Neutron Activation Analysis
of Archaeological Pottery from Long Beach

Gary S. Hurd and George E. Miller

Abstract

Archaeological investigations at CA-LAN-2630 produced 642 prehistoric potsherds. Of these, 63 specimens were subjected to neutron activation analysis (NAA) so as to determine whether they were of local origin or imported. Concentration values of 14 elements, Al, V, Th, Co, Ca, Na, La, Sm, Sc, Fe, Ce, Cr, Mn, and Hf, from the sherd specimens were compared to local soils, excavated daub, and to pottery from regional sites. The results indicated that the LAN-2630 pottery was made from local clays.

Introduction

Archaeological investigations at CA-LAN-2630 (Figure 1) on the California State University campus at Long Beach in 1993 resulted in the recovery of 642 potsherds. The pottery from this site has been identified as Southern California Brown Ware (Boxt and Dillon, this double-issue; see Van Camp 1979:67-68; Griset 2009:122). The LAN-2630 ceramic assemblage consists primarily of small, friable body sherds lacking surface decoration, precluding precise evaluations of vessel morphology or function. By applying neutron activation analysis (NAA) to the LAN-2630 assemblage, we sought to understand the selection and procurement of clay in order to garner information about production and exchange. Unlike descriptive studies that focus on stylistic criteria, vessel characterization by clay chemistry typically uses information that may be irrelevant to the potter yet critical to modern analysts. Our objectives were to identify trace element profiles (TEP) for the excavated potsherds and to compare them with local clay sources. It was hypothesized that a concordance of these data could establish the origin of LAN-2630 ceramics. Conversely, a disparity of these data would support an exchange model.

Sherd Selection and Preparation

A stratified sherd sample of just under 10 percent of the total recovered by unit and level was drawn from the study site. Two specimens of daub and two samples of soil from LAN-2630 also were selected for analysis so as to test the possibility of localized pottery production. If the trace element signatures of daub and soil matched those of the earthenware pottery, there would be very strong evidence that the LAN-2630 ceramics were produced locally. Prior to analysis all potsherds were washed in deionized water. Surfaces were scrubbed with a soft bristle brush and dried at room temperature in a covered container to ambient humidity. Prior to washing, catalogue marks (when present) were removed with a tungsten carbide burr. Potsherd surfaces were penetrated with a tungsten carbide bit to remove an approximately 200 mg sample from drill holes. Some very small potsherds were ground to a coarse powder in a mortar and pestle. Polyvials that held the specimens were washed in ethanol followed by a rinse in deionized water. Approximately 100 mg of material was placed in each one-quarter dram polyvial, which was then labeled with a laundry marker and sealed by melting the cap of the vial to its body. Neither the potsherds nor the vials were touched by hand after they had been cleaned.
Neutron Activation Analysis, Irradiation, Gamma Counting, and Standards

All irradiations were performed at the UC Irvine Nuclear Reactor Facility using the TRIGA Mark I reactor. The reactor generates a core neutron density of $2 \times 10^{12}$ neutrons per cm$^2$ per second at a thermal energy of 250 kW. Trace element determinations for the study samples incorporated the three irradiation schedules discussed below.

A Short-Lived Isotope Determination

Irradiation occurred for one minute or less in the Pneumatic Transfer facility at fluxes from $1 \times 10^{11}$ to $2 \times 10^{12}$ neutrons/cm$^2$ per second, depending upon the sample size. Gamma ray spectrometry followed a six-minute cooling period, using an HPGe end window detector (Canberra Nuclear) with 30 percent efficiency and 2.2 keV resolution at 1332 keV. Data collection time was 4 minutes. This schedule was utilized to generate data on short half-lived isotopes of titanium (Ti), vanadium (V), aluminum (Al), manganese (Mn), and sodium (Na). There were 78 unknowns and three standards analyzed under this condition.

An Intermediate Lifetime Isotope Determination

Irradiation occurred for 10–15 minutes while rotating in a lazy Susan at a flux of $1 \times 10^{12}$

Figure 1. Location of study site CA-LAN-2630 (solid triangle to east of Long Beach) and other locations mentioned in text. Map by Rusty van Rossmann and Matthew A. Boxt.

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neutrons/cm²-second. Gamma ray spectrometry followed using an HPGe Well Detector (Princeton GammaTech) with a 23 mm ID well x 44 mm high, (active volume approximately 115 cm³), approximately 20 percent efficiency, 2.8 keV resolution; 15 minutes count time was employed. This schedule was utilized to generate data on samarium (Sm), tungsten (W), lanthanum (La), scandium (Sc), and potassium (K). The large number of specimens resulted in the loss of potassium (K) values for a significant number of potsherds. This occurred because the entire data acquisition run of 63 samples allowed the 12.36 hour half-life K-42 to decay below detection range. This problem could be avoided by others needing potassium data by irradiating the sample in two lots, which will nearly double the required reactor costs. There were a number of additional isotopes detected during this data acquisition run. Some were present in only a small number of specimens, some were available with greater accuracy from other analyses, and some had unacceptable errors. The Appendix presents the element concentration assignments and proveniences for the study specimens.

**A Long Lifetime Isotope Determination**

Irradiation for one to four hours in the lazy Susan at a flux of 1 x 10¹² neutrons/cm²-second was implemented. Gamma ray spectrometry followed using the same well detector after a decay of two to three days and a count time of one hour. A final data acquisition run was made following a 30-day decay period. Each specimen’s gamma spectrum was collected for 4,000 seconds (1.1 hours), using approximately four days of detector time. Data errors were greatly reduced for long half-lived isotopes. Others, in particular, chromium (Cr), cobalt (Co), cerium (Ce), hafnium (Hf), and thorium (Th) measured from the daughter product (Pa-233), were only detectable after the more active short half-life isotopes had decayed below detection limits. Both spectrometer systems are AccuSpec Model A or B boards with 8K channel memory operated at approximately 0.7 keV per channel. The boards are in PC systems and operated by an ASAP (Analyzer Spectroscopy Application Program) package from ND/Canberra Nuclear. This package provides peak areas, isotope identification, and decay computation capabilities, as well as providing for system calibration. The 30 percent detector system is provided with a Gated Integrator Fast Amplifier (Canberra Model 204) and Fast ADC (8715). It also can be used with a Loss Free Counting module for high count rate correction. Isotopes and the calculated values fell within the standard deviations (Table 1).

**Data Reliability**

Various procedures were performed to guarantee internal data reliability. The first was to prepare blanks that were run with each lot of specimens. Blanks were empty polyvials that were washed, labeled, and irradiated and counted along with the specimen samples. None of the blanks showed gamma activity above background. One potsherd specimen contaminated by the white paint used during cataloguing was analyzed and showed a significant increase of gamma activity from titanium. This contaminated specimen had approximately 20 times the titanium concentration found in the other samples, but there were no other data

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<th>Element</th>
<th>Half Life</th>
<th>Standard Deviation</th>
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<tr>
<td>Vanadium</td>
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<td>±3.0 %</td>
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<td>Titanium</td>
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<tr>
<td></td>
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<td>Samarium</td>
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<td>Tungsten</td>
<td>23.9 hours</td>
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<td>Lanthanum</td>
<td>40.27 hours</td>
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</tr>
<tr>
<td>Scandium</td>
<td>83.9 days</td>
<td>±4.0 %</td>
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</table>

Table 1. Isotopes and Relative Standard Deviations for the Proposed Key Elements.
abnormalities. We decided to report but not analyze the titanium data. Similarly, comparison of the data generated from potsherds ground versus those drilled revealed that only drilled potsherds returned positive tungsten values. Consequently, data values for tungsten are not reported, as the drill bit was clearly the source of the detected values. Multiple standards were run with each batch of specimens. A linear transformation of peak areas to counts per second per mg provided the data for element concentration calculations relative to the coal fly ash standard specimens. By preparing multiple standards, the standards themselves could be relatively cross-checked against their published element concentrations.

The data resulting from the chemical analysis were used to address the local production hypothesis. We began the current procedure by examining the Spearman rank order correlation matrix (Table 2); from simple inspection we observe two subsets of highly intercorrelated elements, Na, La, and Sm, and Fe, Sc, Cr, Ce, Th, Mn, and Hf, with the remaining elements, Al, Ca, V, Tm, and Co, uncorrelated. This suggests that the intercorrelated subsets represent the element concentrations of minerals within the clay matrix. Regardless of the origin of these subsets, it is necessary that they be reduced to single data points, such as a calculated centroid. In this case with the average subset intercorrelation above .9, we ultimately selected just one isotope from each subset to represent that subset.

Analysis

We next examined the sample distribution of each of the measured isotope concentrations. The uncorrelated elements, Al, Ti, V, Tm, and Co, are basically unimodal and approximately normal (Figure 2 a–e). The exception is the strongly bimodal distribution obtained from the calcium data (Figure 2f). The first intercorrelated subset, Na and La, is strongly bimodal (Figure 2g,h), and the data for samarium appears to be weakly trimodal (Figure 2i). Accordingly, we examined the relationship between Na, La, and Sm by splitting the sample at the inflection point of the sodium distribution, fitting a simple regression line to each of the resulting subsets. The regression lines are very different for the two data subsets. The upper distribution regression (e.g., high sodium values) is \( Y(\text{La}) = 0.45X(\text{Sm})+25 \) (Figure 3a), and the lower distribution (e.g., low sodium values) is \( Y(\text{La}) = 0.20X(\text{Sm})+42 \) (Figure 3b). The \( R^2 \) for the regression line in Figure 3a is very low, indicating that those data should be interpreted cautiously. However, the overall result indicates that varying amounts of two minerals are contributing to the trace element profiles of the clay matrix. One of these minerals is present in small amounts and has a lanthanum to samarium ratio of 5:1, while the other is more common and has a lanthanum to samarium ratio of 4:1. Naturally, we recognize that some potsherds may contain both hypothetical minerals and in various amounts and that this may account for the appearance of a third mode in the samarium distribution.

Data distributions for the remaining set of intercorrelated elements, Fe, Sc, Cr, Ce, Th, Mn, and Hf, are presented in Figure 4 with iron representing the group. We note clear representations of bimodal, potentially trimodal, element concentration distribution patterns. However, when the data are examined, we find that a single regression line fits both the upper and lower parts of the distribution patterns (Figure 5). We interpret these results to indicate that a single mineral enriches these elements in the clay matrix and that this mineral specie is bimodally distributed. We favor this interpretation over the alternative explanation that these elements constitute the substitution elements in the base clay and that a relatively pure silicate, such as quartz, is bimodally diluting such clay. Such a strong result should have produced obvious textural differences in the potsherds, yet these were not observed. Petrographic analysis might resolve this issue (Plymale-Schneeberger 1993). The elements identified in this study and potential
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Table 2. Spearman Rank Order Correlation Coefficient on the NAA Trace Element Data.

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mineral species that could serve as sources and are known from Los Angeles County are given in Table 3 (Pemberton 1983).

**Comparisons and Interpretations**

Published NAA results for coastal southern California ceramics are rare, prompting us to look for reports from inland settlements. Frierman (1987) analyzed four Southern California Brown Ware potsherds, or 45 percent of the total assemblage from CA-RIV-2778 (Aros-Serrano Adobe), including a potsherd from the Ontiveros Adobe (CA-LAN-1016/H). These Historic period potsherds differ by a factor of two to as high as 10 for isotopic concentrations that we found to be significant source identifiers for the LAN-2630 pottery. Since ceramic potsherds had been reported from archaeological sites in the vicinity of LAN-2630, we selected five samples from CA-LAN-182H, the Native American ranchería associated with the Pío Pico Rancho Adobe, which is located roughly 10 km to the northeast. Although these sites are not coeval, we chose LAN-182H because it is related geologically to the study site, within the same sedimentary basin. Indeed, this becomes an important indicator of the regional origins of the LAN-2630 ceramics.

Analysis of the trace element composition of pottery potsherds from LAN-2630 indicates that they can be categorized by the presence of at least three to as many as four minerals that enrich the clay matrix of the pottery; these minerals introduce far
Figure 2. Trace element concentration distributions in the CA-LAN-2630 potsherd sample tested. Aluminium (Al), titanium (Ti), vanadium (V), thulium (Tm), cobalt (Co), calcium (Ca), sodium (Na), lanthanum (La), and samarium (Sm). By Gary S. Hurd and Rusty van Rossmann.

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Figure 3. Regression analysis of rare earth element distributions in the CA-LAN-2630 pottery sample tested for sodium (Na), lanthanum (La), and samarium (Sm). Figure by Gary S. Hurd and Rusty van Rossmann.

Partitioning the sample on the inflection points of polymodally distributed element concentrations accounted for most of the sample variance. The partition produced subsets of the sample that included potsherds from LAN-182H, which is geologically comparable but temporally and, in all likelihood, culturally distinct from the study site. The variance in the potsherd trace element profiles is hypothesized to result from two principle sources: (1) the presence of differing amounts of mineral inclusions within the potsherd matrix and (2) the variations in the trace element composition of the actual clays. Thin section analysis of the potsherd sample could be used to further test this hypothesis.

On the basis of NAA, we argue that the study specimens were produced near LAN-2630. There appear to be three elements or groups of elements in the samples that are at least bimodally distributed and independent of each other. Simply splitting the sample at the appropriate inflection points might partition the specimens into interpretable groupings, which account for the majority of data variance.

Looking at the contingency tabulation in Table 4, we favor this approach to the data partition. For example, there are a number of near empty cells indicating that this is not merely a random number exercise. A remaining issue is whether such a partition maximally utilizes the sample variance. This is evident when contrasting Figure 6 with the “residual” trend plotted from the unimodal, uncork-related element distributions such as aluminum, vanadium, and cobalt presented in Figure 7. The distant exchange hypothesis may be further tested by the application of Student’s t-test to the trace element data from Los Angeles County, Orange County, Riverside County, and LAN-2630.

The Orange County ceramic data were from prehistoric site CA-ORA-119A on the upper Newport Bay (Koerper et al. 1978; Hurd et al. 1990) (Table 5). The Riverside County trace element data derive from Andreas Canyon (Palm Springs) Cahuilla pottery (Hurd and Miller 1973) (Table 6). We are “asking” the data if the trace element compositions of the ceramics
Figure 4. Trace element concentration distributions in the CA-LAN-2630 potsherd sample tested. Scandium (Sc), iron (Fe), cerium (Ce), thorium (Th), chromium (Cr), manganese (Mn), and hafnium (Hf). Figure by Gary S. Hurd and Rusty van Rossmann.
Table 3. Elements Identified in Sherd Samples and in Minerals from Los Angeles County.

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<th>Element</th>
<th>Associated Minerals</th>
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<tbody>
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<td>Al</td>
<td>Aluminium, Clay, feldspar</td>
</tr>
<tr>
<td>Au</td>
<td>Gold, Placer deposits in San Gabriel Canyon</td>
</tr>
<tr>
<td>Ca</td>
<td>Calcium, Common from shell, bone, limestone etc...</td>
</tr>
<tr>
<td>Cd</td>
<td>Cadmium, With zinc ores, e.g., sphalerite</td>
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<tr>
<td>Ce</td>
<td>Cerium, Monazite, bastnasite, allanite, orthite</td>
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<tr>
<td>Cr</td>
<td>Chromium, Chromite, chromatin, magnesiochromite (especially with serpentine)</td>
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<tr>
<td>Co</td>
<td>Cobalt, Cobaltite, smallite, erythrite</td>
</tr>
<tr>
<td>Fe</td>
<td>Iron, Hematite, magnetite, substitution metal in clay</td>
</tr>
<tr>
<td>Gd</td>
<td>Gadolinium, Monazite, bastnasite, gadolinite</td>
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<tr>
<td>Hf</td>
<td>Hafnium, Zircon (1% to 5%)</td>
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<tr>
<td>Ho</td>
<td>Holmium, Monazite, gadolinite</td>
</tr>
<tr>
<td>La</td>
<td>Lanthanum, Cerite (25%), monazite (35%) allanite, see cerium</td>
</tr>
<tr>
<td>Mn</td>
<td>Manganese, Iron/manganese nodules, many others</td>
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<td>Na</td>
<td>Sodium, Ubiquitous</td>
</tr>
<tr>
<td>Pd</td>
<td>Palladium, Associated with gold, silver, and platinum minerals</td>
</tr>
<tr>
<td>Ru</td>
<td>Ruthenium, Pyroxinite, with platinum ore, pentlandite</td>
</tr>
<tr>
<td>Sb</td>
<td>Antimony, Stibnite, or antimonides of heavy metals</td>
</tr>
<tr>
<td>Sc</td>
<td>Scandium, Euxenite, gadolinite</td>
</tr>
<tr>
<td>Sm</td>
<td>Samarium, Samarskite, monazite (2.8%), gadolinite</td>
</tr>
<tr>
<td>Sn</td>
<td>Tin, Cassiterite (Sn O₂)</td>
</tr>
<tr>
<td>Th</td>
<td>Thorium, Monazite</td>
</tr>
<tr>
<td>Ti</td>
<td>Titanium, Common, TiO in white paint</td>
</tr>
<tr>
<td>Tm</td>
<td>Thulium, Monazite with thorium</td>
</tr>
<tr>
<td>W</td>
<td>Tungsten, From drill bit</td>
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</table>

Figure 5. Regression analysis of iron-to-scandium concentrations in the CA-LAN-2630 ceramic sample. By Gary S. Hurd and Rusty van Rossmann.
Table 4. Contingency Tabulation of Sherds Partitioned Along the Concentration Distribution Inflection Points for (1) Iron, (2) Samarium, and (3) Calcium.

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<td>2</td>
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<td>3</td>
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<td>17</td>
<td>19</td>
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<tr>
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<td>Calcium = High</td>
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<td>7</td>
</tr>
<tr>
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<td>6</td>
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<td>16</td>
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<td>Total</td>
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from these different locations could have come from the same clay source, which is another way of asking if the CSULB specimens could have arrived on-site through long-distance exchange from the previously tested sources. Also, this analysis should result in the mutual grouping of the soil and daub samples, supporting the notion that post-depositional processes have not significantly altered the trace element profile of the study potsherds. While recognizing that these data do not categorize the only possible distant pottery sources, we find that these results reject the long-distance exchange hypothesis, favoring the local production theory. Only those elements substantially present for all samples are included in the analysis. Chi square tests on presence/absence data also support the local production hypothesis, although they are not presented. A final test of the local production hypothesis is a one-way analysis of variance applied to the NAA generated trace element data from three independent samples. Here we are asking whether or not locale is a statistically significant predictor of trace element data. The results presented in Table 7 further support a local production hypothesis concerning the pottery of LAN-2630.

Conclusions

Our analysis revealed that the potsherds from archaeological sites along the San Gabriel River drainage differ significantly from pottery recovered from archaeological pottery within the Santa Ana River system (RIV-2778 in Corona and ORA-119A at
Neutron Activation Analysis of Archaeological Pottery from Long Beach

Table 5. T-Test Result for Common Elements Found in Ceramics Recovered from CA-LAN-2630 and CA-ORA-119.

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<tr>
<td>V</td>
<td>-2.3</td>
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Table 6. T-Test Result for Common Elements Found in Ceramics Recovered from CA-LAN-2630 and Andreas Canyon, Riverside County.

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Table 7. Results of a One-Way Analysis of Variance Testing Locale as a Predictor of Sherd Trace Element Composition.

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<tr>
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Newport Bay). This provides further support for the argument that the study potsherds from LAN-2630 were produced within the San Gabriel River drainage. It was also noted that the LAN-2630 soil and burnt daub samples share the same chemistry as the potsherds, thus encouraging us to accept the reliability of the potsherd assignments. Our data are unambiguous and lead us to the conclusion that pottery vessels were made within the vicinity of the LAN-2630 archaeological site itself. None of the ceramic samples represent exotic imports.

Acknowledgments

The Pío Pico specimens were recovered during excavations by Cypress College under the direction of Mr. Paul Langenwalter, and permission to use them is gratefully acknowledged. The authors wish to thank the Cahuilla Tribal Council and Tribal Historian Anthony Andreas for providing some of the potsherds discussed in this report. We are grateful to Brian Stokes, Axel Matthias Kern, and Ann Miller for their enthusiasm and tireless efforts at the UC Irvine Radiochemistry Laboratory.

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1973 Analysis of Prehistoric Ceramics by Neutron Activation. In Reports of the Undergraduate Research Fellows to the Regents of the University of California, Irvine. On file, University of California Irvine Library, Special Collections.

Hurd, Gary S., George E. Miller, and Henry C. Koerper

Koerper, Henry C., Christopher E. Drover, Arthur E. Flint, and Gary S. Hurd

Pemberton, H. Earl

Plymale-Schneeberger, Sandra

Van Camp, Gena R.
### Neutron Activation Analysis of Archaeological Pottery from Long Beach

**Unit Concentration Assignment and Provenience for the CA-LAN-2630 Pottery Specimens.**

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**PCAS Quarterly, 47(3&4)**

101
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<th>Depth (cm)</th>
<th>Al (%)</th>
<th>Ca (%)</th>
<th>Ti (PPM)</th>
<th>V (PPM)</th>
<th>Mn-56 (PPM)</th>
<th>Na (%)</th>
<th>La (PPM)</th>
<th>Sm (PPM)</th>
<th>Sc (PPM)</th>
<th>Cr (PPM)</th>
<th>Mn-54 (PPM)</th>
<th>Fe (%)</th>
<th>Co (PPM)</th>
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Element Concentration Assignment and Provenience for the CA-LAN-2630 Pottery Specimens (continued).
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<th>Ti (PPM)</th>
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Element Concentration Assignment and Provenience for the CA-LAN-2630 Pottery Specimens (continued).

* Daub.
** Soil sample.
*** Sherds from CA-LAN-182H.