source materials that outcrop outside the Upper Basin region.

Second, TGW displayed greater compositional variability in elemental concentrations than SFMGW sherds. This finding suggests that TGW vessels were produced from a wider variety of source materials than was the case for SFMGW sherds, an interpretation consistent with Carter and Sullivan's findings (2007).

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