

Chemical Fingerprinting of
Clays and Pottery Sherds from
Western Imperial Valley, California

by
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INTRODUCTION

The following report outlines three research problems dealing with the chemical characterization of three clay and six sherd samples. It also briefly describes the x-ray fluorescence technique as it was used in characterizing the clays and sherds and presents the results of the chemical analyses as they apply to three research problems.

The three analyzed clay samples are from larger clay samples collected by Malcolm Rogers, most likely in the 1930s. At that time, Rogers was the archaeologist at the San Diego Museum of Man and one of only a handful of archaeologists working in southern California. He surveyed from central Arizona to the Pacific Coast and from central Baja California to the northern Mojave Desert. In 1936 Rogers published his now well-known article entitled "Yuman Pottery Making", which details the manufacture and firing of Kumeyaay pottery. Presumably, the clays come from sources that he believed were used by prehistoric and protohistoric potters. With the concurrence of Ken Hedges, the curator of archaeology, I obtained the clay samples about a year ago.

The following analyses would have been impossible without the direct assistance of Dr. Douglas Mose at George Mason University and Ken Hedges at the San Diego Museum of Man. I am very thankful for their help. Dr. Mose kindly volunteered to look at the clay and sherd samples using the x-ray fluorescence technique. He actually ran the tests and patiently explained the steps as he did them. Ken Hedges amiably agreed to sort through the type collection to get the sherds I requested and sent them to me on very short notice. I am also grateful to Jacqueline Olin and Ronald Bishop of the Smithsonian Institution for directing me to Dr. Mose.

RESEARCH PROBLEMS

The following research problems or goals were adopted for this study:

- 1) to chemically fingerprint each of the three clay samples;
- 2) to determine whether or not the six sample sherds could have been manufactured from the clays represented by the clay samples; and
- 3) to determine whether or not there is a chemical difference between pottery types.

The first goal is primary to the study. Two of the clay samples

(SamC-73 and SamC-105) were collected from clay deposits located in the bed of the now extinct, freshwater Lake Cahuilla. Although the exact location of the sites from which the clays were taken (C-73 and C-15) cannot be determined, these clay samples most likely come from the 'Brawley Formation', which is exposed along the western Lake Cahuilla shoreline (See Figure 1).

The non-marine Brawley Formation consists of light gray clays, sandstone, and pebble gravels; and probably dates to the middle Pleistocene (Morton 1977:18-19). The Brawley Formation clays have not been identified mineralogically (Morton 1977:35).

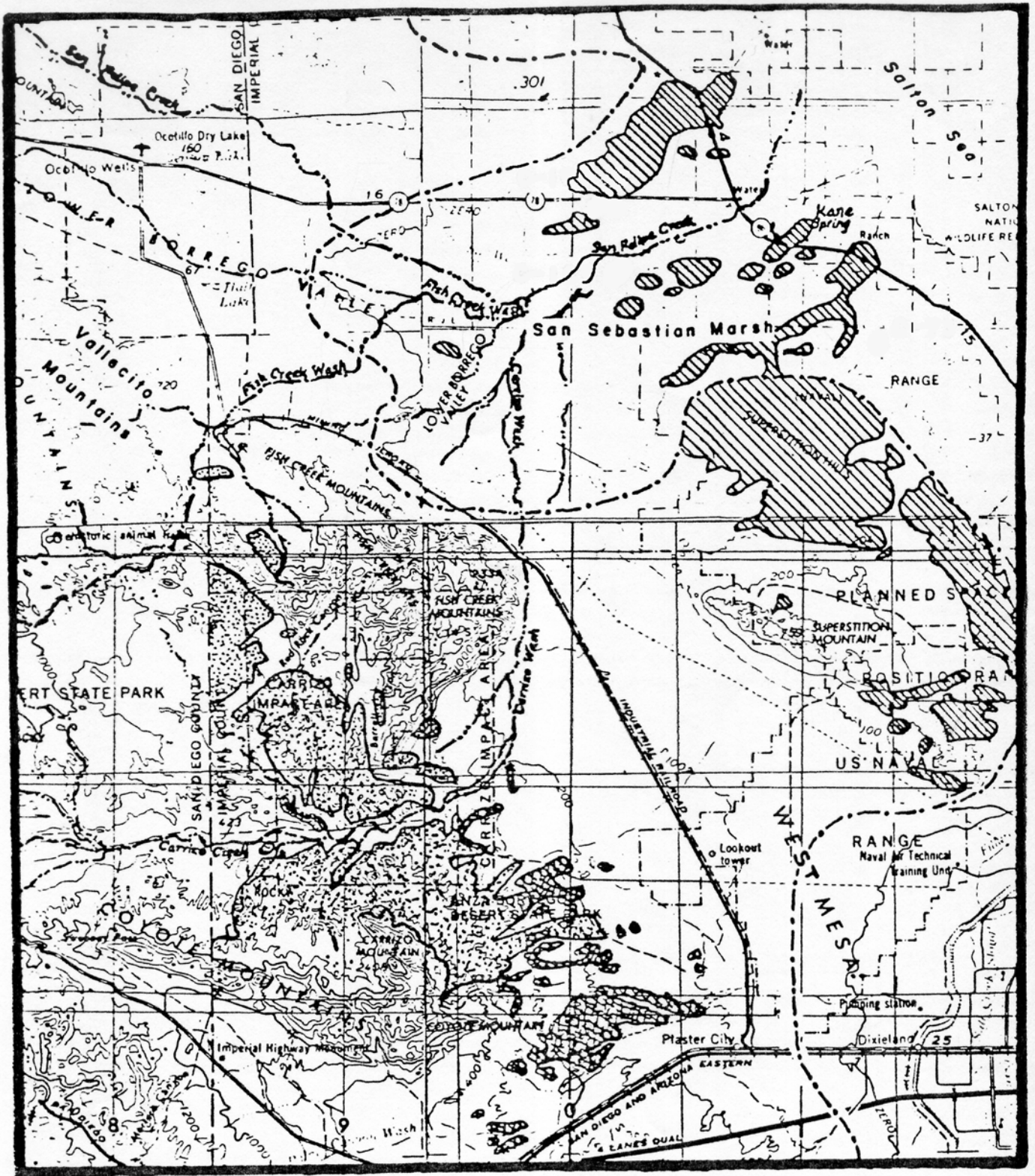
The third clay sample was labeled only as "Coyote Mountain." There are two formations on and around Coyote Mountain that include clay. The first, the Palm Springs Formation, has reddish clays and is very limited in distribution. The second, the Imperial Formation, includes yellow and gray clays and is extensive, being 22 miles long and from 3 to 11 miles wide. The Imperial Formation, which is the only dominantly marine formation known to occur in Imperial County, yields clays that are very homogeneous and of potential commercial value (Morton 1977:17, 34). Since the Palm Springs and Imperial formation clays have not been analyzed (Morton 1977:17,18), the formation origin of SamCyoMtn is uncertain. Nevertheless, the evidence (i.e., the color of the clay, which is "pale yellowish brown"; the extent of the exposed formation and the high quality of the clay) suggests that the clay sample SamCyoMtn derives from the Imperial Formation.

Because of the different origins (i.e., marine versus non-marine), the following hypothesis is adopted for the first research problem.

1. SamC-73 and SamC-105 will be most similar to one another and most dissimilar when compared to SamCyoMtn.

The above hypothesis is supported by the work of Landström, Samsahl and Wenner (1967:1). Through a neutron activation method, these scientists were able to distinguish between marine and lacustrine clay deposits in the Viskan Valley on Sweden's coast. The sea and a river alternately laid down the clay deposits during post-glacial times. Landström, Samsahl and Wenner (1967:3-4) found that boron, chromium, copper, gallium, nickel and vanadium were more abundant in marine than freshwater sediments. They (1967:) also noted that in Pennsylvanian sediments from the Appalachian Basin, the concentrations of boron, lithium, fluorine, strontium, sulphur, and manganese are higher in marine shales; and gallium and chromium are higher in the freshwater shales. The precedent has been set to expect a chemical difference between marine and non-marine clays.

The second research problem focuses on links between the six

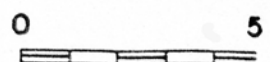


Kane Spring/Coyote Mountain Area

- ▨▨▨▨ Brawley Formation
- ⋯⋯⋯ Imperial Formation
- ⊠⊠⊠⊠ Palm Spring Formation

--- Lake Cahuilla shoreline
 Site locations not shown

SCALE Miles



pottery sherds provided by the San Diego Museum of Man and the three sampled clay deposits. The intent is to assess the possibility that the sherd clays derive from the above marine or non-marine clays. In reality, it is generally impossible to show that a sherd or group of prehistoric sherds were produced from a specific clay source. It is possible, however, to show that a particular sherd or group of sherds could not have been manufactured using a certain clay. The evidence would consist of major chemical differences between the clay and the sherd(s).

Prior to the analyses, the following hypothesis was adopted for the second research problem.

2. Chemically, the six sherds will be most similar to the SamC-73 and SamC-105 clay samples and least similar to the SamCyoMtn clay sample.

To explain the background on the above hypothesis it is necessary to backtrack in time to the Southwest Powerlink Project archaeology studies. The primary purpose of the project was construction of a 500kv transmission line from San Diego, California to Phoenix, Arizona. During the course of compiling the ceramics chapter for the data recovery report on southeastern California, a significant discrepancy in the data appeared. It seemed that there were no Colorado Buff sherds in the entire southeastern California project collection and yet, the Colorado Buff ware type site (C-27) was located within our project area. Michael Waters (1982b), who claims that C-27 is the type site (based on data he has from Rogers), was also the analyst who classified the Southwestern Powerlink Project sherds from southeastern California.

Compilation of raw data in Waters' (1982) Appendix H showed that of the 11 sites in Arizona and California with over 100 Colorado Buff sherds, 10 were west of ancient Lake Cahuilla and 4 of these 10 were in the San Sebastian Marsh/Kane Spring area. A review of Waters' buff ware type collection housed at the San Diego Museum of Man indicated a similar distribution pattern for Colorado Buff sherds. Of his 49 type sherds (which are of the finest quality), all but 4 were from the west side of the Salton Sea. None were from C-27. Also, 8 of the 21 sites from which Waters selected his Colorado Buff ware type sherds were located below the shoreline¹ of ancient Lake Cahuilla in the San Sebastian Marsh/Kane Spring area. Sixteen of the 49 type collection sherds; and all, except one of the sherds specially labeled "typical" Colorado Buff were from the San Sebastian Marsh/Kane Spring area. Additionally, the Imperial County geologic map (Morton 1966) shows that the Brawley Formation consisting of largely of clay is exposed throughout the San Sebastian Marsh/Kane Spring area.

Given the above evidence, one can conclude that Colorado Buff ware as defined by Waters is a western Imperial County/eastern San Diego County phenomenon. The above evidence also suggests

that the San Sebastian Marsh/Kane Spring area might be the focus of Colorado Buff ware production. All of the six sample sherds are from this area. Therefore, the sherds were expected to be chemically similar (or at least not very dissimilar) from the clay samples SamC-73 and SamC-105. At the least, the sherds are expected to be chemically different from the Coyote Mountain marine clay sample, SamCyoMtn.

The third problem centers on ceramic type. What constitutes each type is open to debate, and this issue needs to be discussed before proceeding to the hypotheses regarding the chemical differences between pottery types. The discussion will focus only on the specific types of buff wares that make up the sample.

Malcolm Rogers was the first to classify prehistoric pottery from San Diego and Imperial counties. Within his classification scheme, most of the buff ware sherds from western Imperial County and eastern San Diego County fall into one of two categories--Carrizo Buff I or Carrizo Buff II. Van Camp (1979:85-86), using his museum notes, published Rogers' descriptions of Carrizo Buff I and Carrizo Buff II. They are as follows:

Carrizo I

- Paste: fine to medium with occasional coarse inclusions
- Temper: 15% - 40% crushed barite and biotite (mica) very low to equal half of the barite at 40%.
- Inclusions: microbarite pellets. Sometimes has vugs, twig casts and carbon, with Blake Sea (Lake Cahuilla) gastropods occasionally present. Biotite occurs in barite crystals.
- Color: fresh core break has greasy look and is blue-black...
- Decoration: incising, rim notching. Rarely, cylindrical coiled necks.

Carrizo II

- Paste: same as Carrizo I
- Temper: less and ground more fine
- Inclusions: micro-rounded pellets of oligoclase feldspar
- Attrition: medium to finest of all Yuman pottery...
- Core: pink to peach if oxidized throughout. Blue-black, if not fully oxidized.
- Surface: scummed, whitest of all desert types

Decoration: rims sometimes have the "Salton groove" on their flat faces (i.e., a groove parallel to the edge).

Waters (1982a,b) has published the most recent ceramic typology. In spite of the claims that he is putting forward Rogers' typology, Waters basically ignores Rogers' classification scheme for western Imperial and eastern San Diego counties. Waters uses the type names Colorado Buff and Tumco Buff. [This discussion excludes Salton Buff, which has rounded beach sand as temper and is recognized as a distinct type by Waters and Rogers.] Rogers also used the terms Colorado Buff and Tumco Buff but with a much different meaning. For example, Rogers, who never officially defined Colorado Buff, wrote to E.W. Gifford "that in late Yuman times [post A.D.1500] a buff and red on buff ware which I call Colorado Buff was made from the Needles Valley [along the Colorado River] to the delta and from here up the Gila to Phoenix" (Rogers 1945:3). Unlike the sherds from Waters' Colorado Buff type collection, which almost all come from western Imperial and eastern San Diego counties, only 4 of the 36 Colorado Buff sherds in Rogers' type collection come from sites west of the central Imperial valley. In fact, all of the four sherds are from mountain sites in San Diego County rather than sites on the desert floor, where most of Water' Colorado Buff sherds were found.

Both Waters (1982b) and Rogers (according to his own typed and handwritten notations about the type--Tumco Buff) agree in writing on their definition of Tumco Buff and the distribution of this pottery type (i.e., eastern Imperial County and into southwestern Arizona). Nevertheless, about a year ago Waters typed a ceramic collection from West Mesa, located along the southwestern Lake Cahuilla shoreline. WESTEC Services, Inc. collected the West Mesa sherds as part of a large areal survey for the Bureau of Land Management (Gallegos 1983). At the time that I reviewed the West Mesa collection, of the buff ware sherds (N=665), Waters had classified 28 percent as Tumco Buff, 2 percent as Colorado Buff and 70 percent as Salton Buff. Three buff ware sherds could not be classified. Twenty-eight percent is fairly significant when, the presence of Tumco Buff west of the Lake Cahuilla shoreline was a rare occurrence when Waters (1982c) published his data in Appendix H.

After visually inspecting the Rogers' and Waters' type collections housed at the San Diego Museum of Man and collections from southeastern California and West Mesa, I concluded that 1) Water' Colorado Buff type closely corresponds to Rogers' Carrizo Buff II; and 2) Waters' Tumco Buff (as he designated it for the West Mesa collection) generally corresponds to Rogers' Carrizo Buff I.

Given the above, the following hypotheses were proposed for the

third problem of this investigation.

3. Sherds (#1 and #2) from Rogers' Carrizo Buff I type collection will be chemically more similar to each other than to sherds (#3 and #4) from Rogers' Carrizo Buff II type collection.
4. The sherd (#5) from Waters' Colorado Buff type collection chemically will be more similar to Rogers' Carrizo Buff II sherds (#3 and #4) than to Rogers' Carrizo Buff I sherds (#1 and #2).

[Note that sherd #6 was not identified as to type and was too fragmentary to classify.]

The above hypotheses are not based solely on the name distinctions used by Rogers and Waters. Rogers (1945:1), for example, believed that the focus of Carrizo Buff I was on the old terraces of the south and west shores of Lake Cahuilla, and Carrizo Buff II was on the western shore and in the post-Lake Cahuilla silt and dune country (which is the San Sebastian Marsh/Kane Spring area). Rogers dated (with no absolute chronological data) Carrizo Buff I to pre-Lake Cahuilla and Carrizo Buff II to after the high stand of Lake Cahuilla. The lake was at its final high elevation about A.D.1400 and had desiccated by A.D.1550 (Wilke 1978). Waters' (1982a) dates Colorado Buff to after A.D. 1500 and Tumco Buff from A.D.1000 to A.D.1500. Thus, according to Rogers, not only are Carrizo Buff I and Carrizo Buff II distinct in type but each type has its own geographic distribution and temporal placement. Waters assumes the same about Tumco Buff and Colorado Buff pottery types.

METHODS

All three research problems and their associated hypotheses were investigated. The analytic methods used are briefly described below, and results of the analyses follow.

As mentioned earlier, the clay samples were taken from three large samples of clay at the San Diego Museum of Man. The large samples were up to about 1 liter in volume. They are currently in plastic or paper bags, and are stored in a curatorial drawer. Each large sample of clay was labeled by Rogers. For the purposes of analysis, about 1.5 to 3.0 teaspoons of clay were obtained. The first, SamC-73, was taken from a sample labeled "From Pleistocene Lake Beds, near C-73, Elev.-50?"; the second, SamC-105, from a sample labeled "Below Red Level, C-105"; and the third, SamCyoMtn, from a sample only labeled "Coyote Mountain". Clay sample SamC-73 can be characterized as being very fine in texture. SamC-73 has whitish streaks and small organic black inclusions and no mica. Its color is "grayish orange pink" (5 YR

7/2). Sample SamC-105 is crumbly and has small white fossiliferous inclusions and occasional specks of mica. Its color is "yellowish gray" (5 Y 7/2). Clay sample SamCyoMtn is extremely fine grained with whitish streaks and no mica or black organic inclusions. This sample is waxy to the touch and is "pale yellowish brown" (10 YR 6/2).

The six sherds to be analyzed were judgementally selected. First, I wanted sherds that came from close to where the clay samples were obtained. Secondly, I wanted at least two sherds from each of the Carrizo Buff I and Carrizo Buff II pottery types. Having tallied the sherds in the Rogers' and Waters' pottery type sherd lots, it was simple to identify where the sherds were that fit the above criteria. Six was the minimum number of sherds required to meet the criteria. Ken Hedges selected the sherds given the above guidelines and sent them to me.

One sherd, #5, is from C-105, the site where clay sample SamC-105 was obtained. It is also from Waters' Colorado Buff type collection (SL-116). Two sherds, #1 and #2, are from Rogers' Carrizo Buff I type collection (SL-52); and two sherds #3 and #4 are from his Carrizo Buff II type collection (SL-54). All of the Carrizo Buff I and II sherds are from site C-124, which is located between C-105 and C-73 and is at the heart of the San Sebastian Marsh/Kane Spring area. Sherd #6 is really fragments from a larger sherd from C-73, which is near to the source of SamC-73. Since it is the only sherd from C-73, Hedges broke off fragments for use in the analyses. The physical characteristics of each sherd are provided on Table I.

The clay samples and sherds were analyzed using x-ray fluorescence, the same technique often used to chemically characterize obsidian for sourcing purposes (see Ericson 1983; Hughes 1983; Nelson, Sidrys and Holmes 1978; Nelson and Voorhies 1980; Stross, Sheets, Asaro and Michel 1983; and Zeitlin and Heimbuch 1978). X-ray fluorescence requires no sample preparation; if the sample is larger than a quarter and smaller than about 6cm by 6cm, then the technique can be completely non-destructive, and analysis of certain trace elements can be done in a few minutes (Hughes 1983:21).

In order to clean the surface and to remove the scum coat (which was particularly thick on sherds #1 and #2), a surface area of about 2.5cm by 2.5cm was ground on each sherd. Only one sherd, #2, had to be broken; it was too large. All of the rims, artifact numbers, and most of the surface of each sherd remained intact. The clay samples were not altered at all.

The x-ray emission spectrometer is located in George Mason University's Geology Department. Dr. Mose described the process and manipulated the equipment. The tungsten-target x-ray tube

TABLE I

Sherd Sample - Physical Characteristics

Sample	Oxidation	Color-Outside • Color-Inside	Paste Texture	Inclusions/Temper	Comments
#1 (C-124, SL 52, rim)	complete	very pale orange 10 YR 8/2 • moderate yellowish brown 10 YR 5/4	a bit flakey; generally ranges from coarse (1-½mm) to fine (¼- 1/8mm)	probably sherd temper (reddish in color com- pared to the surround- ing paste, which is more yellowish); no mica	scum coat; inside burned; Carrizo Buff I
#2 (C-124, SL 52, notched rim)	complete	yellowish gray 5 Y 7/2 • moderate brown 5 YR 4/4	somewhat grainy in appearance; very coarse (2-1mm) to fine (¼-1/8mm)	orthoclase (1½ to 1/8 mm)- probably temper	scum coat; Carrizo Buff I
#3 (C-124, SL 54, direct rim)	complete	light brown 5 YR 6/4 • light brown 5 YR 5/6	medium (½-¾mm) to very fine (1/8-1/16 mm)	orthoclase (less than ½ mm)- may be inclusions or temper. Sherd temper may also be present-if so, then they were ground very fine	3 notches on direct rim; Carrizo Buff II
#4 (C-124, SL 54, rim flared)	in- complete	light brown 5 YR 6/4 • moderate reddish brown 10 R 4/6 to dusky yellowish brown 10 YR 2/2	coarse (1-½mm) to very fine (1/8-1/16 mm)	same as above, but ortho- clase pieces are gener- ally larger	slight scum coat; outside burned; Carrizo Buff II
#5 (C-105, SL 116)	complete	light brown 5 YR 6/4 • pale red- dish brown 10 R 5/4	medium (½-¾mm) to very fine (1/8-1/16 mm)	orthoclase (<½mm) may be inclusions or temper. Sherd temper may be pre- sent-if so, then they were ground very fine	slight scum coat; weathered; Waters Colorado Buff
#6 (C-73)	in- complete	grayish orange 10 YR 7/4 • light brown 5 YR 5/6 to dusky yellowish brown 10 YR 2/2	grainy appearance; medium (½-¾mm) to fine (¼-1/8mm)	sherds temper; occasional bit of orthoclase- probably inclusions	sample consists of very small pieces of a sherd; very little surface evident; no sherd type given

was operated at 38 Kv and 40 mA. As it is set up, the spectrometer was best suited for identifying the elements from the fourth through the sixth periods. To identify the most distinct elements to be used for comparative purposes, sherd #1 was scanned. The angle was noted for each fluctuation in intensity from about 10 to 90 degrees. The most significant angles obtained were 51.7, 45.0, 43.1, 37.1, 31.7, 25.0, and 22.3. Of these, 51.7(K α) is iron (Fe), 45.0(K α) is copper (Cu), and 25.0 and 22.3 (K γ and K β) are strontium (Sr). The angle 43.1 is probably nickel (Ni). The angles 37.1 and 31.7 could not be identified with a specific element. According to Dr. Mose, these latter angles may represent zinc, but there is enough uncertainty to drop them from further analysis.

The intensity values for Fe (K α), Sr (K α), Cu (K α), and Ni(?) (K α) were determined for each clay and sherd sample for the purposes of calculating the ratio of these elements to one another. The absolute amount of each element per sample was not determined. The baseline adjustment was calculated for each element and subtracted from each intensity reading.

After the spectrometer was calibrated, the elements for study were selected, and the sherds were ground, it required less than 30 minutes to obtain the intensity readings for all clay and sherd samples.

RESULTS

The results of the analyses are interesting and point in unexpected directions. They are presented below vis-a-vis each of the three research problems and the corresponding hypotheses. First, however, a strong caution is in order. Only three clay and six sherd samples were analyzed and all were judgementally selected. The samples cannot be considered representative of a larger sample universe. For example, SamC-73 and SamC-105 are not necessarily representative of the clays found in the lakebed and two Carrizo Buff I sherds do not constitute a representative sample of that class of pottery. The intent of the analyses is to see if my initial ideas about pottery types and their distribution seem to hold up given a chemical analysis of the sherds and three clay samples. If the results are as expected, then considerable work still will have to be done to prove them. If the results do not turn out as expected, then perhaps the ideas are wrong and need modification before more rigorous testing can be done. The latter situation actually applies to this study.

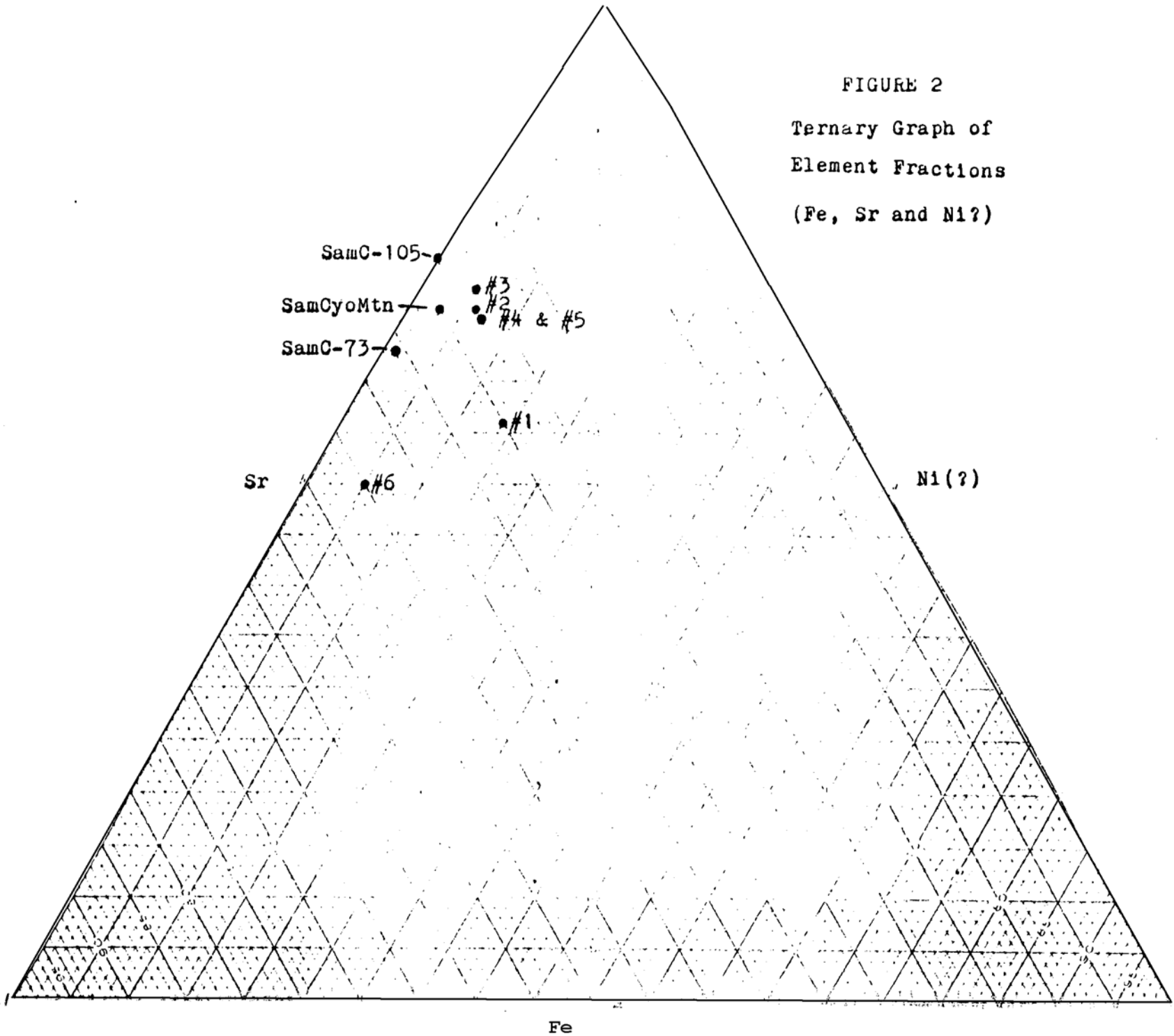
The original and adjusted intensity values are presented in Appendix A. Table II shows the adjusted intensity values and element to element ratios, which are based on the adjusted intensity values. Figure 2 shows the element fractions of iron (Fe), strontium (Sr) and nickel (Ni). [For each sample the three elements were normalized to 100 percent.] Although the

TABLE II

Adjusted Intensity Values and
Element to Element Ratios

Adjusted Intensity Values	#1	#2	#3	#4	#5	#6	Sam C-73	Sam C-105	Sam CyoMtn
Strontium (Sr) (25.0)	2.0	.8	.7	.9	.8	.3	.1	-.3	.4
Nickel (Ni) (43.1)	4.1	3.7	3.6	4.1	3.8	2.7	3.0	1.7	4.0
Copper (Cu) (45.0)	.8	.8	.9	.8	.7	.8	.5	.3	.8
Iron (Fe) (51.7)	7.8	9.1	9.6	9.6	9.0	3.0	5.3	4.4	8.9
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Ratios									
Fe/Sr	3.9	11.4	13.7	10.7	11.3	10.0	53.0	na	22.3
Fe/Ni(?)	1.9	2.5	2.7	2.3	2.4	1.1	1.8	2.6	2.2
Fe/Cu	9.8	11.4	10.7	12.0	12.9	3.8	10.6	14.7	11.1
Ni(?)/Sr	2.1	4.6	5.1	4.6	4.8	9.0	30.0	na	10.0
Ni(?)/Cu	5.1	4.6	4.0	5.1	5.4	3.4	6.0	5.7	5.0
Cu/Sr	.4	1.0	1.3	.9	.9	2.7	5.0	na	2.0

FIGURE 2
Ternary Graph of
Element Fractions
(Fe, Sr and Ni?)



calculations for copper are included on Table II and Appendix A, Dr. Mose recommended dropping copper from further analytic manipulations because the intensity values are in the range one might expect from machine noise. (Apparently because of copper wiring and other structural factors, the spectrometer can generate its own copper intensity values independent of that found in the sample.) Although the identity of the element with a angle reading of 43.1 is uncertain, the 43.1 element (probably nickel) is retained in the analyses because of the consistent and relatively high intensity values for each sample.

Chemical characterization of the clay samples did not support the first hypothesis, which claimed that the lakebed samples SamC-73 and SamC-105 would be most similar to one another and least similar to SamCyoMtn, the clay of marine origin. The ratio data on Table II indicate that, in fact, SamC-73 and SamC-105 are each relatively more similar to SamCyoMtn than to each other. (Figure 2 graphically shows the relationship between each of the three clays.)

Although the absolute intensity values are not directly comparable between clay samples (because of sample size and perhaps because of differences in the topology of each sample), the marine clay sample, SamCyoMtn, does appear to have a greater amount of strontium and nickel, which is consistent with the data presented by Landström, Samsahl and Wenner (1967). Nevertheless, when the percentages of elements (Fe, Ni?, Sr) are compared, the marine clay is not that different from the freshwater clays; and the freshwater clays are very different from one another. The latter is not that difficult to explain because even adjacent clay deposits can vary in terms of mineral content. Clays laid down by various fillings of the Colorado River might be quite distinct. Why the marine clay is not more distinct, however, is not as easily explained.

The question may be better posed as why are the lakebed clays so similar to the marine clay? There is one simple explanation, but whether it is right or not cannot be determined. The portion of the Lake Cahuilla lakebed from which the clay samples were collected is at the terminus of three major drainages -- Carrizo Wash, Fish Creek Wash and San Felipe Creek. All three drainages carry runoff from the surrounding hills, which commonly have outcrops of the marine clay deposits. Carrizo Wash actually bisects the Coyote Mountain Pliocene marine deposits that consist largely of the fine clays. Thus, in spite of the fact that the lakebed clays were laid down by freshwater, many of the particles that actually went into forming the clays probably came from surrounding marine sediments.

Another explanation may be that there simply are not consistent differences between freshwater and marine clays given the three elements of iron, strontium and nickel (?). Perhaps other elements would be better distinguishers. Obviously, more work has to be done in order to determine this. The answer is not

readily available in the literature.

The results of the analyses did not support the second hypothesis either. It predicted that the chemical characterization of the sherds would be more similar to the lakebed clays than to the Coyote Mountain clay. Figure 2 shows the relationship of the sherds to the clays. Given the three elements, sherds #1 and #6 are obviously chemically different from all the clay samples and sherds #2, #3, #4, and #5 cluster fairly close to the Coyote Mountain sample, SamCyoMtn.

The chemical characterization of sherd #1 will be addressed later. Before going on to provide some explanations for the above results, however, some comment on sherd #6 is necessary. Unlike the other sherds which were fairly large and could be inserted into the spectrometer in a way that the entire or almost all of the sample area was covered, sherd #6 was in small fragments and did not cover the entire sample area exposed to the x-rays. Also, unlike the other sherds, which had relatively flat surfaces exposed for analysis, the fragments of sherd #6 were angular and there was no continuous flat surface. This may have significantly affected the results. There is, however, no way to be certain. For this reason, although the data are presented, sherd #6 is generally excluded from the following analyses.

That sherds #2, #3, #4, and #5 are very similar to one another and to SamCyoMtn may be an artifact of small sample size. If so, however, one would normally expect more of a random than a clustered distribution as shown on Figure 2. Another possible explanation has to do with the actual formation of the clay vessels and their firing. Although it is unlikely that elements would be lost (in the way that mineral crystal structures are), both the forming and firing of the pottery vessels could redistribute the elements. For example, the strontium in SrSO_4 [the form of strontium mined in the Fish Creek Wash area and commonly found in clay] might be drawn to the surface of the vessels along with the sulfur, which forms with other salts to produce a surface scum coat. If this were the case, then strontium would always show up in large quantities when analyzing the surfaces of sherds. Nevertheless, although it is conceivable that the process of forming and firing clay vessels could naturally bring certain elements to the surface in given ratios, it is highly unlikely. Sherd #1 would support this argument.

Lastly, perhaps sherds #2, #3, #4, and #5 were manufactured from clays chemically very similar to SamCyoMtn. Perhaps the Pliocene marine deposits, which extend from the northeast side of Coyote Mountain well into the Vallecito Mountains to the northwest, are the primary source of the clay used by San Sebastian Marsh/Kane Spring potters to make fine buff wares. The clay deposits would not have been far away; and, of the three samples, SamCyoMtn appears to be the best quality clay in terms of texture. Use of the Pliocene marine clays for pottery manufacture might also help

explain why, of the sites recorded by Rogers, C-160 in the Vallecito Mountains appears to have the greatest range of buff ware pottery types. The marine clays would have been close at hand.

The third hypothesis was partially supported by the analyses. (See Figure 2) In terms of the percentage of iron, strontium and nickel (?), sherds #3, #4, and #5 are very similar chemically. They were all classified as Carrizo Buff II by Malcolm Rogers. Carrizo Buff sherds #1 and #2, on the other hand, are very dissimilar. Sherd #2, in fact, is chemically very similar to the Carrizo Buff II sherds. The fourth hypothesis was definitely supported by the analyses. Waters' Colorado Buff sherd #5 was chemically most similar to Rogers' Carrizo Buff II sherds. Sherds #5 and #4 are actually identical in terms of their proportions of iron, strontium and nickel (?). Thus, the results suggest (although not conclusively simply because of sample size) that there is more variability in chemical makeup within the sherd type Carrizo Buff I and very little in Carrizo Buff II (or Waters' Colorado Buff).

CONCLUSIONS

In spite of the unexpected results, the clay and sherd analyses were extremely productive. Using the x-ray fluorescence technique to chemically fingerprint clays and pottery sherds seems to have considerable potential. Unless there is some fatal flaw of which I am unaware, x-ray fluorescence could be used as a standard technique in pottery analysis. In order to match pottery with specific clay sources, the two best methods seem to be x-ray fluorescence and neutron activation. Neutron activation has been used to analyze ceramics (e.g., Perlman and Asaro 1969 and Bishop, Harbottle and Sayre 1982); but according to Bishop (1984), it is a very expensive technique (about \$600 per sample). I do not know the exact cost to analyze a sherd using x-ray fluorescence, but it would certainly be much less. The Peabody Museum CARD lab charged \$20 per obsidian sample for chemical fingerprinting. After watching for a day, I could not have grasped all the subtleties; nevertheless, operating the spectrometer did not seem to be particularly difficult. The technique can be virtually non-destructive. On the surface, x-ray fluorescence appears to be the more useful technique for pottery analysis.

Actually, I believe x-ray fluorescence could be useful in almost all pottery studies, not only pottery sourcing studies. The reality of what appears to be real pottery types could be tested. Regional as well as inter-site and intra-site pottery analyses could be done. [It would be interesting to apply this technique to Longacre's famous Carter Ranch Pueblo ceramic collection.] More work is necessary in order to determine the usefulness of x-ray fluorescence in pottery analyses. If the technique is sound, then the ceramic analyst will be able to chemically

characterize sherds quickly. This, in conjunction with petrographic analysis should provide the analyst with invaluable quantitative as well as qualitative data.

Even though the results contradicted the proposed hypotheses, they do suggest directions to take in future analyses of buff wares in southern California. Some are presented below.

1. This is not restricted to analysis of southern California buff wares but is a first step in determining the applicability of the x-ray fluorescence technique to pottery analysis. Clays and pottery need to be analyzed to see what the chemical correspondance is between raw clay and fired clay.

2. Clay samples from marine and non-marine deposits need to be systematically analyzed and compared to determine if there are qualitative or quantitative chemical differences between the two types of clay. The range of variability within each of the types of clays also has to be studied. It is possible that there is as much variability within as between each type of clay.

3. A comparison of Rogers' or Waters' various pottery types would be particularly interesting. For example, there should be a chemical difference between Rogers' Carrizo Buffs and his Colorado Buffs, which are primarily found in Arizona. Rogers' Vallecito Buff is very distinctive and if a chemical analysis showed that sherds labeled as Vallecito Buff are chemically similar, this pottery type would be very useful to adopt (it is not generally recognized as a type) because it could be easily identified during field survey.

4. The suitability of Pliocene marine clays for producing buff ware pottery has to be investigated.

There are many lines of research that can be pursued in addition to the four listed. One's imagination is the limiting factor. The above, however, are what I see as the next steps that should be taken. They build on the results of the x-ray fluorescence analysis presented in this report.

In concluding, I would like to reemphasize a point that was made earlier. These analyses do not constitute a "test" of any general hypothesis regarding pottery types or clay sources. The results presented apply to a very small, very judgemental sample. What is described in this paper are the very first small steps in a series of steps that would (or should) constitute a test of pottery types and their affiliation with particular clay sources.

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APPENDIX A

Original and Adjusted Intensity Values

<u>Sample</u>	<u>Strontium (25.0)</u>	<u>Nickel? (43.1)</u>	<u>Copper (45.0)</u>	<u>Iron (51.7)</u>
#1	4.4/2.0	4.9/4.1	1.5/.8	8.4/7.8
#2	3.2/.8	4.5/3.7	1.5/.8	9.7/9.1
#3	3.1/.7	4.4/3.6	1.6/.9	10.2/9.5
#4	3.3/.9	4.9/4.1	1.5/.8	10.2/9.6
#5	3.2/.8	4.6/3.8	1.4/.7	9.6/9.0
#6	2.7/.3	3.5/2.7	1.5/.8	3.9/3.3
SamC-73	2.5/.1	3.8/3.0	1.2/.5	5.9/5.3
SamC-105	2.1/-.3	2.5/1.7	1.0/.3	5.0/4.4
SamCyoMtn	2.8/.4	4.8/4.0	1.5/.8	9.5/8.9
Baseline Adjustment	2.4	.3	.7	.6