

# Glaze and slip pigment analyses of Pueblo IV period ceramics from east-central Arizona using time of flight-laser ablation-inductively coupled plasma-mass spectrometry (TOF-LA-ICP-MS)

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## Abstract

This paper presents the results of glaze-paint and slip analysis of 161 White Mountain Red Ware ceramic samples (AD 1275–1325) from east-central Arizona. Time of flight-laser ablation-inductively coupled plasma-mass spectrometry (TOF-LA-ICP-MS) analysis is used (1) to establish viability of the technique for measuring chemical compositions of glazes and slips, and (2) to establish a methodology for inferring this structured variability, specifically delineating the presence of specific pigment mixtures or “recipes” used by prehistoric potters in the Greater Southwest. These data bear on archaeological questions about craft production, exchange, technology, and social organization.

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## 1. Introduction

Archaeologists working in the Greater Southwest have long been interested in glaze-painted wares, beginning with A.V. Kidder and Anna Shepard’s analyses of the Rio Grande glaze ware sequence at Pecos Pueblo [21,40]. The study of glaze-paints has been popular because the advent of these wares coincided with important behavioral changes, such as migration, the expansion of exchange networks, and changing social organization with aggregation.

Although the distribution of glaze-painted pottery has been used to address exchange and mobility, the compositional aspects of glaze-paints and their associated slips have been generally understudied over the past seventy years. Notable exceptions include Shepard’s research which used optical petrography and experimental tests to understand the

composition of the pigments as well as their properties [39,40], De Atley’s [6] and Fenn et al.’s [8] electron microprobe analysis of Ancestral Puebloan ceramics from the Silver Creek area, Huntley’s [20] and Herhahn’s [19] electron microprobe work at Zuni and the Rio Grande, respectively, and Habicht-Mauche and colleagues [12,13] use of ICP-MS on Rio Grande glaze wares. These studies have contributed greatly to an understanding of the technology of glaze wares, especially at the inter-site level, but have left questions of ceramic slip composition and fine-grained chemical variations of pigments across a single site unanswered.

Chemical compositional techniques that focus on ceramic pastes and clays have been used widely in provenance studies that have addressed questions about ancient economy, migration, and socio-political organization [see papers in 10]. Less attention has been paid to the pigments applied to the exterior of pottery, although the analyses of paints [41] but not slips have appeared in the literature of the past twenty years. The analysis of these pigments offers obvious advantages in compositional studies, such as a more holistic approach to

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understanding raw material procurement and exchange systems. This type of analysis can also contribute to the understanding of ceramic technology, and the *chaîne opératoire* of the potting process, and the ways in which “potting communities” are formed and interact [8,20].

Creating and using an appropriate methodology to analyze these pigments is another matter. Traditional chemical composition analyses have relied on bulk sampling, which has focused on ceramic pastes and hence the provenance of the primary body clay. Although it is possible to examine surface treatments on pottery with these techniques by removing small portions of paint and slip for analysis [12], efficient measurement requires the use of quantitative spot-testing of surface contexts. An appropriate technique would target a small area on the exterior of a ceramic sherd and measure its chemical composition at high resolution. Past research on glazes and paints using surface testing methodologies have relied on scanning electron microscopy (SEM), X-ray fluorescence (XRF) [1], and the electron microprobe [6,8,19,20]. In recent years, laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) has become a widely used tool by archaeologists in chemical composition studies [13,30,41]. This technique has the promise to fulfill the criteria stated above: efficient spot-testing at high resolution.

The present project has two goals. The first is to evaluate the usefulness of time of flight-laser ablation-inductively coupled plasma-mass spectrometry (TOF-LA-ICP-MS) for the analysis of paints and slips, which previously have not been subjected to extensive chemical analyses. The second is to create a methodology for inferring structured variation in chemical data generated from this technique. We examined samples of White Mountain Red Ware (WMRW) from east-central Arizona to evaluate the possibility of specific pigment mixtures, or recipes, at a single site, which will allow researchers to test for and infer the presence of potting communities and their anthropological interpretation.

## 2. Technical background

### 2.1. White Mountain Red Ware

WMRW was made over a broad region from the Acoma area of New Mexico to the Mogollon Rim in east-central Arizona [45]. Paste is generally characterized as light, being made from kaolinitic clay, and temper inclusions are primarily crushed sherd, with some sand or crushed rock [16]. WMRW has a thick red-slip made from limonite [15]. Paint is composed of a black, mineral-based mixture. The ware can be classified into stylistically different types that develop through time between AD 1100 and 1400, but which interests us here is Pinedale type, which was manufactured in east-central Arizona between AD 1260 and 1325 [5]. Pinedale style includes Pinedale Black-on-red and Pinedale Polychrome (the latter type has an additional kaolinitic white paint). Bowls are the most common vessel type, decorated with fine-line geometric decoration in black on the interior, and with black

motifs framed in white on the exterior [16], although jars are also present with geometric designs on their exteriors.

Pinedale type WMRW paint (but not slip) has been noted to have a “matte glaze” appearance. Although the black paint does not have the brilliant luster of the later glaze-wares of Zuni or the Rio Grande [19,20], these paint appears to be lightly vitrified and appear to reflect light differently than paints on earlier styles of WMRW. Using an electron microprobe Fenn et al. [8] showed that although these early glaze-paints may have begun as the results of accidents or experimentation, by AD 1275 at Bailey Ruin these glaze-paints were intentionally made due to high values of lead in their compositions.

Glaze-paints are compositionally and technologically complex. These paints are primarily composed of silica ( $\text{SiO}_2$ ) which acts as a “network former,” or primary constituent [35]. However, because the melting point of silica is  $1700^\circ\text{C}$  a “network modifier” or flux is added to lower the melting point of the silica and create a glass, thus giving the paint a luster. Appropriate flux materials world-wide are rich in sodium, potassium, calcium, manganese, and lead [18]. For low-fired pottery ( $800\text{--}1000^\circ\text{C}$ ) such as Pueblo ceramics, lead sulfide bearing minerals such as galena were necessary ingredient, as well as being available across the landscape of the Greater Southwest [40]. Fluxes such as copper and lead are also important for their role as colorants, with lead in some instances creating a clear luster and copper creating a green coloration [34]. Due to our current knowledge of ethnographic Pueblo pottery traditions and archaeological research, we are confident in arguing that the addition of lead sulfide bearing minerals will be the determining factor in identifying any meaningful structured variability in the ceramic sample set of Pinedale type WMRW. Mineral samples of galena were found in the ceramic production areas of Bailey Ruin, adding to our hypothesis that galena was being used as a flux material for the paint on Pinedale types of WMRW in east-central Arizona in the late 11th and early 12th centuries [27].

It appears that prehistoric potters in some contexts were mixing different mixtures or “recipes” of WMRW paints [8]. Fenn and his colleagues identified differences in chemical compositions of glaze-paint on WMRW between assemblages at the early Pueblo IV period site of Bailey Ruin located in east-central Arizona (Fig. 1). These data, although promising, were low resolution and pointed to the need for further investigation of the degree to which the compositional values in glaze-paints differ across the pueblo, and whether meaningful compositional groups (e.g., recipes) might exist.

Pigment mixing and application (especially that of glaze-paint) differs in some respect from other aspect of ceramic technology. Unlike clay, which can be procured from many places on the landscape, the sources of flux-bearing minerals such as lead are relatively scarce. This limits the degree of natural chemical variation and gives researchers the opportunity to explain variation of pigments in behavioral terms. Also, because these sources may be long distances away from where a pot is made, potters may have had different exchange partners or differential access to these raw materials. This has been demonstrated by

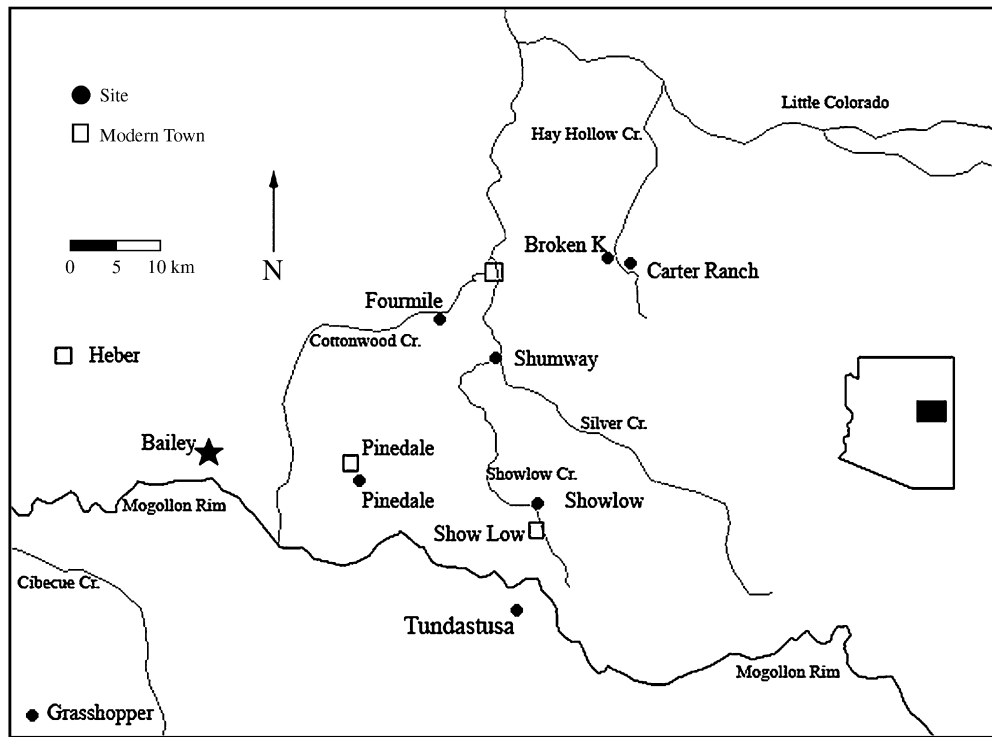


Fig. 1. The location of Bailey Ruin in east-central Arizona (adapted from Ref. [25], Fig. 1.1).

Habicht-Mauche et al. [12,13] who focused on Rio Grande glazes from northern New Mexico in an attempt to source the lead flux material used in pottery across the region. In their analysis, the flux was most likely galena from the Cerrillos area near present day Santa Fe. Using both acid dissolution ICP-MS and LA-ICP-MS to look for lead isotope signatures, the authors found it possible to delineate flux mineral provenance, hence allowing for modeling of social and economic systems. This study also implies that pigment mixing recipes and traditions is not just the result of how communities of practice make and teach pottery, but also reflect the role, status, and social signaling present in these communities.

The addition of minerals to glaze-paint can have other technological importance besides acting as glaze fluxes but can also act as colorants. WMRW needs to be fired in an oxidizing atmosphere to make its limonite-based slip reach its desired red–orange color. Paints with high iron contents would also change color, not to the desired dark black, but to brownish-orange and red. Therefore, paints with lower iron contents but higher lead and copper additives were required for the sought-after dark black paint appearance on WMRW [8].

Associated with paints are ceramic slips, which are made from a slurry of clay that is thinly applied to a vessel surface before it is painted and fired [35]. If anything, analysis of slips has been even more neglected than analysis of glazes. On WMRW pottery, slips apparently are mixed using yellow limonitic clay, which fires to a red color [8]. The use of limonite is substantiated by the discovery of an unfired WMRW bowl by Haury and Hargrave [15] at Showlow Ruin in east-central Arizona. Although it has never been tested, slip composition may

also be mixed in patterned ways that may identify potting groups.

## 2.2. Time of flight-laser ablation-inductively coupled plasma-mass spectrometry (TOF-LA-ICP-MS)

An alternative to acid dissolution in sample preparation for inductively coupled plasma-mass spectrometry (ICP-MS) became available in the mid-1990s [23,30,32]. LA-ICP-MS uses a pulsed laser that ablates a small portion of a solid sample that is entrained into the plasma stream by a carrier gas [30]. A Nd:YAG laser can either be scanned over a sample's surface or aimed at a specific area, yielding both bulk and point-specific data [11].

Despite the LA-ICP-MS technique's advantages over acid dissolution, this technique has not escaped the problems of a developing methodology [7,30]. Despite variation in ablation yield, approaches to data calibration that rely on "standardized signals" (ratios to an internal standard) have been found to yield reproducible results that are consistent with other techniques [2,30,42]. Studies of ceramic surfaces have been perhaps of the most common application of LA-ICP-MS. In one study, Speakman and Neff [41] used laser ablation to analyze mineral and organic paint on pottery from the Mesa Verde region, and were successful in distinguishing between the two. Habicht-Mauche and colleagues [13] determined lead–isotope ratios in glaze-paints from the Rio Grande valley with both acid dissolution and laser ablation, although they found the acid dissolution results to be more reproducible. A

recent edited volume [43] contains several other studies of ceramic surface materials by LA-ICP-MS.

Most applications of LA-ICP-MS in archaeology so far have involved the coupling of laser ablation systems with scanning ICP-mass spectrometers, either quadrupole or magnetic sector devices. On a number of counts, however, time of flight-ICP-MS (TOF-ICP-MS) is the ideal instrument to use with laser ablation. Rather than scanning the mass range, in TOF-ICP-MS ions from the plasma are sampled at a single instant in time and different masses are detected by monitoring how long it takes them to reach a detector, the heavier ions taking longer than lighter ions. Many snapshots of the entire mass spectrum can thus be obtained in a fraction of a second. By sampling ions produced by the plasma at a single instant in time, TOF-ICP-MS eliminates variation in ion production over time due to plasma flicker and variation in the sample stream reaching the plasma [see technical discussion in 42]. The speed and immunity from variation in ion production make TOF-ICP-MS ideal for analysis of transient signals, such as the signals produced by laser ablation sample introduction. Analyses reported in this paper were undertaken on a GBC Optimass TOF-ICP-MS; specifics of the analysis are listed in a later section of the paper.

3. Methods

3.1. Research area

The Pueblo III – Pueblo IV period transition was a time of settlement reorganization, with both aggregation and migration affecting the size and social composition of communities in the Greater Southwest [24,25,33]. Excavations and subsequent analyses at Bailey Ruin, a large aggregated Ancestral Puebloan site located in east-central Arizona and dating to the late 13th and early 14th century, have provided insights into a dynamic population in transition from regionally dispersed to centrally aggregated settlement and behavioral patterns.

Bailey Ruin (AD 1275–1325) is a compact, 200–250 rooms masonry pueblo that encloses a central plaza (Fig. 2) [27]. The site is ringed by multiple middens and it is estimated that the site housed a maximum of over 200 people. Excavations fully or partially exposed seven rooms, delineated plaza boundaries, and tested the central plaza and surrounding middens. Excavations have established that Bailey Ruin was a mid-range sized site in comparison to other local Pueblo IV sites that include Fourmile Ruin, Pinedale Ruin, and Showlow Ruin [24].

3.2. Sampling strategy of White Mountain Red Ware (WMRW) ceramics

The data set consist of WMRW sherds sampled from the seven excavated rooms at Bailey Ruin (Table 1, also included in full as supplemental data). Fenn et al. [8] interpreted their findings of WMRW at Bailey Ruin as having intentionally manufactured glaze-paints with high lead contents. We selected 161 samples for analysis using TOF-LA-ICP-MS. The sherds sampled in this study were selected because they were large enough

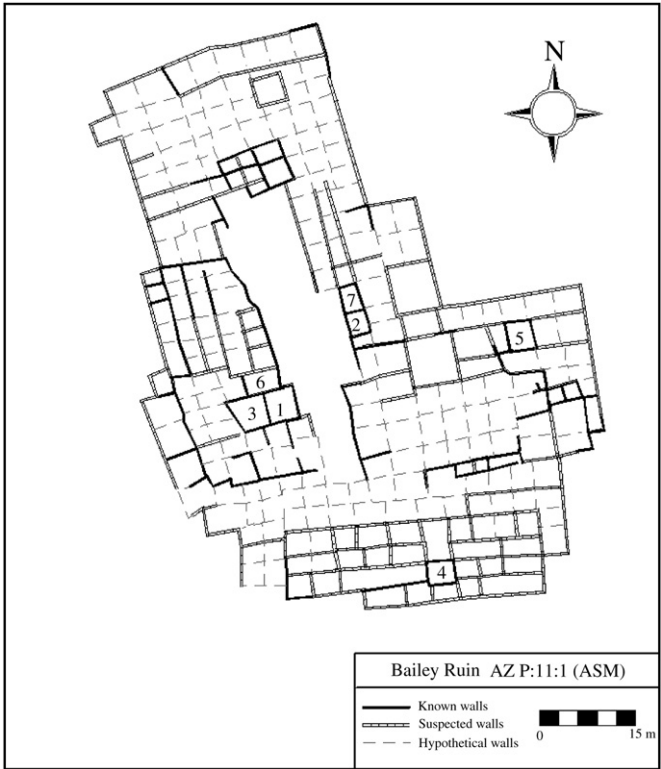


Fig. 2. Plan view of Bailey Ruin (adapted from Ref. [27], Fig. 6.1).

to recognize design style; Pinedale Black-on-red and Pinedale Polychrome. All paint and slip testing were on identical ceramic samples. Due to missing values six red slip measurements were discarded (53-R, 123-R, 129-R, 134-R, 135-R, 251-R) thus totaling the number of slips measured to 155.

3.3. TOF-LA-ICP-MS analysis

The California State University, Long Beach GBC Opti-Mass time-of-flight ICP-mass spectrometer with a New Wave UP213 laser at 60% power was used to analyze the 161 samples. The analysis measured and recorded two pigments from each sherd. Data for 40 elements were recorded,

Table 1 Number of WMRW samples and provenience	
Provenience	Samples
Room 1, strat 0	1
Room 1, strat 2	12
Room 1, strat 3	12
Room 1, strat 4	14
Room 1, strat 5	14
Room 1, strat 6	10
Room 2, strat 6	4
Room 3, strat 6	23
Room 4, strat 6	3
Room 5, strat 4, 3	9
Room 6, strat 4	35
Room 7, strat 3	24
Total	161



including: Na, Mg, Al, Si, K, Mn, Fe, Ba, Pb, Ca, Sc, Ti, V, Cr, Ni, Co, Cu, Zn, As, Sn, Sb, Cs, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, Th, and U. Na and Cr were discarded because of the large number of missing values, a result of high background peaks at the relevant mass. Five standards were analyzed between every 15 samples: (1) Robert Brill's standard glass B; (2) Brill's standard glass D; (3) NIST SRM612; (4) NIST SRM610 and (5) Ohio Red Clay.

Signal intensities data were calibrated by fitting standardized concentrations (ratios to silicon) in the standards to standardized counts (ratios of raw counts to silicon raw counts). High abundance elements (Na, Mg, Al, Pb, K, Ca, Ti, Mn, Fe, Ba, and Pb) were calibrated to concentrations by converting the standardized counts to standardized oxide concentrations and summing to 100%. The silicon concentrations determined from this run were then used to convert the standardized concentrations determined in a second run of low-abundance elements to actual concentrations. This approach to data calibration is similar to that described by Gratuze [11], and is described in more detail elsewhere [30,42].

To evaluate the usefulness of TOF-LA-ICP-MS as an analytical technique for the materials examined we compared the compositions of the standards used here against their known chemical compositions. We compared the consensus values for the Brill [4] and NIST glass standards [31] to the means obtained from back-calculation during the Bailey Ruin study. Due to limitations in space we have included this table as [supplemental data](#). The main discrepancy is the underestimate of most rare-earth element (REE) concentrations in the SRM612. Since REEs in natural geological materials tend to be closer to SRM612 (~40 ppm) than to SRM610 (~440 ppm), more accurate measurements would probably be obtained by omitting SRM610 from the calibration. In the present case, REEs play little role in the definition of compositional groups, so the absolute accuracy of their measurement is of little importance. However, future analyses must take these concerns into consideration.

Although laser ablation can be non-destructive, small pieces that had full pigment representation (approximately 5 mm×5 mm) were removed from each sherd using a geological rock saw. The samples were then affixed to a glass slide. By separating many small fragments of samples and inserting them into the laser chamber at the same time, analyses time was reduced dramatically. In the chamber, each sample was pre-ablated with the laser to remove any surface contamination that may have resulted from post-depositional contact with surrounding soil or subsequent handling and preparation. The sherds were then ablated along small paths (<1 mm) across each pigment type (paint and slip) on each sherd.

### 3.4. Developing a methodology for interpreting ceramic surface pigments

Finding statistically meaningful compositional groups in a ceramic assemblage is one thing, making meaningful behavioral inferences from these groups is another. There are multiple factors that could affect the variability and distribution of

pigment composition in a single site. In this section, we divide these factors into two categories (non-behavioral and behavioral/technological) and create a methodology that attempts to control for both.

To account for the possibility of non-behavioral formation processes such as ceramic mobility (bioturbation or erosion) and other *n-transforms* [36], we sampled ceramics from excavated units with no evidence of disturbance [27]. By establishing that ceramics were situated in their original depositional contexts, we are able to argue for contemporaneity amongst samples and their initial depositional position on room floors.

Although it is generally accepted that post-depositional effects (or ceramic diagenesis) influence the chemical composition of the archaeological ceramic, few studies have quantified these influences. Post-depositional additions/subtractions of chemical elements in archaeological ceramics due to interactions with soil waters have been neglected. Notable exceptions are Hedges and McLellan [17] tests in alteration simulation experiments and Schwedt et al. [38] analysis the surface and core of Greek ceramics. The latter found evidence of calcium leaching and severely altered alkali metal concentrations in sampled sherds. The authors conclude that ceramic alteration happens from the outside in. This problem is especially pertinent in the arid American Southwest due to the extreme additions of salts and carbonate by evaporation and eolian additions. Although this is a natural process that has not been well studied, this research indicates that elements that may be leached or deposited onto ceramics from groundwater are either highly soluble such as calcium or sodium, or mobile cations. Because this study examines the presence and absence of lead-bearing flux materials, we are confident that diagenetic processes will have little effect on the compositional analyses. However, to account for the high probability of surface deposition, samples were pre-ablated with the laser before measurement.

TOF-LA-ICP-MS is a spot-testing technique that relies on a laser to ablate a small amount of sample off the surface of a ceramic sample. This project's aim is to examine both paints and slips on WMRW, both which are pigments applied in thin layers (relative to the paste) superimposed on the main clay body. One concern in using this type of analysis is actually ablating through the target pigment and into the next deeper material, skewing the results of the chemical characterization. To account for this, we measured the thickness of the paints and slips on WMRW using a binocular microscope and found them to be approximately 40 and 200 µm thick, respectively. Prior analysis using the same technique and instrument found tested ablation on similar samples to be upwards to 30 µm [41,42], well within acceptable depth to assure us of the techniques appropriateness for analysis of WMRW pigments. However, to test this assumption both the paints and slips are compared in Section 4.4 to understand if compositional variability can and does occur with the use of TOF-LA-ICP-MS on studies of paints and slips.

There are numerous possible sources for behavioral variability in ceramic pigment recipe diversity. First and foremost, we make the assumption that the ceramics that were sampled for pigment analyses were locally produced. This is an

important distinction when making anthropological and technological inferences based on ceramic production. Previous ceramic sourcing analysis from room floor contexts of Bailey Ruin has shown an overwhelming majority of locally produced pottery [27,45], and three of the rooms tested had evidence of ceramic production [28]. Although some variation in chemical composition may be attributed to ceramic imports, it is unlikely that this will contribute to any strong patterned variability.

To ensure that time is not a variable in explaining compositional diversity, ceramics were sampled from floor proveniences and were not part of the post-occupational fill. The occupational sequence of Bailey Ruin was approximately fifty years in length. Multivariate ceramic seriation and use of tree-ring cross-dates from other sites in the area have been used to assign dates to the assemblages of each stratum and room that was sampled [26]. These data show that all rooms were occupied simultaneously, and hence the samples are contemporaneous. There is the possibility that recipe variation was the result of “accidents” or experimentation by potters. Although this may have been the case with early glazes, the conclusions of Fenn et al. [8] show that Bailey Ruin potters were intentionally producing glaze wares. If there is any kind of structured variation in the chemical composition between samples, these accidents will most likely appear as outliers.

Our sampling strategy tested negativity against Schiffer’s [37] “missed-pot hypothesis,” which postulates that multiple sherds from a single whole vessel are sometimes recorded as representing multiple pots. This phenomenon could serve to skew the data and create artificial chemical groupings. We used a 20× binocular microscope to analyze paste consistency and other unique phenomenon such as the presence of a “carbon core” which occurs when the paste is not fully oxidized, as well as measuring vessel wall thickness in all samples. Because we only had 161 samples we feel confident that this testing indicates that we have not sampled multiple times from the same vessel.

Although it is likely that the flux material originated in lead sulfide deposits such as galena, it is beyond the scope of this paper to begin to identify these sources. We acknowledge that raw material availability very well could affect the recipes of paint composition, as shown by Habicht-Mauche et al. [12] who demonstrated that availability was related to social and political behavior. We define “recipes” broadly, allowing that the differences in pigment compositions are affected by both specialized knowledge in pigment mixing and application, but also that certain potting communities may have had differential access to materials. Both are meaningful as the result of prehistoric behavior. Future work will seek to the understanding of the source of these materials (which could be locally procured or exchanged as far away as the northern Rio Grande in New Mexico), which will further resolve the behavioral meaning behind recipe groups.

Lastly, another possible source of variation is based not in overt prehistoric behavior but instead in the homogeneity of the paints and slip over an entire vessel. This project measures individual sherds as representing whole vessels. To test these

assumptions, the paint of a large sherd (over 20 cm<sup>2</sup> in area) of White Mountain Red Ware was analyzed in five places and is examined in the next section.

## 4. Results

In this section, we first present results of the LA-TOF-ICP-MS measurements of ceramic surface treatments. We then describe patterns in the data for both the paints and slips.

### 4.1. Testing the precision of the instrument and the homogeneity of applied pigments

As described earlier, these analyses are based on the assumption that Ancestral Puebloan potters mixed compositionally homogeneous paints and applied these across the entirety of a vessel. It is also assumed that the precision of the TOF-LA-ICP-MS technique is great enough that multiple analyses on the same pigment will be chemically and statistically similar. If these assumptions are correct, measurements on a sample sherd (that is representative of a single pot) can be interpreted as representing the whole vessel’s paint mixture composition, or recipe.

The multiple analyses show similar chemical compositional signatures, with all five falling into the same chemical group. For comparison, these samples are plotted along with the confidence ellipses for the three glaze-paint recipe groups described in the next section (Fig. 3). We explain the one sample that does not cluster tightly with the other four others to be from an area of black pigment that was applied thinly such that the analysis picked up the background signature of the vessel’s slip. This test strengthens the assumption of vessel pigment homogeneity and that each ceramic samples analyzed represents a single whole vessel.

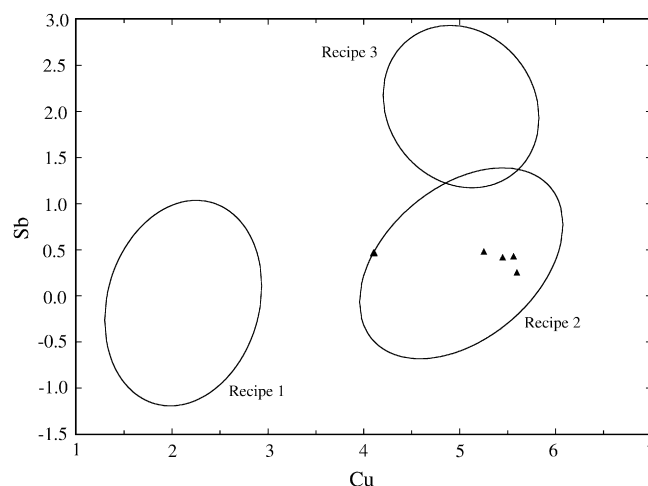


Fig. 3. Bivariate plot of Cu and Sb (base-10 log concentrations) in five replicate analyses from a single sherd, with 90% confidence ellipses for the compositional groups of paints.

#### 4.2. Trace element variations and groupings in White Mountain Red Ware glaze-paints

The statistical analyses to generate these results followed procedures developed for analysis of INAA data [3,9,29] and were performed using a set of programs written in GAUSS by Neff. Steps included missing data replacement, data reduction, group formation, and comparison amongst pigments. Two elements with a majority of missing values, Na and Cr, were removed from the database. Base-10 logarithms were used to express all concentrations. Groups were initially recognized by principal components analysis (PCA), and were subsequently refined using jackknifed Mahalanobis distances [29]. Table 2 displays the mean elemental concentrations of the paint samples. Principal components were generated for the paint samples of the WMRW ( $n = 161$ ). Table 3 lists the eigenvalues and percentage variance subsumed by each

Table 2  
Mean elemental compositions of White Mountain Red Ware paint compositional groups 1–3 in ppm

Element	Group 1 ( $n = 22$ )		Group 2 ( $n = 65$ )		Group 3 ( $n = 74$ )	
	Mean	St. Dev.	Mean	St. Dev.	Mean	St. Dev.
Mg	5313	2946	2941	2272	1685	1863
Al	98,456	30,549	103,070	36,717	55,247	27,686
Si	268,022	86,121	204,063	79,586	131,445	54,505
K	29,453	16,185	28,420	16,251	20,631	57,008
Mn	7084	26,597	98,397	136,452	17,898	60,462
Fe	68,827	83,150	51,506	40,715	22,542	20,288
Ba	3806	2612	1596	1428	711	746
Pb	449	1888	50,818	105,673	467,912	172,102
Ca	31,620	32,710	19,405	22,986	9795	8091
Sc	28	11	25	15	13	8
Ti	4657	2902	3154	1837	1795	1257
V	110	157	81	38	43	19
Ni	144	97	241	731	62	54
Co	38	48	54	153	14	14
Cu	160	163	166,708	171,557	151,451	150,496
Zn	384	535	1301	2572	498	314
As	66	205	43	35	51	49
Sn	9	8	17	11	11	8
Sb	2	2	4	5	164	129
Cs	12	7	28	20	9	8
La	61	31	45	26	25	13
Ce	105	47	96	106	45	25
Pr	13	5	10	6	6	4
Nd	65	27	60	48	31	21
Sm	10	4	10	6	5	4
Eu	2	1	2	2	1	1
Gd	10	5	10	9	4	3
Tb	1	1	1	1	1	1
Dy	8	4	9	8	3	4
Ho	2	1	2	2	1	1
Er	4	2	5	5	2	2
Tm	1	0	1	1	0	0
Yb	5	3	5	5	2	2
Lu	1	0	1	1	0	0
Hf	8	11	4	5	2	1
Ta	2	2	1	0	0	0
Th	19	8	13	7	7	3
U	6	7	6	3	3	3

Table 3

Principal eigenvalues and associated variance of the paint from White Mountain Red Ware

	Eigenvalue	%Variance	Cum. %Var.
1	5.7027	53.2599	53.2599
2	1.8597	17.3688	70.6288
3	0.974	9.0967	79.7254
4	0.4592	4.2889	84.0143
5	0.2932	2.7383	86.7526
6	0.2188	2.0439	88.7965

component. Three major compositional groupings appeared on the first two components. The groups were refined by calculation of Mahalanobis distances. Fig. 4 shows the three groups plotted on the first two principal components along with coordinates for the variables. Fig. 5 indicates that Group 1 is high in iron but low in lead and copper content, Group 2 is high in copper but low in lead and iron, and Group 3 is low in iron but high in copper, antimony, and much higher in lead.

As stated earlier, some Pueblo IV period paints are usually thought to be mixed with a lead base, which serves as a flux. This is most-definitely the case for two of the three recipe groups (2 and 3). Both Groups 2 and 3 have high copper contents but Group 3 is unique because it appears that a large amount of a lead-bearing material was also used as flux material in this group, possibly in the form of galena. Upon visual inspection, Group 3 paints tended to have the most luster of all the samples, with some having a vitrified texture. Group 1 represents a contemporaneous paint that while has similar visual characteristics as the other samples lack the large proportion of Fe and Cu additions, which probably resembles the chemical composition of pre-glaze WMRW paints and the appearance of different types of recipes variability as illustrated by Fenn et al. [8]. The possibility that glaze-paints of different recipes are made side-by-side in a contemporary setting is intriguing, and although the reasons for this behavioral difference are unknown it points to the stark differences in paint mixing by the prehistoric potters at Bailey Ruin. The technological importance of this high iron, low lead group begs further analysis at both a mineralogical and chemical scale. As Tite et al. [44] has shown, the appearance of a highly reflective pigment does not necessarily have to relate to its chemical composition but rather its physical properties. We propose the use of SEM and petrographic analysis to further explore both the technological and behavioral meaning for Recipe 1 paints.

Three distinct paint recipes were discovered in the WMRW samples. These recipes primarily vary in levels of iron, copper, antimony, and lead. Although there is some overlap between Groups 2 and 3, there were no problematic outliers that might suggest the overt signs of mixing “accidents” or diagenetic effects. These samples originated from both bowls and sherds, with no functional vessel type correlating with recipe type. There, we are confident in arguing that three specific black paint recipes were used at Bailey Ruin for the manufacture of WMRW, with two of these recipes intentionally manufactured as glaze-paints.

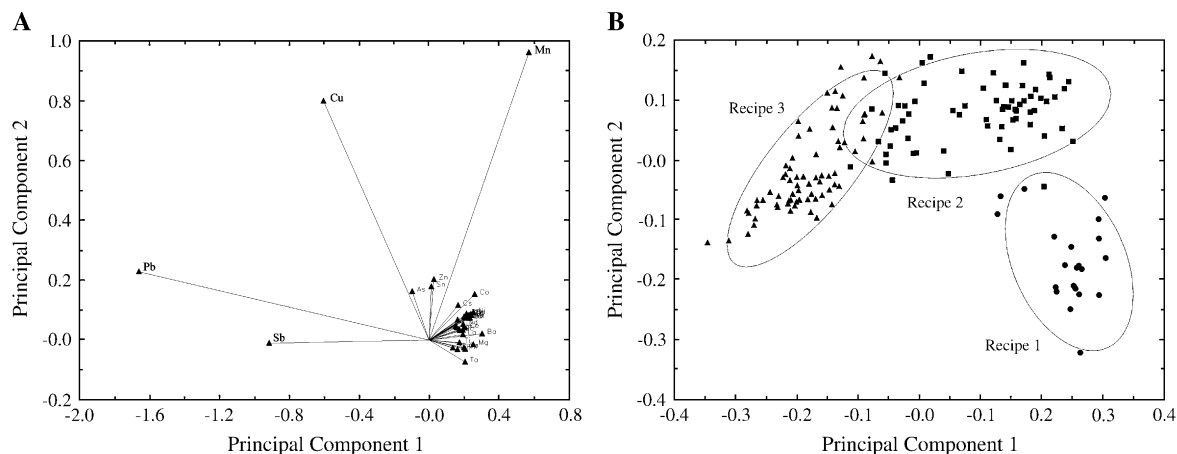


Fig. 4. Bivariate plot of principal components 1 and 2 of the paint data, with (A) elemental variables and (B) paint samples from the entire data set shown. Vectors connect variable coordinates to the origin in order to represent the pattern of inter-element correlation. Ellipses represent 90% confidence level for membership in the three groups.

#### 4.3. Trace element variations and groupings in White Mountain Red Ware slips

Principal component analysis generated no clear separation amongst samples of the WMRW slip. However, two separate slip groups can be recognized on bivariate projections of the data (e.g., Fig. 6). These groups were further refined using Mahalanobis distance analysis. Group 1 is substantially smaller than Group 2; it is characterized by lower silica and higher aluminum (Table 4 and Fig. 6). Also interesting are the slightly diminished rare-earth element concentrations in Group 1. The two slip groups may be derived from different clay sources and/or they may represent different ways of mixing the clay for the slip, as evident by the strikingly different concentrations of silica in Group 2.

In summary, two red-slip compositional recipes can be recognized in the WMRW assemblage at Bailey Ruin. When the samples are analyzed chronologically (between the strata in

Room 1) no structured variation in paint and slip recipes occurred through time. Again, there were no correlations between vessel function (bowl or jar) and slip type. Because of this, we are confident in our assumption that both pigment recipe suites were being manufactured contemporaneously across Bailey Ruin around the turn of the 14th century.

#### 4.4. Testing for variation in paint composition due to possible ablation into underlying slip

Although WMRW paint thickness is approximately 40  $\mu\text{m}$ , more than the 30  $\mu\text{m}$  depth that the laser ablation technique penetrates in sampling, we were concerned with the possibility that TOF-LA-ICP-MS sampling of surface paints could be skewed by interference with underlying material (i.e. slip). We had some indication of this phenomenon with the analysis of five independent analyses of paint from a single pot sherd in Section 4.1 where one sample area showed variation with the

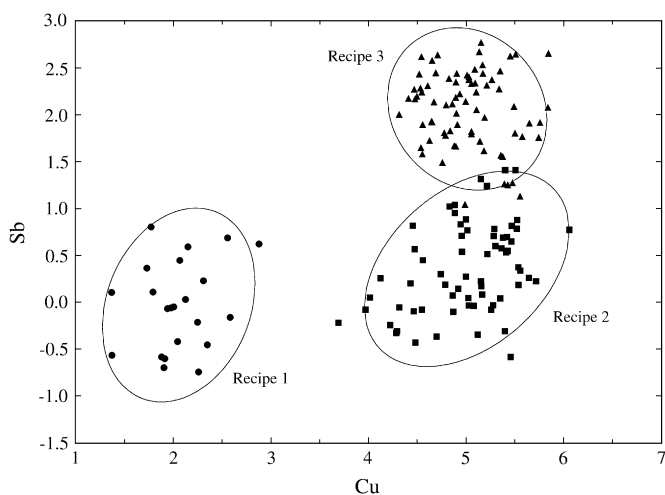


Fig. 5. Bivariate plot of Sb and Cu (base-10 log concentrations) in WMRW paint Groups 1, 2, and 3. Ellipses represent 90% confidence level for membership in the three groups.

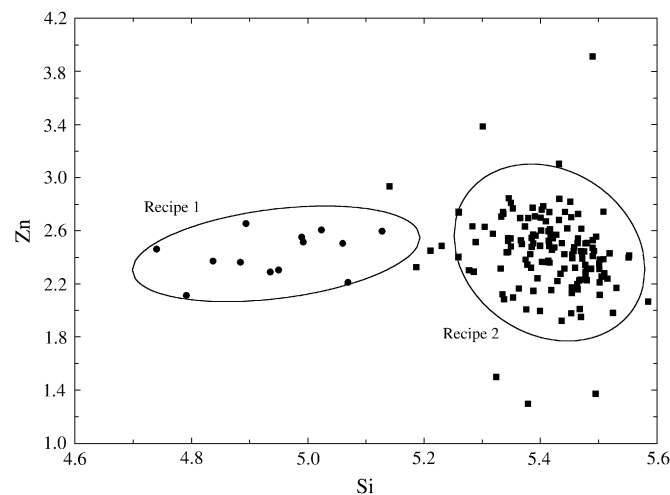


Fig. 6. Bivariate plot of silicon and zinc (base-10 log concentrations) in WMRW slip Groups 1 and 2. Ellipses represent 90% confidence level for membership in the three groups.



Table 4  
Mean elemental compositions of White Mountain Red Ware slip Compositional Groups 1 and 2 in ppm

Element	Group 1 ( <i>n</i> = 13)		Group 2 ( <i>n</i> = 142)	
	Mean	St. Dev.	Mean	St. Dev.
Mg	1685	1863	3295	2271
Al	55,247	27,686	119,857	27,672
Si	131,445	54,505	264,152	43,457
K	20,631	57,008	27,699	10,283
Mn	17,898	60,462	469	797
Fe	22,542	20,288	63,341	39,257
Ba	711	746	2964	8394
Ca	467,912	172,102	27,387	64,525
Sc	9795	8091	14181	9516
Ti	13	8	29	11
V	1795	1257	5783	2705
Ni	43	19	101	74
Co	62	54	179	180
Cu	14	14	30	17
Zn	151,451	150,496	4659	6977
As	498	314	380	706
Sn	51	49	31	51
Sb	11	8	7	5
Cs	164	129	3	5
La	9	8	26	18
Ce	25	13	77	94
Pr	45	25	131	129
Nd	6	4	15	15
Sm	31	21	77	73
Eu	5	4	10	8
Gd	1	1	2	2
Tb	4	3	10	10
Dy	1	1	1	2
Ho	3	4	10	11
Er	1	1	2	2
Tm	2	2	6	7
Yb	0	0	1	1
Lu	2	2	7	10
Hf	0	0	1	1
Ta	2	1	10	22
Th	0	0	2	1
U	7	3	25	15

others, and was probably the result of a thin application of paints that was ablated through in testing. Rather than dismissing this as an isolated problem we were able to test the appropriateness of the technique by comparing both the paint and slips from the 155 samples (the number of sherds with both recorded paint and slip compositions) to understand if this “over-ablation” affected our results in a dramatic fashion.

To test for this possibility, the WMRW paint samples that were associated with both slip recipes were plotted to verify that the compositional groups established as paint recipes were not skewed by the underlying slip material. Fig. 7A is a bivariate plot of the first two principal components that plots the paint composition of samples associated with Recipe 1 slip. Although only 13 samples belonged to this group, paints with Recipes 2 and 3 separated in much the same way as when all of the paint samples were plotted regardless of slip background. Interestingly paint Recipe 1 is not included on this plot. We have interpreted this as not the result of chronology (the samples are from contemporary deposits) or over-ablation

(the other two paint recipes are represented) but rather due to behavioral factors and considerations beyond the scope of this paper, such as differing “traditions” of pigment application in the potting process amongst potting groups at Bailey Ruin.

Fig. 7B is a bivariate plot of the first two principal components that plots paint compositions of the remaining 142 samples that are associated with the Recipe 2 slip background. Paint Recipes 2 and 3 plot in a similar way to those samples associated with slip Recipe 1, with the addition of paint Recipe 1. Because all three paint recipe groups are found on the same slip type, and for paint Recipes 2 and 3 on multiple slip types, we conclude that it is not likely that these groupings are not the inadvertent result of surface reaction between paint and underlying slips. Rather they represent distinct and tightly bound recipes that are not dramatically skewed by ablation into other material during analysis. The possibility of this occurring on any surface pigment analysis is always present, however, and we suggest that great care be taken in accounting for this phenomenon by understanding pigment thickness and comparing both paint and slip elemental values.

## 5. Discussion and conclusions

### 5.1. TOF-LA-ICP-MS considerations

Time of flight-laser ablation-inductively coupled plasma-mass spectrometry (TOF-LA-ICP-MS) is a new and potentially powerful analytical technique in archaeology. The advantages include minimal preparation time and rapid analysis, both of which are necessary for a large compositional data set. Using a time of flight (TOF) ICP-mass spectrometer with laser ablation is a particularly powerful combination, since it enhances transient signal capabilities. Will this technique work on paints and different types of slips at the level of precision necessary to delineate pigment recipes? The potential to generate a large database with TOF-LA-ICP-MS proved especially advantageous in this study. Because of the possibility that some compositional groupings would be represented in low frequencies, a large sample size was necessary; this proved especially crucial in identifying Recipe 1 of the limonitic slip, which only had 13 samples. A smaller sample size may not have revealed this pattern in the data. The criteria set forth as appropriate technique and methodology to measure ceramic surface treatments were this: spot-testing with high resolution. We have demonstrated the delineation of distinct chemical groups in the ceramic assemblage while producing a large amount of data in minimum time. We have also been able to accurately analyze the surface pigments with confidence, using the spot-test laser ablation method. The potential problems of ablating through targeted pigments were addressed and while noted as a worthy concern did not appear to affect the results of this analysis. Future studies must be ready to compare both slip and paint data to test for this, however, and not leave it as untested assumption. We conclude that the use of the TOF-LA-ICP-MS methodology is appropriate for future studies dealing with slip and paint on ceramics.

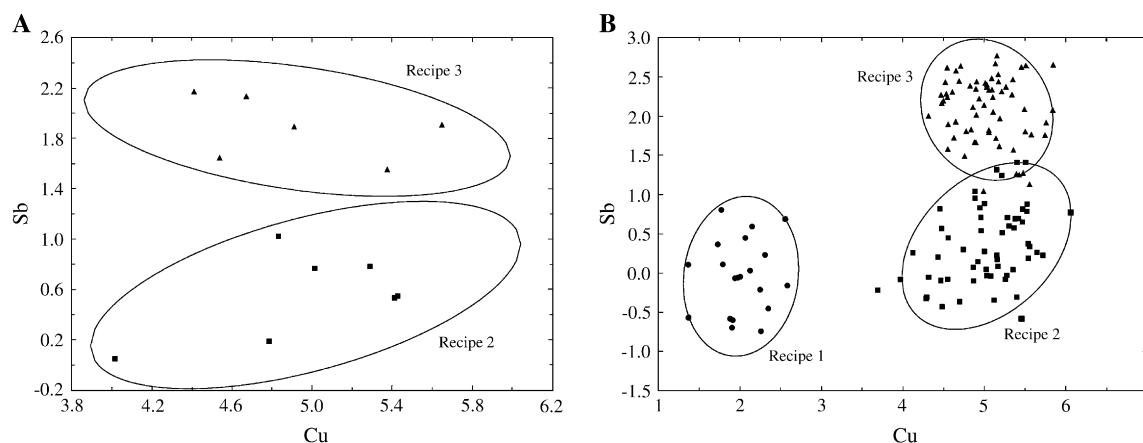


Fig. 7. Bivariate plots of Principal Components 1 and 2 (base-10 log concentrations) of the WMRW paint data associated with both (A) slip Recipe 1 and (B) slip Recipe 2. Ellipses represent 90% confidence level for membership in the three groups.

### 5.2. Pigment recipes and their implications

The three paint and two slip mixtures are inferred here to be recipes or specific ways that pigments were mixed and applied to pottery in the Greater Southwest. Although the main point of this project is to define these groupings and their probable behavioral meaning, we have taken pains to elaborate on a methodology appropriate for the analysis of surface pigments on pottery. In careful sampling we were able to control for the non-behavioral formation processes of turbation and erosion and behavioral processes such as non-contemporaneous samples, imported pottery, and “missed-pots”. We tested for potential behavioral variation in the homogeneity of pigments over the surface of an entire vessel, as well as seeing no evidence for “accidents” or diagenetic effects.

This sort of analysis, especially at a single site, is important to researchers because it is possible that pigment recipes correspond to communities of potters. In the study region, ethnographic and ethnohistoric literature documents that potting is performed primarily by females and that pottery is made and learned within the household. If pigment recipes characterize a form of knowledge, it is likely that this knowledge is passed down family lines in the form of teacher–student apprentice relationships. Therefore, it is possible that this elemental patterning and inferred existence of potting communities represent different households, which allow researchers to view Pueblo social organization at a very high resolution. Although this case study focuses on one small part of the American Southwest, the methodology used has wide application potential for archaeological research in general.

Future research will seek to understand how pigment (and specifically glaze-paint) recipes are spatially related across a single pueblo, leading to interpretations of the possible residences of household groups. Ethnographic research has provided the possibility that potting traditions are passed amongst extended Pueblo households [14]. The spatial distribution of pigment recipes likely will be related to the extended family, and thus clusters of rooms at a single village. Also, the pigment recipes can be compared against known locally

produced ceramics that were made from nearby clay sources to infer technological and social processes. These multiple lines of evidence will help researchers construct the *chaîne opératoire* of potting manufacture and understand ceramic production on a small scale.

The learning and practicing of pottery skills seen by mixing specific recipes appears to have become visible in the archaeological record. It is not unreasonable to argue that these same communities practiced and shared other traits amongst one another. These may include concrete life-skills such as food procurement, architecture building and maintenance, agricultural skills, and survival skills. They also may include more abstract yet extremely important knowledge such as religion, cosmology, oral traditions, and social obligations and traditions. Lave and Wenger [22] argue that it is not always the social structure that influences the learning process, but that the learning process may structure the society. This study is limited to only one small portion of the material remains from a single craft, but perhaps we are seeing household clusters that are formed by a shared learning experience.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jas.2006.06.001.

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