

AN ASSESSMENT OF THE ACID-EXTRACTION APPROACH TO
COMPOSITIONAL CHARACTERIZATION OF
ARCHAEOLOGICAL CERAMICS

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We criticize the acid-extraction approach to chemical characterization of ceramics previously advocated in this journal by Burton and Simon (1993). The instrumental technique used by Burton and Simon (inductively coupled plasma emission spectroscopy [ICP]) is a highly precise chemical characterization technique, but noise introduced by characterizing acid extracts from sherds nullifies the usefulness of the resulting elemental concentration data for archaeological sourcing.

Criticamos el uso de extractos de ácido en la caracterización química de la cerámica, que Burton y Simon (1993) defendieron recientemente en esta revista. La técnica instrumental utilizada por Burton y Simon (espectroscopía de plasma de acoplamiento inductivo) es una técnica de caracterización química altamente precisa. Sin embargo, la interferencia introducida al caracterizar los extractos de ácido de los tiestos anula la utilidad de las concentraciones de elementos como datos que pueden reflejar las fuentes de cerámica arqueológica.

“Good, fast, cheap; pick any two.” – anonymous

Burton and Simon (1993) advocate chemical characterization of acid extracts as an alternative to bulk sample characterization in pottery sourcing studies. The main advantages claimed for this approach are low cost, instrumental availability, and ease of sample preparation. In contrast, bulk characterization by neutron activation analysis (NAA) is “expensive and beyond the reach of many” (p. 45), while bulk characterization by atomic absorption (AA) and inductively coupled plasma emission spectroscopy (ICP) entails high labor investment in sample preparation and a necessity to work with hazardous toxic chemicals.

One cannot quarrel with Burton and Simon’s desire to find a fast, inexpensive, widely available, and clean (nontoxic) technique for characterizing the chemical composition of archaeological pottery. Numerous studies demonstrate the potential of chemical characterization to yield reliable

ceramic source determinations. And, as Burton and Simon (1993:45–46) point out, a capability to analyze large samples of pottery would help extend the scope of ceramic sourcing research to fine-grained questions about interaction on an intraregional or even intrasite level. If other things were equal, then the advantages of speed, low cost, and compatibility with widely available instrumentation would surely establish the superiority of the acid-extraction approach.

Unfortunately, as we demonstrate here, other things are not equal. The acid-extraction sample preparation process introduces so much uncontrolled variation into ceramic compositional data sets that even the most conspicuous distinctions may remain hidden, and this is likely to lead to distorted or incorrect conclusions about prehistoric exchange systems. Consequently, we recommend against use of the acid-extraction approach in chemistry-based ceramic provenance investigations. The potential distortions are so serious that we do not even think that acid-extraction ICP

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should be used as an initial screening tool or that the data might usefully complement data produced by other chemical or mineralogical characterization techniques.

We emphasize that our recommendations pertain only to the sample preparation techniques advocated by Burton and Simon and not to their choice of analytical instrumentation—ICP. Under appropriate conditions, ICP, NAA, AA, and other techniques will yield highly precise multi-element compositional characterization of a wide range of materials.

Ceramic Sourcing by Bulk Analysis and Acid-Extraction Analysis

The basic goal in any sourcing study is to link characterized artifacts with sources or source zones where raw materials used in their manufacture originated. In chemistry-based sourcing studies of pottery, forming groups of chemically similar pottery specimens is a crucial step in the analysis. Sometimes raw materials may be compared directly to such groups; more often, the “criterion of abundance” (Bishop et al. 1982:301–302) is used to differentiate local from nonlocal groups and to infer production zones for the various identified groups.

Groups of specimens may be picked out of data derived from any kind of measurement on a collection of pottery. In sourcing studies based on elemental concentration measurements, one seeks to define groups that form recognizably distinct centers of mass (areas of high point density) in the elemental concentration space. Methods for defining and interpreting compositional groups are largely beyond the scope of this paper. The main topic of concern here is how the measurement process itself affects the potential to recognize chemically distinct groups.

Whether source-related groups are recognizably distinct from each other depends not just on the separation between their centroids but also on the total chemical variation of each group. Harbottle (1976:37) reports that total variation for homogeneous compositional groups of Greek Bronze Age pottery ranges from 4–9 percent for many elements determined by NAA, but that Mesoamerican ceramic compositional groups show total variation in the 10–20 percent range for most elements. In NAA data for three groups

of ethnographic pottery from the Valley of Guatemala (Arnold et al. 1991:Table 5), standard deviations are below 15 percent of mean concentrations for 37 of 51 reported concentrations (17 elements in three groups), while in three compositional groups of Aztec Black-on-orange pottery (Hodge et al. 1993:Table 5), standard deviations are below 10 percent of mean concentrations for 37 of 57 reported concentrations (19 elements in three groups) and below 15 percent for 53 of 57 reported values. In bulk (complete-dissolution) ICP data on New York bricks from a single source, Gilbert et al. (1993:Table 4) found coefficients of variation (C.V.s, i.e., standard deviation expressed as percentage of mean) under 10 percent for 27 out of 31 elements. These and many other bulk characterization studies suggest that total variation in source-related compositional groups may be expected to remain far below 20 percent of mean concentrations for the vast majority of elements.

In the case of bulk chemical data (such as NAA data or complete-dissolution ICP data), total variation of a group may be partitioned into (a) natural variation in the “source,” which here includes variation related to cultural practices, such as tempering, together with use and diagenetic effects; (b) variation introduced by sampling of each individual specimen; and (c) variation in the analytical measurements (Bishop et al. 1982; Harbottle 1976). In the acid-extraction approach, an additional source of variation is introduced by the extraction procedure itself. This is evident in Burton and Simon’s statement of what the acid-extraction data represent: the data for each sherd represent “micrograms of *extractable* ion per gram of sherd” (Burton and Simon 1993:48 [emphasis added]). “Extractability” is an additional, recognized source of chemical variation in the acid-extraction approach.¹

The natural chemical variation within and between groups is the “signal” of interest in ceramic sourcing studies, while the other contributions to total variation in a data set may attenuate the signal or render it ambiguous. Analytical errors can be evaluated by repeated analyses of a carefully homogenized sample. Analytical error in bulk chemical data produced by NAA remain below about 3 percent for many elements and below 10 percent for the majority of elements

(Glascok 1992; Harbottle 1982; Bieber 1977:Table 5). ICP spectrometry yields comparable precision, judging from the instrumental and procedural precision values reported by Burton and Simon (1993:Table 1; also see Hart et al. 1987:Table 1).

Individual specimen sampling variation can be evaluated by analyzing repeated samples from the same batch of ceramic paste (in most cases, this would mean the same pot). In one study, NAA of separate vessels within a single fused waster stack from Tel Leilan (Syria) yielded C.V.s below 3 percent for 12 of 25 elements and below 10 percent for 21 of 25 elements; these C.V.s are actually below those obtained with a homogeneous reference material for 19 of 25 elements (Blackman et al. 1993:Table 1). In another study, repeated neutron activation analyses of two large Godin III (Iran) storage vessels yielded C.V.s slightly higher than homogeneous reference material C.V.s but still under 5 percent for 11 of 25 elements in one vessel and for 10 of 25 elements in the other vessel; C.V.s were below 10 percent for 18 elements in one case and for 15 elements in the other (Henrickson and Blackman 1992:Table 9.4). Assessment of sampling variation in full-dissolution ICP (Hart et al. 1987:Table 1) yielded C.V.s below 5 percent for 15 of 23 elements and below 10 percent for 22 of 23 elements. Bishop et al. (1982) point out that the magnitude of added variation from sampling vagaries depends on sherd texture, fine-paste ceramics showing less variation than coarse-paste (highly tempered) vessels. The studies just cited suggest, however, that even conservative estimates of the variation from analytical error plus sampling (measured as coefficient of variation) would be far below 10 percent for a majority of the elements determined by bulk techniques such as NAA or full-dissolution ICP.

Variation in "extractability," which is unique to the acid-extraction approach, is more difficult to evaluate than analytical variation or individual specimen sampling variation. The "procedural precision" reported by Burton and Simon (1993:Table 1) indicates variation in repeated extractions from the *same ceramic material*. In this case, such potential determinants of extractability as firing temperature and atmosphere, mineralogy, and conditions in the burial environment are held constant. As Burton and

Simon (1993:46) note, "the acid-extraction method . . . is more sensitive to technological parameters such as firing temperature, and probably to postdepositional alteration, than are methods that measure total elemental abundances." A realistic assessment of the added chemical variation introduced by variation in extractability must allow for variation in conditions that might affect extractability. (Besides the technological and burial conditions mentioned above, variation in particle size of the powdered sample subjected to the acid soak might also affect extractability; it is unclear whether calculation of "procedural precision" by Burton and Simon involved regrinding of the repeated analyses).

Burton and Simon discuss one possible determinant of extractability, firing temperature, at some length and conclude that "[f]iring influences on the chemical signature are minor" (Burton and Simon 1993:52). Test tiles made from the same clay sample were fired to four different temperatures (0, 400, 600, and 800°C) and analyzed by acid-extraction ICP. Histograms of \log_{10} data for 12 elements are presented for three of the clays. The \log_{10} scale effectively conceals a great deal of the chemical variation related to firing temperature, but conversion of the log concentrations (read from Figures 1–3 in Burton and Simon 1993) back to ppm concentrations indicates that the firing influences are anything but minor: for the Roosevelt gray-green clay, measured aluminum concentration varies from about 2,950 to about 12,500 ppm (about 400 percent), strontium varies from about 18 to about 200 ppm (about 1100 percent), and titanium varies from about 9 to about 35 ppm (about 390 percent); for the Shoofly clay, aluminum varies from about 7,950 to about 39,800 ppm (about 500 percent), potassium varies from about 890 to about 3,200 ppm (about 350 percent), titanium varies from about 25 to about 200 ppm (about 800 percent), and zinc varies from about 6 to about 35 ppm (about 580 percent); the Vosberg clay concentrations are more stable, the maximum variation being only about 300 percent for titanium. C.V.s calculated from the firing temperature data (four measurements) for these elements would range from about 60 percent to about 100 percent, and presumably the C.V. would drop with larger sample sizes. Clearly, however, Burton and Simon's

own data demonstrate tremendous differences in extractability as a result of varying *just one* of the potentially relevant conditions.²

In summary, when natural (within source) variation is held constant in bulk analysis by NAA, even the most conservative estimates of remaining analytical and sampling variation are less than one-tenth of mean concentrations for most elements. In acid-extraction ICP, in contrast, Burton and Simon's own data indicate variation due to analytical error, individual specimen sampling, and extractability may be as high as 100 percent for some elements. This not only exceeds (by up to one order of magnitude) the conservative 10 percent figure for analytical and sampling variation in NAA data, but it also exceeds (by up to a factor of five) the conservative limit of 20 percent total variation expected for most elements in compositional reference groups.

Burton and Simon (1993:46) suggest that "for a first approximation," acid-extraction data characterize the fired clay component of ceramic pastes. However, the huge observed differences in extractability based on firing temperature alone imply that acid-extraction data characterize *different* components of the ceramic fabric in different sherds; the compositional profile of one sherd may express mainly clay composition, that from another may express more temper than clay, and that from a third may express mainly the composition of diagenetic products. In short, there is no means to control what really is being measured in the acid-extraction approach. Obviously, this situation contrasts starkly with bulk chemical characterization, in which each and every measurement expresses the total concentration of an element in the fabric (which includes, of course, cultural additives and diagenetic additions together with clay). The implications of this contrast for the recovery of "archaeologically significant information" (Burton and Simon 1993:45) from compositional data sets are addressed in the following section.

Comparison of NAA and Acid-Extraction ICP Data on Tanque Verde Red-on-brown Ceramics

Chemical characterizations of 366 Tanque Verde Red-on-brown ceramics from the Tucson Basin and neighboring parts of south-central Arizona

were recently undertaken by both acid-extraction ICP and NAA. The study was initiated by Paul Fish, who selected the samples for analysis (Fish et al. 1992). Acid-extraction ICP was conducted by James Burton at the Laboratory for Archaeological Chemistry, University of Wisconsin, Madison, using procedures described by Burton and Simon (1993). NAA was carried out at the Archaeometry Laboratory, Missouri University Research Reactor Center (MURR), using procedures described by Glascock (1992). Results of the latter study are reported by Fish et al. (1992). Besides the 366 bulk neutron activation analyses carried out at MURR, 40 specimens were sonically disaggregated (Gaines and Handy 1977) and the various size fractions subjected separately to NAA (Elam et al. 1992). Given the claim that acid-extraction ICP measures the clay matrix (Burton and Simon 1993:46), the clay fraction NAA data are of special interest here. Compositional data were exchanged between the two labs to facilitate comparison of approaches to compositional characterization. Ten elements were determined by both NAA and acid-extraction ICP and thus provide a basis for comparing the two approaches to characterization (note that only two elements determined by ICP are excluded, whereas 23 elements determined by NAA, including many of those measured most precisely, had to be excluded).³

Table 1 shows descriptive statistics and Pearson's correlation coefficients for the bulk NAA vs. ICP data ($n = 366$), the clay fraction NAA vs. ICP data ($n = 40$), and for a homogeneous compositional reference group identified by NAA (Marana-BC, $n = 78$) for the 10 elements analyzed by both techniques. Both the whole Tanque Verde Red-on-brown data set and the subset of analyzed clay fractions are heterogeneous collections of analyses representing a number of production centers in the Tucson Basin and elsewhere. Therefore, natural variation is expected to be much greater than variation within a single compositional group; this high natural variation is reflected in many coefficients of variation in the 15–40 percent range for NAA data in Table 1. Comparison of the C.V.s for NAA and ICP data reveals that the acid-extraction approach magnifies this high natural variation even further, the

Table 1. Summary Statistics and Correlation between Acid-Extraction ICP and NAA Data.

Element	ICP			NAA			Pearson's Corr.
	Mean	S.D.	C.V.	Mean	S.D.	C.V.	
Bulk data (n = 366)							
Al (%)	2.22	.66	29.9	7.88	.69	8.8	.07
Ba (ppm)	320.	210.	64.1	770.	160.	20.6	.59
Ca (%)	3.16	1.48	46.8	3.85	1.39	36.	.94
Fe (%)	1.12	.45	40.2	3.13	.57	18.2	.40
K (%)	.44	.24	54.6	2.866	.27	9.6	.19
Mn (ppm)	350.	160.	45.3	690.	180.	26.6	.59
Na (%)	.11	.05	41.	1.36	.29	21.6	-.08
Sr (ppm)	180.	140.	78.4	380.	150.	40.3	.89
Ti (ppm)	250.	90.	35.6	2890.	760.	26.4	.14
Zn (ppm)	47.	20.	42.1	74.	17.	22.6	.43
Clay fraction data (n = 40)							
Al (%)	2.40	.72	30.3	8.85	.69	7.8	.34
Ba (ppm)	375.	159.	42.4	1080.	340.	31.3	.76
Ca (%)	2.86	1.05	36.7	5.13	1.54	30.	.92
Fe (%)	1.04	.34	32.5	3.83	.27	7.	-.06
K (%)	.42	.25	59.4	2.66	.26	9.8	.34
Mn (ppm)	360.	112.	31.2	1080.	210.	19.1	.50
Na (%)	.12	.03	27.1	.94	.17	17.7	-.04
Sr (ppm)	160.	180.	110.6	420.	240.	57.1	.97
Ti (ppm)	220.	60.	25.5	3150.	460.	14.5	-.15
Zn (ppm)	45.	17.	37.5	115.	16.	14.4	.43
Marana-BC Group (n = 78)							
Al (%)	2.04	.52	25.6	7.62	.44	5.7	-.02
Ba (ppm)	280.	120.	44.2	750.	110.	14.3	.51
Ca (%)	2.76	1.16	42.1	3.49	1.10	31.5	.95
Fe (%)	1.04	.32	30.9	2.83	.22	7.7	.05
K (%)	.37	.19	51.3	2.89	.20	6.8	.18
Mn (ppm)	310.	90.	29.8	670.	90.	13.7	.45
Na (%)	.11	.04	33.7	1.47	.11	7.4	-.20
Sr (ppm)	140.	50.	35.	360.	40.	11.8	.72
Ti (ppm)	270.	70.	26.4	2600.	330.	12.7	-.05
Zn (ppm)	44.	14.	30.5	69.	8.	11.4	.17

ratio of ICP to NAA C.V.s ranging from 1.3 to 5.7 and averaging 2.4 for the bulk data and from 1.2 to 6.1 with an average of 2.7 for the clay fraction data. In other words, chemical variation introduced by variation in extractability *more than doubles* the chemical variation of this data set, which, to reiterate, is already chemically heterogeneous due to the inclusion of multiple compositional groups. This observation leads one to suspect that many if not most between-group differences would be hidden in acid-extraction ICP data.

The descriptive statistics shown for the Marana-BC group in Table 1 provide perhaps the best indication of the additional variation introduced by extractability. With the exception of calcium, C.V.s for the concentrations determined by

NAA are in the 5–15 percent range, which fits the expectations mentioned previously for total variation in a group of ceramics derived from a single source. (The high variation in calcium may be due in part to deposition of secondary calcite in pore spaces and/or to variation in calcium-feldspar content.) The C.V.s for the acid-extraction ICP data, in contrast, range from about 25 percent to more than 50 percent; these C.V.s are far higher than C.V.s of the NAA data for this group and far higher even than the very conservative 20 percent figure cited previously as the upper limit of total variation in bulk chemical data for a source-related compositional group. With the exception of strontium, the ICP C.V.s for the Marana-BC group are also higher than C.V.s for both the total

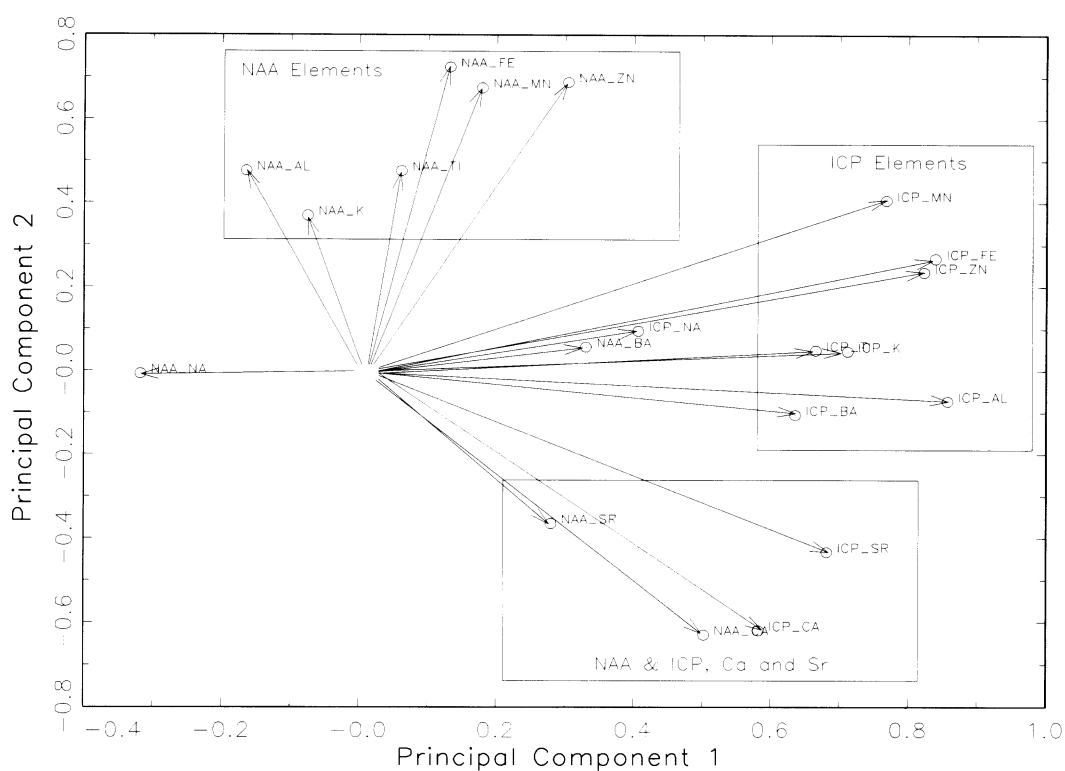


Figure 1. Variable (element) configuration on the first two components derived from PCA of the correlation matrix of NAA bulk plus acid-extraction ICP data on the total Tanque Verde Red-on-brown data set.

bulk and clay fraction NAA data. The ratio of ICP to NAA C.V.s for individual elements in the Marana-BC group range from 1.3 to 7.7 and average 3.7, which implies that variation in extractability *nearly quadruples* the total variation in this compositional group. Parenthetically, it is worth reiterating that the 10 elements being considered here are not among the elements determined best by NAA, so if anything these data *underestimate* the magnification of variation due to extractability.

The large differences between the ICP and NAA concentration means in Table 1 are not bothersome in themselves, since no claim is made that the entire sample enters solution in the acid bath. One would, however, expect very high positive correlation between measurements obtained by the two techniques if both are responding to the same underlying compositional signal (i.e., natural chemical variation within and between sources). One possibility is that acid-extraction

ICP, despite the added chemical variation introduced by variation in “extractability,” is still a rough measure of the bulk composition; however, low and even negative correlations between NAA and ICP measurements in both the total bulk dataset and the Marana-BC group (Table 1, last column) belie this interpretation. Another possibility is that, as claimed by Burton and Simon (1993:46), acid-extraction ICP measures abundances in the finest (clay) component of the ceramic paste; however, the low and negative correlations for the clay fraction data in Table 1 indicate that this is not the case either. The only high correlations in Table 1 are for the alkaline earth elements, calcium and strontium (barium to a lesser extent), which go into solution as divalent cations in the acid bath; for these elements, the acid-extraction ICP analysis appears to approximate what is measured by either bulk or clay fraction NAA. With these exceptions, individual elemental concentrations obtained by acid-extract-

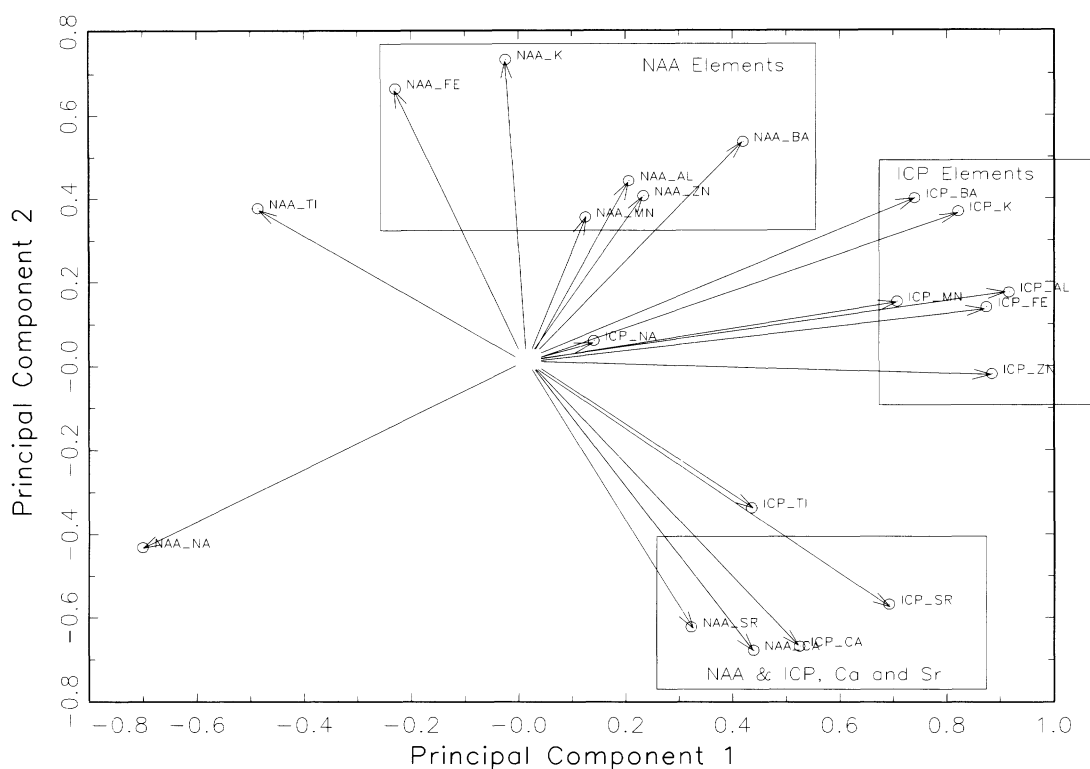


Figure 2. Variable (element) configuration on the first two components derived from PCA of the correlation matrix of NAA clay fraction plus acid-extraction ICP data on the 40 Tanque Verde Red-on-brown specimens for which clay-fraction separates were analyzed by NAA.

tion ICP appear not to reflect either bulk composition or clay fraction composition.

The question of what the acid-extraction ICP data actually measure may also be examined from the perspective of overall structure in the compositional data set. An efficient way to do this is to subject the data set consisting of ICP together with NAA measurements for each sample to a principal components analysis (PCA) and to plot the resulting variable coordinates on the first two components. The resulting h-plots, on which variable coordinates are connected to the origin by vectors, provide the best possible two-dimensional representation of the correlational structure of the data (Baxter and Heyworth 1991); the cosine of the angle between two vectors indicates variable correlation, so vectors to highly correlated variables have very small angles, vectors to uncorrelated variables have angles in the neighborhood of 90° , and vectors to negatively correlated elements have angles in the neighborhood of 180° . Elements

whose coordinates lie closest to the origin are represented most poorly in terms of their correlations with other elements (Tangri and Wright 1993). In the present case, both bulk data (Figure 1) and clay fraction data (Figure 2) show most ICP elements plotting together on the right side of the plot and most NAA elements plotting together at the top of the plot, at roughly 90° from the ICP elements; again, strontium and calcium are exceptions to the overall pattern, the ICP and NAA coordinates for these two elements forming a separate set of positively correlated measurements at the lower right corner in both the bulk and clay fraction plots. Here again it is obvious that, with the exception of calcium and strontium, acid-extraction ICP measures something distinct from what is measured either by bulk NAA or NAA of clay separates; indeed, the offset of approximately 90° between the NAA and acid-extraction ICP elements suggests that the two analytical techniques approach independence of one another.

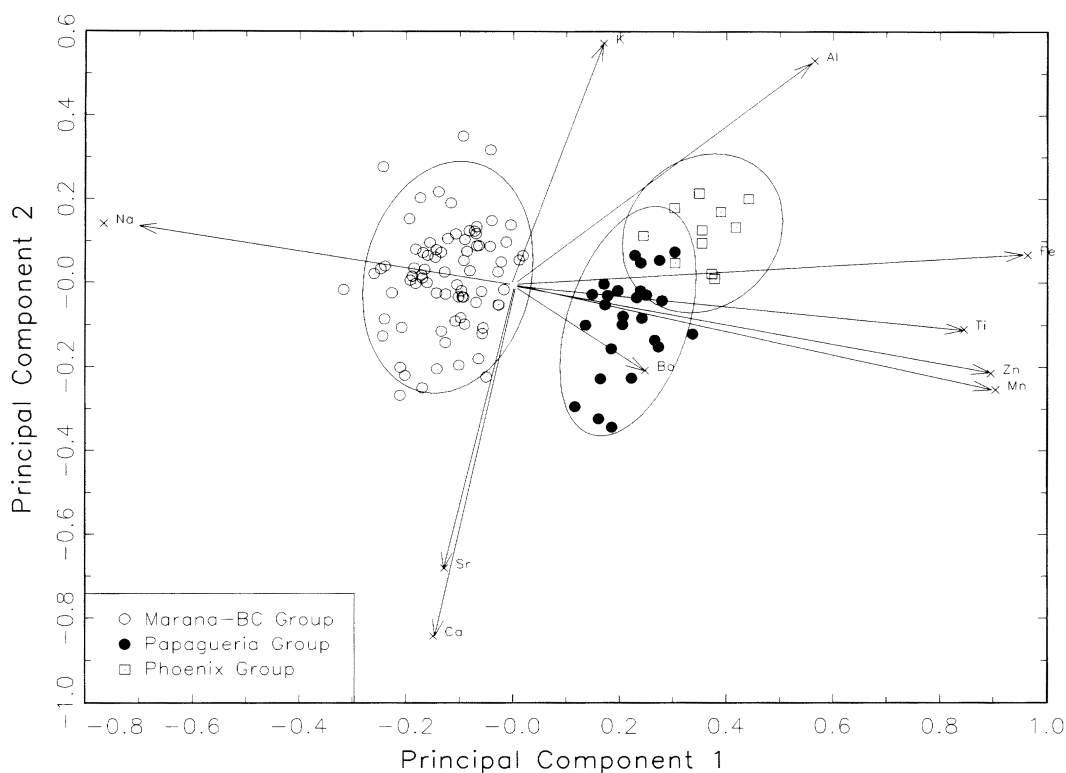


Figure 3. Biplot of the first two components derived from PCA of the correlation matrix of the NAA bulk data for the total Tanque Verde Red-on-brown data set. Ellipses represent 90 percent confidence level for membership in the three known groups.

As a fall-back position, one might claim that—despite the huge increase in chemical heterogeneity due to variation in “extractability” and despite the fact that there is no obvious answer to the question “What does acid-extraction ICP measure?”—compositional characterization of acid extracts can still yield “archaeologically significant information.” It is always possible to find *some* subgroup structure in a compositional data set; might source-related groups still be recognizable in an acid-extraction analysis data set? This question can be addressed with the Tanque Verde Red-on-brown data set, within which there are some compositional distinctions that are so marked that if a characterization technique cannot find them, it is hard to imagine how that technique could ever contribute “archaeologically significant information.”

As discussed by Fish et al. (1992), compositional distinctions within the Tucson Basin are comparatively subtle, and there is considerable

ambiguity in the assignment of specimens to one group or another. There is no such ambiguity when one compares any of the Tucson Basin groups (here we use a group designated Marana-BC) to a group inferred to represent production somewhere in the Papageria region west of Tucson or to a group inferred to represent production in the Phoenix area. Many different projections of the 32-dimensional NAA data set (i.e., many of the 32 elements and/or principal components) reveal this three-way partition. What about the 10 elements determined in common by NAA and ICP? Are the known subgroups recognizable in this space of reduced dimensionality either in the ICP or the NAA data?

If one has no other means to guess what groups might exist in a data set, a reasonable approach to compositional data analysis is to hypothesize subgroups based on some pattern-recognition technique such as cluster analysis or PCA (Bishop and Neff 1989). In PCA, scatterplots of objects on the

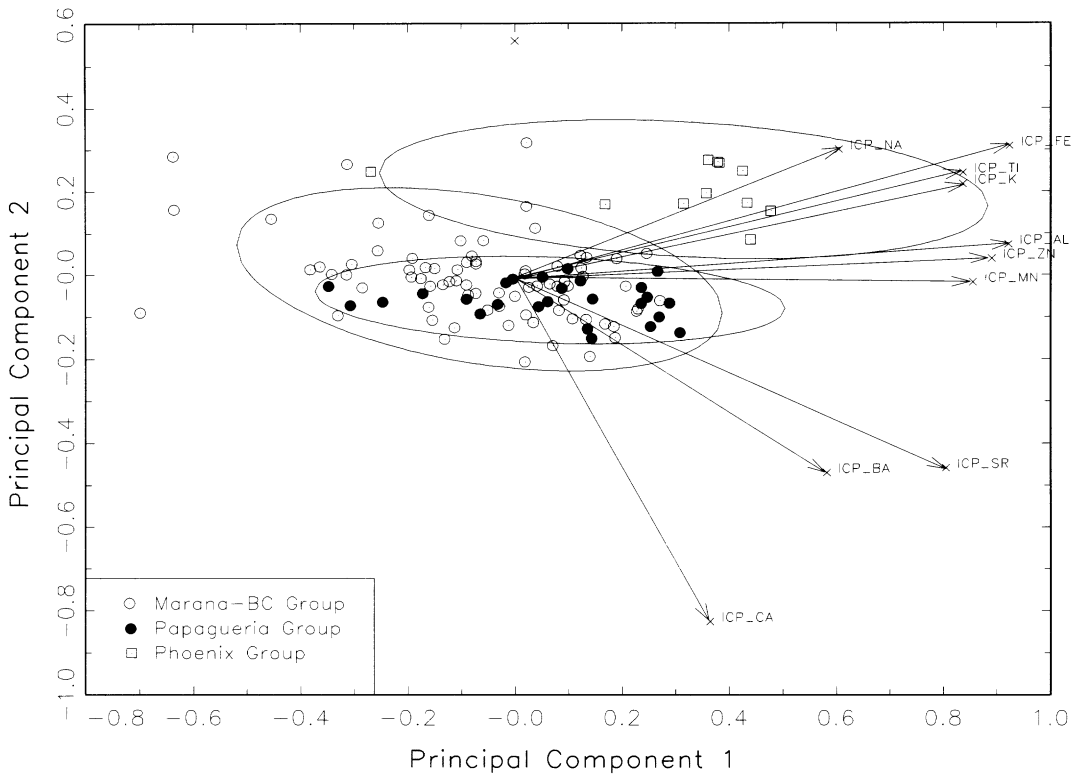


Figure 4. Biplot of the first two components derived from PCA of the correlation matrix of the ICP data for the total Tanque Verde Red-on-brown data set. Ellipses represent 90 percent confidence level for membership in the three known groups.

first several components reveal major subgroup structure. PCA of the NAA and ICP data sets consisting of Marana-BC, Papageria, and Phoenix groups of Tanque Verde Red-on-brown are summarized in Table 2, and the objects and variables are plotted on the first two principal components of each data set in Figures 3 and 4 (the simultaneous display of objects and variables is called a “biplot” [Baxter 1992; Neff 1994]). In accord with the earlier observation that NAA and ICP analyses are nearly independent of one another, the correlational structure of the two data sets revealed by variable vectors in Figures 3 and 4 differ substantially.

The difference in structure between the NAA and ICP data is also evident in the object configurations shown in the biplots derived from the two PCAs (Figures 3 and 4). The NAA data (Figure 3) segregate clearly along the first principal component into two major point clouds, with some over-

lap remaining between the Papageria and Phoenix groups. The ICP data (Figure 4) form one continuous point cloud with some peripheral data points (outliers). If the groups were not differenti-

Table 2. Summary of Principal Components Analysis of Three-group Subset of Tanque Verde Data.

Acid-Extraction ICP			Bulk Neutron Activation		
Eig.	% Var.	Cum. % Var.	Eig.	% Var.	Cum. % Var.
6.11	61.12	61.12	4.30	42.96	42.96
1.41	14.12	75.24	1.97	19.74	62.70
.78	7.83	83.08	1.29	12.94	75.63
.63	6.33	89.41	.69	6.93	82.56
.39	3.87	93.28	.60	6.01	88.57
.27	2.72	96.00	.45	4.55	93.12
.19	1.91	97.90	.32	3.20	96.32
.09	.93	98.84	.22	2.24	98.56
.08	.78	99.61	.10	.99	99.55
.04	.39	100.00	.04	.45	100.0

Note: n = 115; Eig. = Eigenvalue; Var. = Variance; Cum. = Cumulative

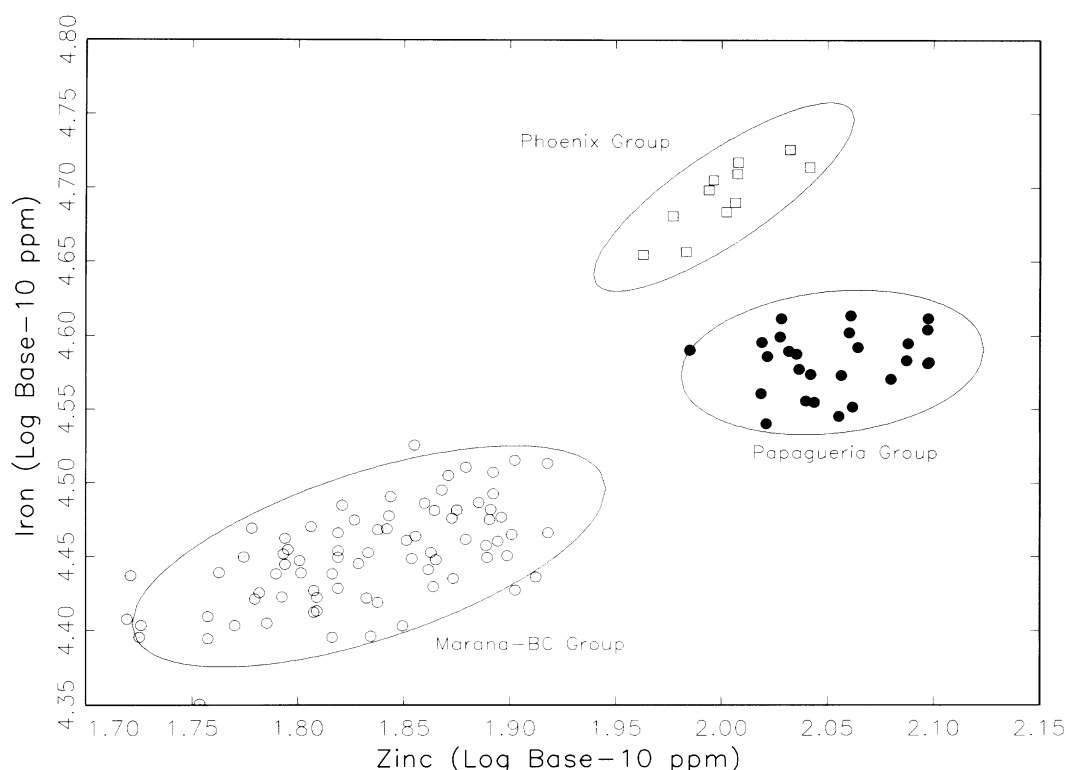


Figure 5. Bivariate zinc-iron log concentration plot showing data for three Tanque Verde Red-on-brown groups obtained by bulk NAA. Ellipses represent 90 percent confidence level for membership in the groups.

ated by symbols (i.e., if this were part of the pattern-recognition phase in a real study), most of the Phoenix specimens probably would be picked out as a peripheral subgroup; the distinction between the Papaguera and Marana-BC groups, however, would remain completely obscured by this approach to pattern recognition. Even if one guessed that the Papaguera specimens should form a distinct subgroup (e.g., because all came from a single site or shared unique decorative characteristics), there is no possible way that Figure 4 could be interpreted as suggesting a source distinct from Marana-BC specimens.

It is remarkable that the major dimension of variance in the ICP data (Principal Component 1), which accounts for over 60 percent of total variance (Table 2), reveals virtually complete overlap of the three groups (Figure 4). Since this component expresses enrichment-dilution of virtually all measured elements (note the direction of all variable vectors in Figure 4), but largely fails to reveal

between-group differences, the most plausible interpretation of this dimension is that it expresses "extractability." That is, the most leachable specimens score high on this component, while less leachable specimens score low. High scores for most of the Phoenix group members may not indicate natural compositional properties of this group so much as greater susceptibility to leaching in an acid bath.

The foregoing interpretation suggests that the single greatest source of chemical variation in the ICP data is noise arising from variation in extractability, which in turn must be due to variation in firing temperature and atmosphere, burial environment, etc. This interpretation accords both with the huge effect of extractability on individual element variation documented in Table 1 and with the fact that Burton and Simon's own data demonstrate the dependence of extractability on firing temperature.

The positions of variable coordinates in Figures

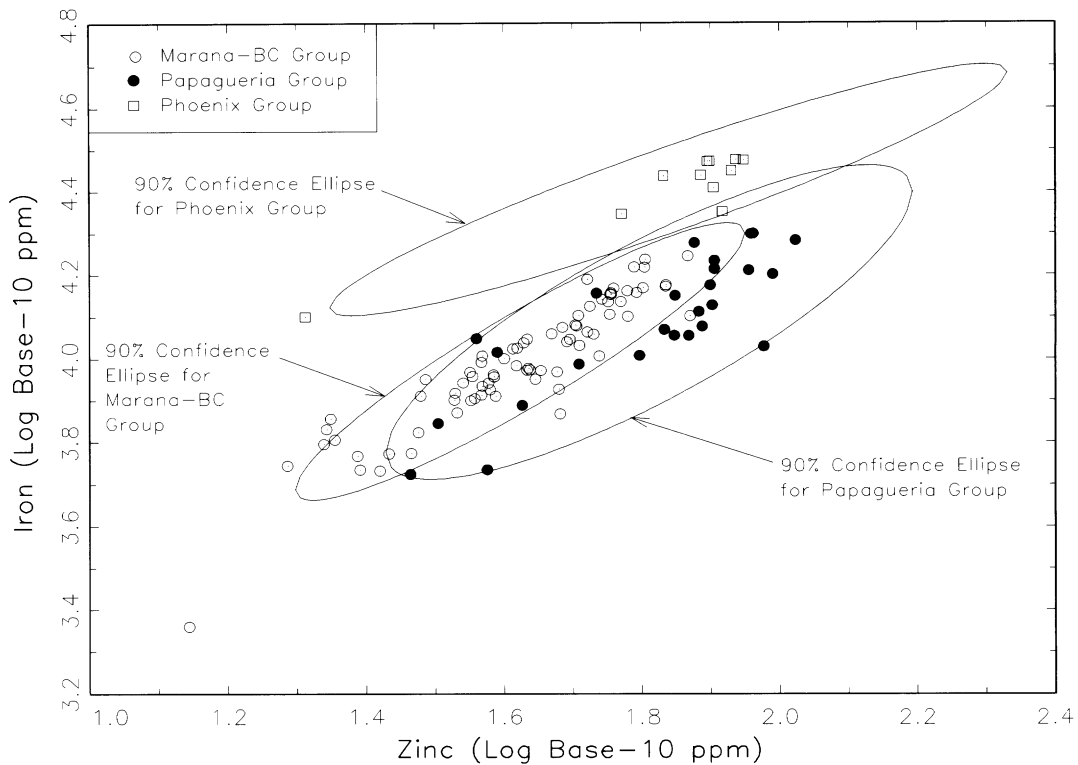


Figure 6. Bivariate zinc-iron log concentration plot showing data for three Tanque Verde Red-on-brown groups obtained by acid-extraction ICP. Ellipses represent 90 percent confidence level for membership in the groups.

3 and 4 indicate contributions to variation along each dimension and can serve as a guide for examining other projections of the data in search of group separation (Neff 1994). In the NAA data (Figure 3), iron and zinc both contribute importantly to variation along the first principal component. As expected, a bivariate plot of these two elements (Figure 5) clearly separates the Papagueria and Phoenix groups from the Marana-BC group. Additionally, the Phoenix group is completely distinct from Papagueria. A plot of the same two elements (iron and zinc) measured by acid-extraction ICP (Figure 6) shows a single point cloud with the Phoenix group located in a peripheral position and potentially distinguishable from the other groups; the Marana-BC and Papagueria groups overlap completely. So far, then, pattern recognition based on inspection of PCA plots and bivariate elemental concentration plots of the ICP data does not seem capable of revealing the known structure in the Tanque Verde data.

What if a different pair of elements is chosen by inspection of the PCA biplot of the ICP data (Figure 4)? Since, as noted, Principal Component 1 reveals virtually no subgrouping tendencies, one would probably look at elements that contribute to Principal Component 2. Calcium and sodium are relatively important in this regard, higher calcium pulling specimens low and higher sodium pulling them high. A bivariate plot of NAA data for these two elements (Figure 7) shows separation of the Phoenix group from the other two, and a bivariate plot of ICP data (Figure 8) reveals the same thing. Unfortunately, the Papagueria group is still contained completely within the Marana-BC group. Also, ironically, separation of the Phoenix group from the others is based on lower concentrations of sodium according to the NAA data (Figure 7), but it is based on higher concentrations according to the ICP data (Figure 8). This might have been expected, of course, in light of the negative correlation of

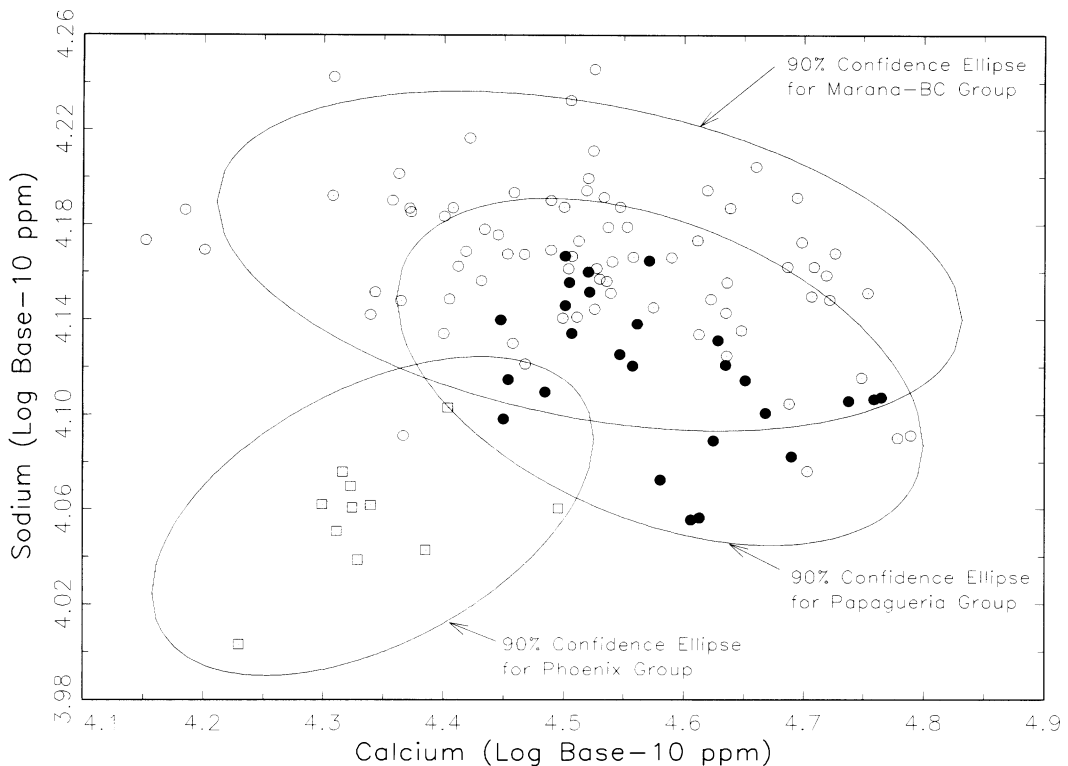


Figure 7. Bivariate calcium-sodium log concentration plot showing data for three Tanque Verde Red-on-brown groups obtained by bulk NAA. Ellipses represent 90 percent confidence level for membership in the groups.

NAA and ICP sodium measurements revealed by Table 1 and Figures 1–2. Again one must question what the acid-extraction ICP analysis is really measuring: yes, the Phoenix group is chemically differentiable based on the ICP data, but the chemical difference apparently arises not from natural chemical variation but from a difference in susceptibility to leaching in an acid bath (which enriches the acid extracts from the Phoenix group in sodium as well as other elements).

To be fair, we examined every single dimension of the ICP data set and most of the 45 possible bivariate projections of principal components or elemental concentrations in a search for dimensions that would separate the Papagueria and Marana-BC groups. The two groups overlap almost completely on all principal components. We finally found that a bivariate manganese-aluminum plot depicts reasonably good separation at the 90 percent confidence level (Figure 9). Still, however, the data form a single point cloud within which the

existence of subgroups would be highly debatable if they were not known beforehand (Figure 10). The fact that the separation appears only in this one projection of the data (out of 45 possible) further diminishes the chance that pattern-recognition techniques would be able to reveal its existence. And, since the Papagueria group is made up of specimens from five sites, and three widely separated sites are major contributors, it would not be possible to recognize the group given an initial working hypothesis of local production and distribution. Finally, manganese, like calcium and strontium, is highly susceptible to modification in the burial environment, so a differentiation based only on manganese (the two groups overlap completely on aluminum alone) would be highly suspect on a priori grounds, and one would hesitate to infer a source difference even if the compositional difference were recognized.

The bulk NAA data, in contrast to the acid-extraction ICP data, reveal an exceptionally clear

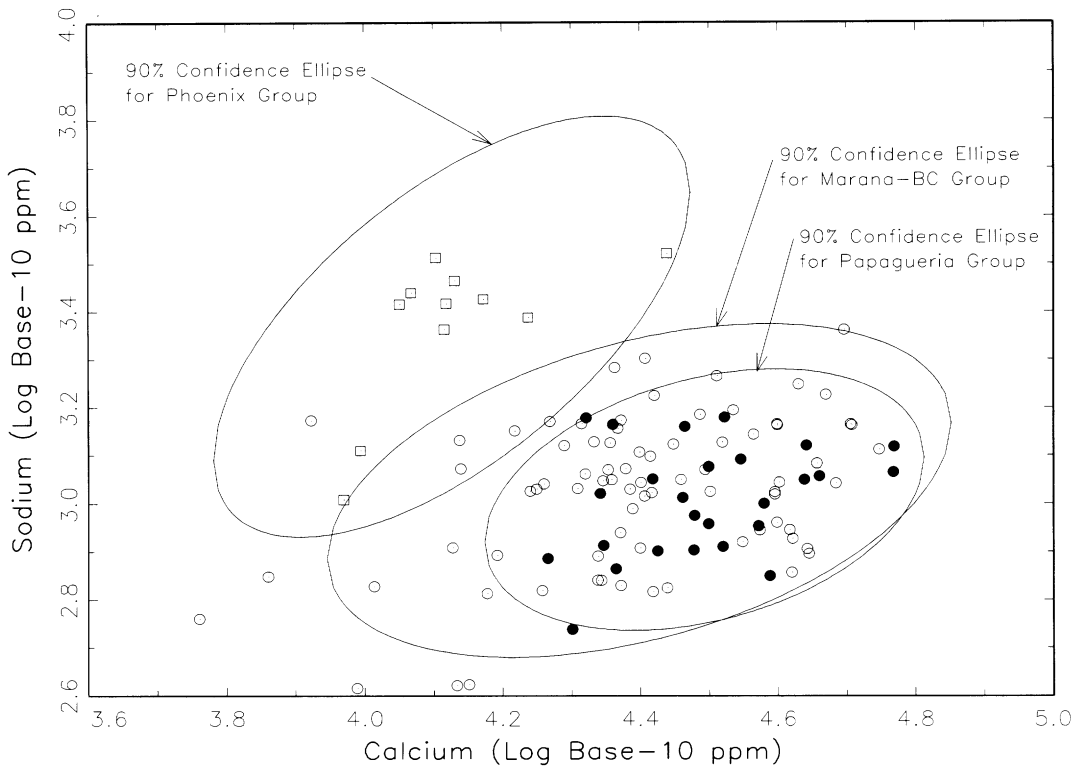


Figure 8. Bivariate calcium-sodium log concentration plot showing data for three Tanque Verde Red-on-brown groups obtained by acid-extraction ICP. Ellipses represent 90 percent confidence level for membership in the groups.

chemical distinction between the Marana-BC and Papageria groups on numerous dimensions (e.g., Figures 3 and 5). Since even this obvious interregional chemical difference probably would not be found in acid-extraction ICP data, it is unreasonable to expect the acid-extraction analysis to reveal subtle intraregional compositional distinctions such as those within the Tucson Basin. We must conclude that the huge additional chemical variation attributable to variation in extractability overwhelms all but the grossest natural interregional differences in ceramic composition.

To return finally to the issue of “archaeologically significant information,” we must comment on the likely failure to identify the Papageria group in an acid-extraction ICP study. This particular group constitutes the clearest evidence derived from the NAA study (Fish et al. 1992) that Tanque Verde Red-on-brown pots moved long distances across the Arizona desert. The group includes specimens from just north of the Tucson

Basin, the Phoenix area, and the Papageria area, the latter two areas being separated by a distance of more than 200 km (Fish et al. 1992). Failure to differentiate this group from the larger mass of Tucson Basin pottery or a spurious assignment of specimens in the group to several different subgroups would contribute toward a highly distorted picture of the circulation of Tanque Verde Red-on-brown pottery. One might argue that the analysis provided “archaeologically significant information,” but the information would be wrong.

Conclusion

In summary, comparison of acid-extraction ICP data with bulk NAA data indicates (1) variation in extractability is a huge additional source of noise in ceramic compositional studies; (2) the compositional signal measured by acid-extraction ICP correlates very poorly with both bulk NAA measurements and NAA measurements on clay-frac-

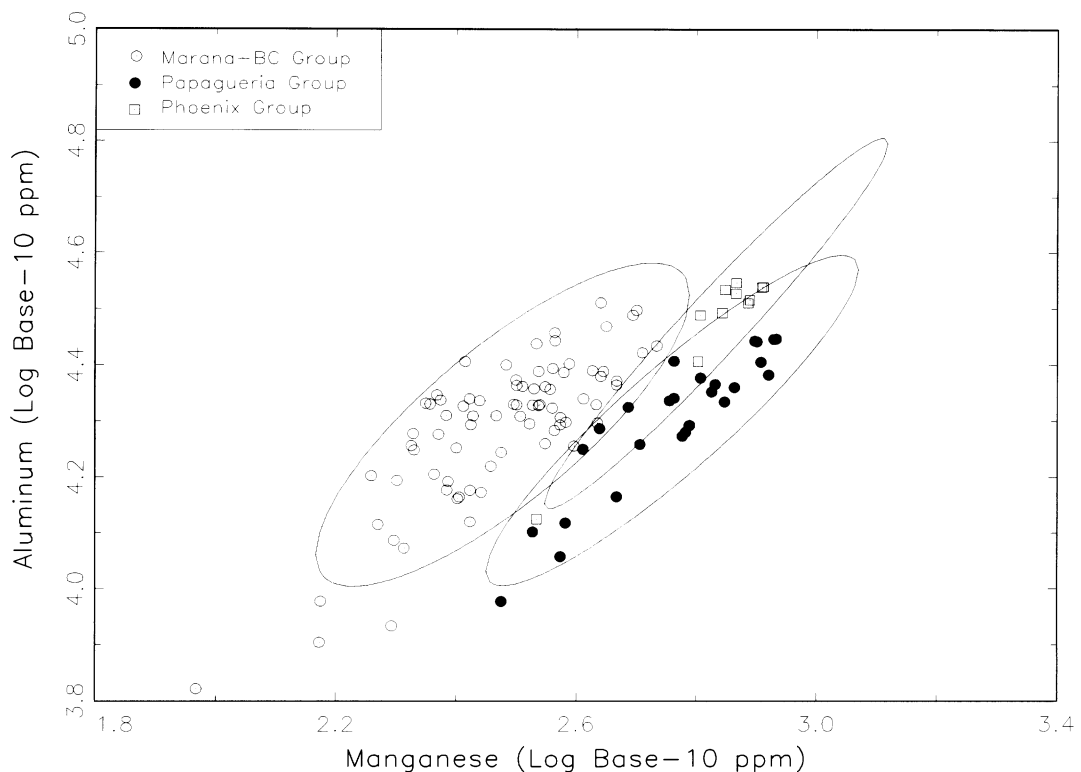


Figure 9. Bivariate manganese-aluminum log concentration plot showing data for three Tanque Verde Red-on-brown groups obtained by acid-extraction ICP, with groups differentiated by symbols. Ellipses represent 90 percent confidence level for membership in the groups.

tion separates; and (3) even the most conspicuous of interregional compositional distinctions may be undetectable in data sets derived from acid-extraction ICP analysis.

In light of these findings, we cannot imagine any viable role for the acid-extraction approach in ceramic provenance research. As illustrated by the Tanque Verde case, using acid-extraction ICP as the primary analytical technique would yield a highly distorted view of compositional similarities and differences. Using it as an initial screening tool or as a complement to other chemical or mineralogical techniques would only increase the noise that would have to be filtered out in order to identify source-related subgroups. For the time being, we regretfully conclude that chemistry-based ceramic provenance research still requires slow and/or costly techniques such as NAA or complete-dissolution ICP.

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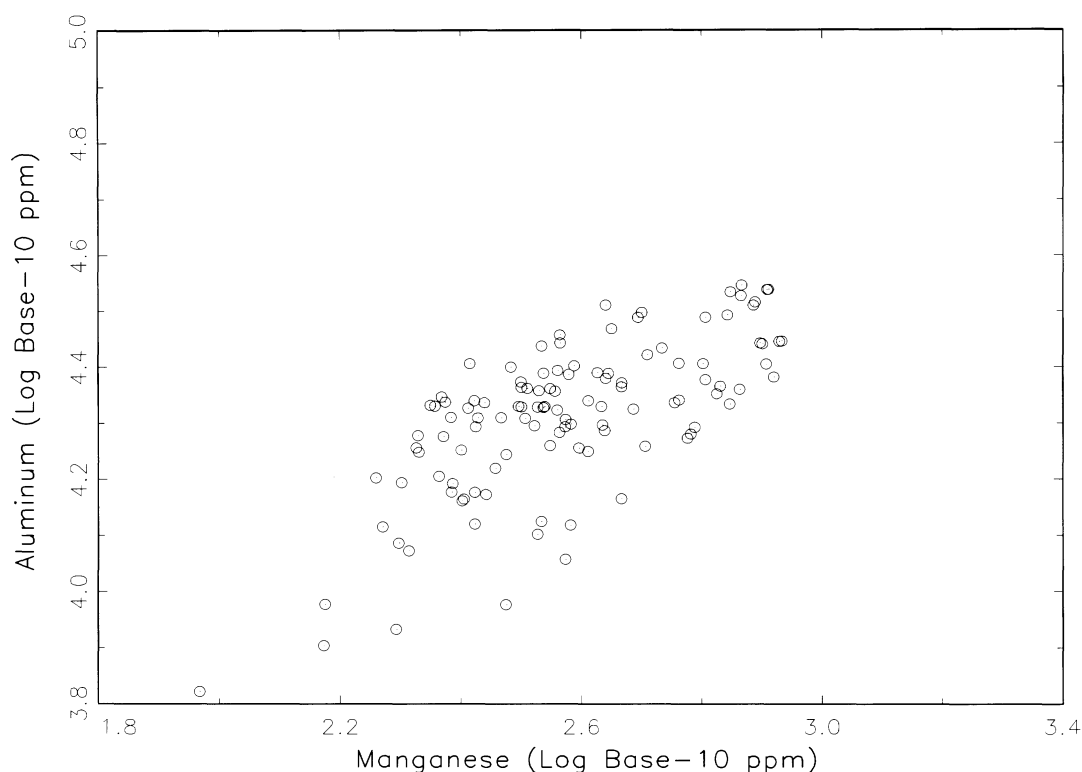


Figure 10. Bivariate manganese-aluminum log concentration plot showing data for three Tanque Verde Red-on-brown groups obtained by acid-extraction ICP. These are the same data plotted in Figure 9, but indications of known subgroup membership by symbols and group confidence ellipses are omitted.

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Notes

1. One reviewer of this paper suggested that variation associated with extractability should be subsumed under that associated with sampling the paste for analysis. We believe this is a moot point. To us, it seems more straightforward to distinguish bulk sampling, which is necessary for any chemical analysis, from weak-acid extraction, which is an additional sampling procedure necessary only in the Burton-Simon approach. Hart et al. (1987) provide a precedent for our point of view: in evaluating the precision of complete-dissolution ICP, they consider separately the variation related to individual specimen sampling, dissolution, and instrumental procedures.
2. It is worth pointing out in connection with this discussion of firing temperature that experiments reported recently by Cogswell et al. (1996) demonstrate that firing temperature has no effect on elemental concentrations determined by NAA (with the exception of bromine, which is rarely reported in NAA studies) through a range of temperatures up to about 1100°C.
3. The data used in this study can be obtained on the World Wide Web at <http://www.missouri.edu/~murrwww/archdata.html>.

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