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Characterization of Maya pottery by INAA and ICP-MS

N. C. Little,[1] L. J. Kosakowsky,[2] R. J. Speakman,[1] M. D. Glascock,[1]* J. C. Lohse[3]

[1] *Research Reactor Center, University of Missouri, Columbia, MO 65211, USA*
[2] *Department of Anthropology, University of Arizona, Tucson, AZ 85721, USA*
[3] *Texas Archaeological Research Laboratory, University of Texas, Austin, TX 78712, USA*

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A total of 81 pottery and 25 clay samples from the archaeological site and hinterland areas of Blue Creek in northwest Belize were analyzed by instrumental neutron activation analysis and inductively-coupled-plasma mass-spectrometry at the University of Missouri Research Reactor. Data generated for this study offers insight into local clay-resource variability and movement of pottery in the transition from Early (A.D. 250–600) to Late Classic (A.D. 600–850) occupation. Comparison of data generated by the two analytical techniques demonstrates the relative strengths and weaknesses of each method.

Introduction

Recent research in the Blue Creek area in northwestern Belize (Fig. 1) has been focused on the social organization of the ancient Maya as it is reflected in settlement patterns, exploitation of natural resources, environmental adaptation, and material culture. The goals of this research include: (1) elucidation of patterns of economic production by focusing on manufacturing technologies, and mechanisms of exchange that provided bases of support for complex socio-political institutions, (2) identification of social coalitions that were organized around the specific requirements for producing certain goods, and (3) reconsideration of social relations between different social entities with respect to traditional anthropological discourses involving centralized political authority versus "dispersed" economies.[1] By focusing on a regional scale, we hope to investigate the organization of and interaction between individual households as well as regional centers and their dependencies. Ceramic compositional data were useful in addressing these questions.[2–4] In order to investigate localized versus dispersed ceramic production, it is important to understand the distribution of finished vessels in relation to the raw materials (e.g., clays and non-plastic additives) used in their manufacture. This research provides an opportunity for examination of the role of ceramic production in the lowland Maya region.

Two initial steps were necessary for ceramic analysis of the Blue Creek area. First, a large sample of ceramics was classified according to their stylistic and decorative attributes using standard type-variety nomenclature. Second, 81 ceramic samples were selected from five sites, including the ceremonial center and the five-mound site of Quincunx along the Blue Creek escarpment. Samples from hinterland sites including the Rio Hondo house mounds, Chan Cahal, and Sayap Ha were also analyzed. In order to identify through chemical means, temporal and stylistic differences in ceramic production, both Early Classic Aguila Orange and Late Classic Achote Black sherds were selected for analysis. This focus on two ceramic types also allows us to narrow potential sources of variability in the INAA results that might arise from selecting a more diversified sample. Several sherds that were presumably non-local to the Blue Creek region were also submitted for analysis. Given that much of northern Belize is situated on a limestone plain, the possibility exists that chemical variability among ceramics will be minimal, thereby making chemical distinctions between wares and sites difficult if not impossible. In order to better understand chemical variability of raw materials from within the Blue Creek region, 25 clay samples were submitted for analysis.

Experimental

Instrumental neutron activation analysis (INAA) and inductively-coupled-plasma mass-spectrometry (ICP-MS) were conducted in the Archaeometry Laboratory at the University of Missouri Research Reactor (MURR). The ceramics were prepared for analysis using standard MURR procedures.[4] Pieces of each sherd were burred with a silicon carbide tool to remove painted or slipped surfaces and adhering soil. Burred samples were washed with de-ionized water and ground in agate mortars to a fine powder. The powdered samples were then oven-dried at 100 °C for 24 hours. For analysis by INAA, portions of approximately 150 mg were weighed into polyethylene vials for short irradiations. At the same time, 200 mg of each sample was weighed into a high-purity quartz vial for long irradiations. Along with the unknown samples, reference standards of SRM-1633a (Coal Fly Ash) and SRM-688 (Basalt Rock) were similarly prepared, as were quality control samples (e.g., standards treated as unknowns) of SRM-278 (Obsidian

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* E-mail: GlascockM@Missouri.edu

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Rock) and Ohio Red Clay. For analysis by ICP-MS, 100 mg of powdered sample was weighed into a gelatin capsule. Along with the unknown samples, quality control samples of SRM-679 (Brick Clay) were similarly prepared.

Instrumental neutron activation analysis

At MURR, INAA of pottery and clays consists of two irradiations and a total of three gamma counts.[5,6] As described by GLASCOCK,[5] short irradiations involve a pair of samples being transported through a pneumatic tube system into the reactor core for a 5-second irradiation at a neutron flux of $8\cdot10^{17}$ n·m^{-2}·s^{-1}. After a 25-minute decay, the samples are counted using a high-resolution germanium detector for 720 seconds. This count yields data for the short-lived radionuclides related to the elements: Al, Ba, Ca, Dy, K, Mn, Na, Ti, and V. For the long irradiation, bundles of 50 or 100 of the encapsulated quartz vials are irradiated for 24 hours at a neutron flux density of $5\cdot10^{17}$ n·m^{-2}·s^{-1}. Following irradiation, samples are allowed to decay for 7 days, and then are counted for 2,000 seconds (the "middle count") on a high-resolution germanium detector coupled to an automatic sample changer. The middle count yields determinations for seven medium half-life radionuclides, related to the elements: As, La, Lu, Nd, Sm, U, and Yb. After an additional 2-week decay, a second count of 10,000 seconds is carried out on each sample. This measurement permits quantification of 17 long-lived radionuclides, related to the elements: Ce, Co, Cr, Cs, Eu, Fe, Hf, Ni, Rb, Sb, Sc, Sr, Ta, Tb, Th, Zn, and Zr.

Inductively-coupled-plasma mass-spectrometry

Sample preparation for ICP-MS analysis was conducted using a modified version of the method described by KENNETT and colleagues[7] for digestion of archaeological pottery. ICP-MS samples were digested using a combination of acid, heat, and pressure in a Milestone SCI microwave oven. The microwave has a twelve-position segmented rotor that permits simultaneous processing of up to twelve sample digestion vessels at any given time. A computer integrated into the microwave system monitors and controls the internal temperature and pressure of the vessels during MW assisted digestion. For our experiments, ten of the vessels were used to digest archaeological samples, one vessel was reserved for a blank, and the remaining vessel was set aside for the quality control sample (SRM-679).

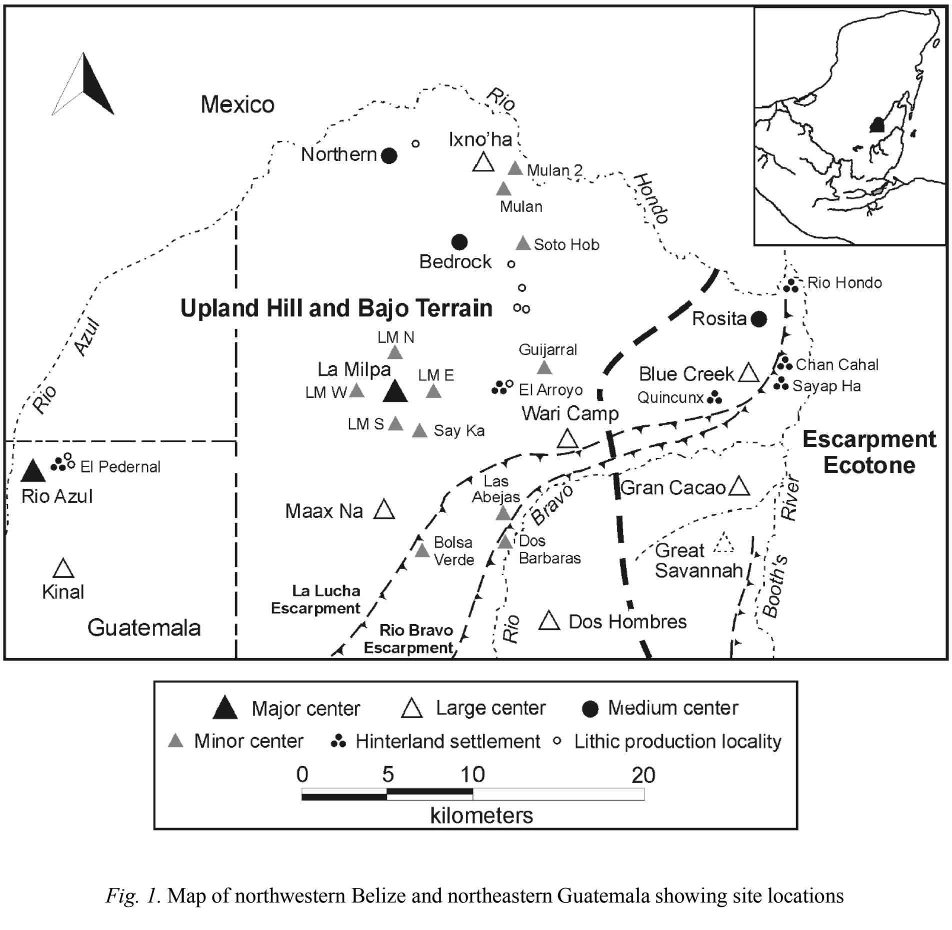

Fig. 1. Map of northwestern Belize and northeastern Guatemala showing site locations

Prior to sample digestion, 10 cm^3 of HNO_3 was sealed in each vessel and heated to 180 °C for a 15-minute cleaning cycle. After heating, the vessels were cooled on ice for 1 hour. After cooling, the acid was removed and a 2% HNO_3 solution was used to rinse the vessels.

For digestion of pottery (and other silicate-based materials), 6 cm^3 of HF, 3 cm^3 of HNO_3, and 1 cm^3 of HCl was pipetted into each of the clean digestion vessels. Gel capsules containing the pre-weighed pottery and quality control samples were added to each vessel. An empty gel capsule was added to the vessel containing the acid blank. Vessels were sealed, heated to 180 °C for 30 minutes, and then cooled on ice for 1 hour. Following the digestion, 25 cm^3 of a 4% boric acid solution was added to each vessel to break up the insoluble fluorides that are created by HF digestions.[7] Vessels containing the boric acid solution were again heated to 180 °C for 30 minutes. Upon completion of the second heating cycle, vessels were cooled for 1 hour and the digestate was rinsed from each vessel into a cleaned centrifuge tube using a 2% HNO_3 solution and topped to 50 g.

A 0.2 g aliquot of digestate from each sample was weighed into clean 15 cm^3 centrifuge tubes. The digestate was then spiked with 1 cm^3 of a 10-ppm concentration solution containing ^{6}Li, In, and Bi internal standards to correct for instrument drift. After the internal standards were added, each sample was topped-off to 10 g with 2% HNO_3. Standard solutions (Spex Certiprep Multi 1 and 2) and blanks were similarly prepared.

The digested samples, quality controls, blanks, and standards were injected into the ICP-MS torch, where argon gas plasma was used to ionize the injected sample. The resulting ions passed though a two-stage interface (sample and skimmer cones) designed to enable the transition of the ions from atmospheric pressure to the vacuum chamber of the ICP-MS system. Once inside the mass spectrometer (in this case a high-resolution magnetic sector ICP-MS), the ions were accelerated by high voltage and passed through a series of ion optics, an electrostatic analyzer (ESA), and finally a magnet. By varying the strength of the magnet, the ions were separated according to mass/charge ratio and passed through a slit into the detector, which records only a small atomic mass range at a given time. Data were generated for the following elements: Ag, Al, Ba, Ca, Ce, Co, Cr, Cs, Cu, Dy, Eu, Fe, K, La, Lu, Mg, Mn, Na, Nd, Ni, Pb, Pr, Rb, Sc, Sm, Sr, Tb, Th, Tm, U, V, Y, Yb, and Zn.

Quantitative analysis

Quantitative analysis was carried out on base-10 logarithms of concentrations for the data, thereby compensating for differences in magnitude between major and trace elements. Transformation to base-10 logarithms also scales the data into a more normal distribution for trace elements.

In order to elucidate source-related subgroups, a pattern-recognition technique called principle components analysis (PCA) was applied to the chemical data. PCA can be applied as a simultaneous R- and Q-mode technique.[8] The RQ-mode technique displays both variables (elements) and objects (individual analyzed samples) on the same plot, making it possible to observe the contributions of specific elements to group separation and to the distinctive shapes of the various groups. The resulting “biplot” can then be verified by inspection of bivariate elemental concentration plots. In order to determine whether a group can be easily discriminated from other groups, a metric known as Mahalanobis distance is utilized.[6]

INAA results

Inspection of the INAA data reveals four compositional ceramic groups in the 81 specimen data set (Fig. 2). The group designated as Blue Creek (BC) 1 contains 30 specimens, 26 of which are classified as Aguila Orange. The remaining four are other Early Classic ceramic types. BC-2, containing 23 samples, is comprized almost entirely of ceramics from the Achote Black Group and only two samples that are from Early Classic blacks. BC-3, the smallest group, contains 3 samples of Aguila Orange pottery that originate from Quincunx and Chan Cahal. BC-4 is comprized of 9 Aguila Orange specimens, of which more than 50% originate from Rio Hondo, with the remaining half representing other hinterland sites. Fourteen samples had low probabilities of membership in any of the groups, and are classified as unassigned (Fig. 2).

One outlier, NCL026, was compared against the MURR ceramic database, which contains data for approximately 34,000 pottery and clay samples from all over the world. Based on Euclidean distance, the closest match was found with samples from the Dos Pilas site in Guatemala (Fig. 3).[11] The Dos Pilas samples are characteristic of the Chablekal Ceramic Group from the Greater Palenque Region of the western Maya Lowlands, the production area for said ceramics is in or around Palenque.[11] If NCL026 is in fact from the same Chablekal Ceramic Group, it may be evidence of the farthest eastern distribution of the ware, indicating long-distance trade into the region.

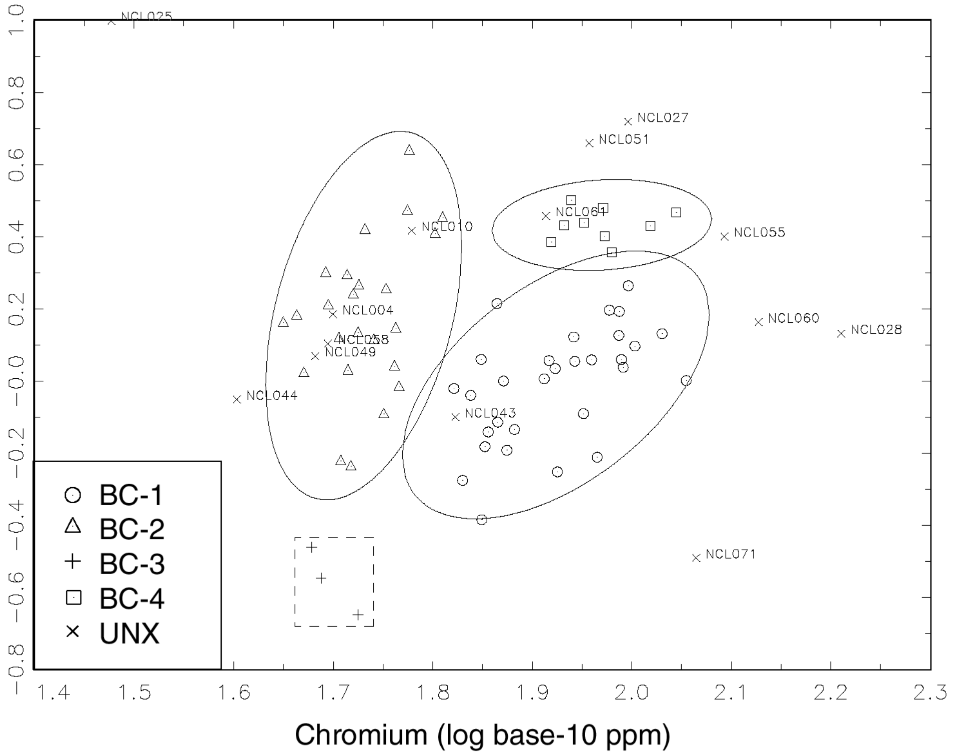

Fig. 2. Bivariate plot of chromium and cesium log-concentrations showing hypothetical subgroup structure within the data set. Unassigned samples are labeled with analytic ID and BC-3 is surrounded with dotted lines. Ellipses represent 90% confidence interval for group membership

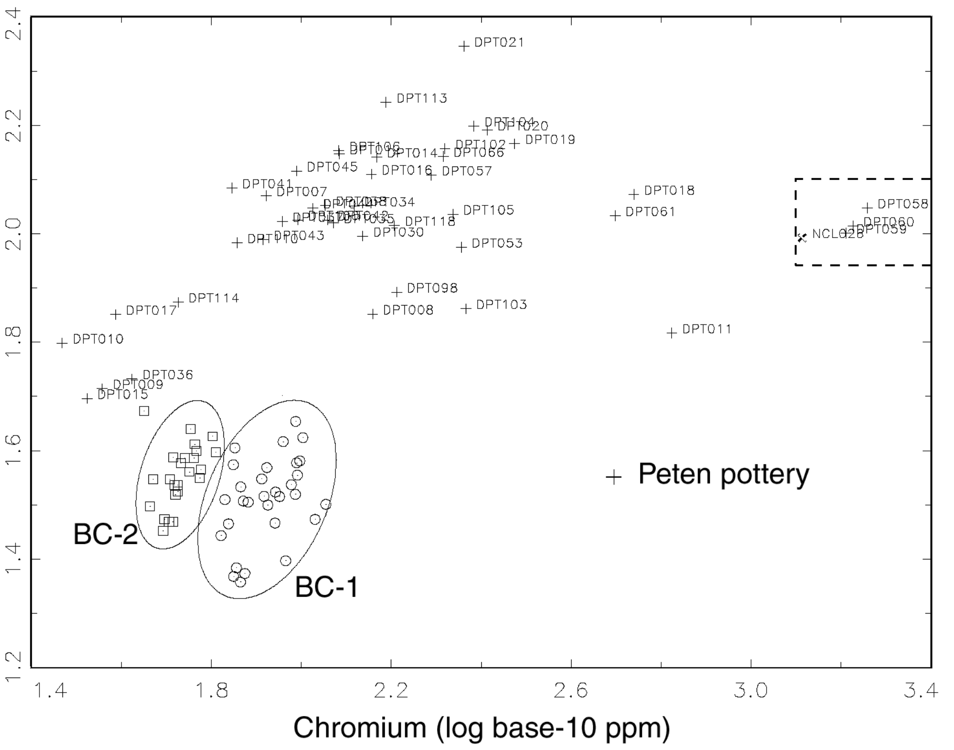

Fig. 3. Bivariate plot of chromium and vanadium log-concentrations displaying the two main Blue Creek groups against Dos Pilas pottery. This indicates possible grouping of NCL026 with Dos Pilas ceramics. Ellipses represent 90% confidence interval for group membership

Additional INAA of pottery from the region should aid in refining groups BC-3 and BC-4, thus providing additional insight into hinterland settlements and their roles in craft production in the region. The heterogeneity found within BC-1 suggests additional group designations will occur with more sampling of pottery from the region.

In order to understand the chemical variability of surrounding locations, the Blue Creek groups were then compared with data generated by MANNING[9] and LYLE.[10] Their samples were obtained from the Rio Bravo area (approximately 20 km to the south and southwest of Blue Creek) in conjunction with the Programme for Belize Archaeological Project.

BC-1 and BC-2 were projected against the Rio Bravo primary groups, here designated as LM1 (various ceramic styles) and LM2 (primarily black wares). Interestingly, BC-2 and LM2 plotted together consistently in all projections (Fig. 4). Such compositional similarity suggests that all settlements represented by these clusters utilized a common clay source for the production of black wares, or that the pottery from both areas originated from geographically separated but chemically similar clays. Although groups BC-1 and LM1 do not correlate as well as the black wares, there is considerable overlap in most projections of the data. This overlap could indicate a chemical continuum of clay composition between the two sites, suggesting local ceramic production in both areas.

Whereas the INAA data demonstrate definite grouping of ceramic samples, statistically the analyzed clays are of poor match, for any of the pottery groups. This could result from a high-calcium clay source and/or the addition of an enriched-calcium temper not yet identified. Also, the apparent homogeneity of the local clay deposits may have influenced the INAA results.

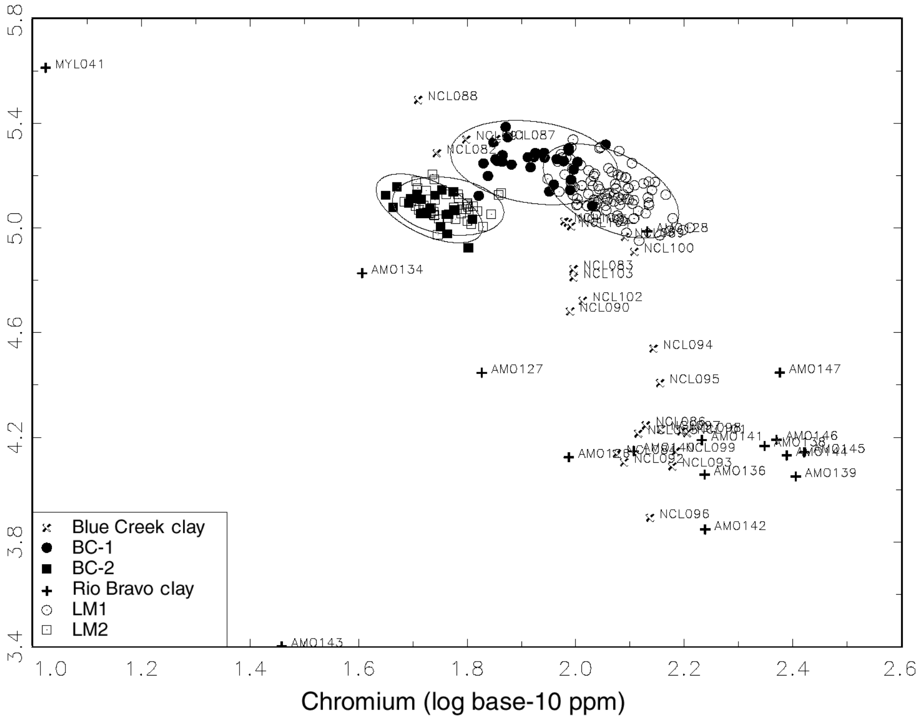

Fig. 4. Bivariate plot of chromium and calcium log-concentrations displaying the two main Blue Creek groups against MANNING's two main groups. Ceramics and clays from Rio Bravo and Blue Creek are projected against BC-1 and BC-2. Ellipses represent 90% confidence interval for group membership

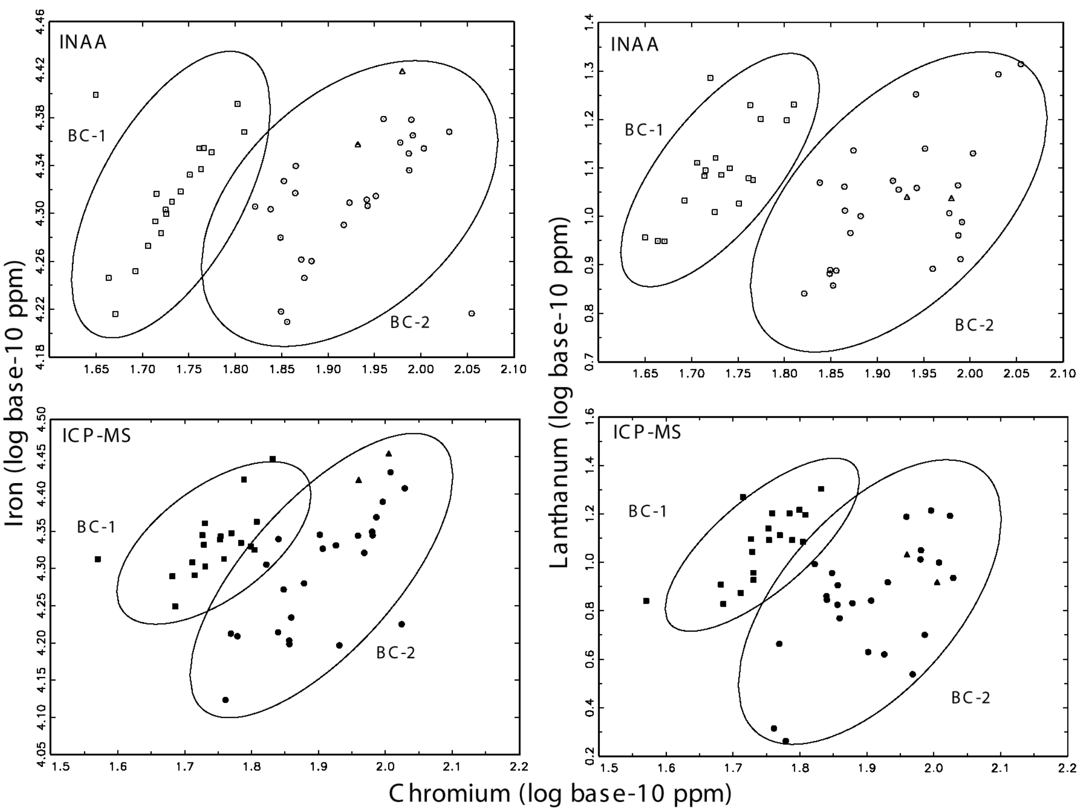

Fig. 5. Bivariate plot comparison of INAA and ICP-MS data using chromium log-concentrations projected against iron and lanthanum log-concentrations. Ellipses represent 90% confidence interval for group membership

Discussion

Time constraints did not permit for the microwave digestion and ICP-MS analyses of all 106 samples analyzed by INAA, instead a subset of 60 samples was analyzed by ICP-MS. The ICP-MS samples formed groupings similar to those found using bivariate plots with INAA data (Fig. 5). Although a different analytical technique, data generated from ICP-MS yielded results similar to INAA data. The means and standard deviations are shown to express similar ranges of variation for those elements measured by both techniques (Table 1). The complementary nature of the two techniques can also be seen in Fig. 5, where bivariate plots compare INAA and ICP-MS data generated for BC1 and BC2. To reiterate, ICP-MS was found to be complementary to the widely accepted technique of INAA. In addition, elements not routinely measured by INAA were measured by ICP-MS. Although these elements did not contribute to the chemical differentiation of pottery in this example, these elements may be of interest for discriminating ceramic groups in other projects.

There are several advantages to analyzing pottery by ICP-MS. First, data can be generated for most elements in the periodic table. Second, the data return for ICP-MS is immediate, whereas with INAA, one must wait for the short-lived radionuclides to decay, allowing for long-lived radionuclides to be measured. This usually takes a minimum of three weeks after the 24-hour irradiation. Finally, access to a nuclear reactor is not necessary to perform ICP-MS experiments. A lab with the proper equipment is all that is required, which can be purchased for any lab in the country.

Although, there are advantages for ICP-MS, there are also disadvantages of ICP-MS for the bulk analysis of pottery. First, the required high-purity acids are expensive, and they expose the lab technician to hazardous chemicals (e.g., hydrofluoric acid). Another drawback is the long preparation time as compared to INAA. Because the sample is microwaved twice, the time required for cooling the vials and cleaning the vessels between each digestion allows for the preparation of only of twelve samples per day. There is also substantial time required for the dilution of the samples, preparation of standards, and the requirement for a trained operator to monitor the instrument during analysis. Although the cost for ICP-MS is comparable to INAA, the increased labor and time required for sample preparation and analysis, as well as the use of volatile chemicals are a hindrance to widespread application.

Table 1. Comparison of data (in mg.kg–1, ppm)generated by INAA and ICP-MS for Blue Creek Groups 1 and 2

Element	Blue Creek 1		Blue Creek 2	
	INAA (*n*=30)	ICP-MS (*n*=25)	INAA (*n*=24)	ICP=MS (*n*=19)
Ag	n.d.	1.46 ± 0.40	n.d.	2.05 ± 0.99
Al, %	5.86 ± 0.69	5.10 ± 0.97	6.13 ± 0.61	5.50 ± 1.03
As	3.58 ± 0.84	n.d.	2.08 ± 0.53	n.d.
Ba	289 ± 162	267 ± 201	302 ± 202	273 ± 188
Ca, %	18.00 ± 2.70	13.70 ± 2.70	12.00 ± 1.40	10.29 ± 1.99
Ce	32.6 ± 18.7	17.5 ± 8.1	31.4 ± 7.3	28.3 ± 8.8
Co	4.48 ± 2.33	3.67 ± 1.08	2.83 ± 0.82	2.95 ± 0.90
Cr	84.8 ± 13.0	82.7 ± 14.9	54.0 ± 5.1	55.9 ± 7.1
Cs	1.04 ± 0.35	1.09 ± 0.41	1.70 ± 0.87	1.14 ± 0.61
Cu	n.d.	11.13 ± 2.21	n.d.	9.50 ± 2.71
Dy	1.97 ± 0.64	1.40 ± 0.62	1.92 ± 0.41	1.70 ± 0.63
Eu	0.41 ± 0.14	0.32 ± 0.14	0.42 ± 0.10	0.41 ± 0.13
Fe, %	2.10 ± 0.25	2.03 ± 0.40	2.07 ± 0.22	2.17 ± 0.23
Hf	4.93 ± 0.55	n.d.	6.58 ± 1.18	n.d.
K	987 ± 809	1502 ± 1125	1602 ± 1050	1714 ± 715
La	11.3 ± 3.5	8.0 ± 3.8	12.6 ± 2.7	12.5 ± 4.0
Lu	0.21 ± 0.05	0.14 ± 0.06	0.20 ± 0.03	0.15 ± 0.06
Mg, %	n.d.	3.40 ± 1.05	n.d.	4.63 ± 1.04
Mn	186 ± 118	140 ± 53	125 ± 52	126 ± 48
Na	1866 ± 1179	1873 ± 1161	1713 ± 1231	1784 ± 1216
Nd	16.3 ± 8.4	7.2 ± 2.8	15.9 ± 7.5	10.6 ± 3.6
Ni	n.d.	14.60 ± 5.49	n.d.	24.6 ± 69.6
Pb	n.d.	16.64 ± 15.77	n.d.	15.1 ± 4.6
Pr	n.d.	1.60 ± 0.65	n.d.	2.38 ± 0.80
Rb	12.1 ± 5.8	9.0 ± 4.2	19.6 ± 6.3	14.2 ± 5.3
Sb	0.81 ± 0.10	n.d.	0.81 ± 0.10	n.d.
Sc	7.51 ± 0.91	6.88 ± 1.42	7.40 ± 0.79	7.10 ± 1.13
Sm	2.55 ± 0.84	1.60 ± 0.67	2.54 ± 0.58	2.09 ± 0.73
Sr	117 ± 64	98 ± 60	85 ± 63	81 ± 61
Ta	0.68 ± 0.08	n.d.	0.79 ± 0.09	n.d.
Tb	0.26 ± 0.10	0.33 ± 0.26	0.27 ± 0.07	0.37 ± 0.11
Th	8.99 ± 1.07	6.50 ± 1.89	9.48 ± 1.29	7.85 ± 2.57
Tm	n.d.	0.13 ± 0.05	n.d.	0.14 ± 0.05
Ti	2422 ± 293	n.d.	2920 ± 367	n.d.
U	1.05 ± 0.31	0.77 ± 0.11	1.26 ± 0.39	0.95 ± 0.14
V	32.9 ± 5.7	31.5 ± 5.2	36.2 ± 4.8	35.7 ± 3.8
Y	n.d.	8.94 ± 2.96	n.d.	9.12 ± 2.44
Yb	1.51 ± 0.41	0.97 ± 0.38	1.44 ± 0.21	1.02 ± 0.37
Zn	46.1 ± 6.8	50.9 ± 17.3	46.7 ± 6.4	51.8 ± 9.6
Zr	109 ± 17	n.d.	15.3 ± 30	n.d.

n.d.: Not detected.

Conclusions and future research

When utilized in conjunction with type-variety and stylistic analyses, the use of INAA and ICP-MS for chemical characterization of Maya pottery stands to contribute significantly to our understanding of the social implications of ceramic design, manufacture, exchange, and consumption. Additional examination in regard to the social complexity of the ancient Maya also allows for the recognition of social units of production, addressing the question of centralized control over pottery production versus dispersed management of manufacture. The analysis of clays from several discrete environmental zones allowed us to not only characterize the chemical variability of raw materials, but also to distinguish between clay resources that may have been utilized by different social groups reliant on localized natural resources. Overall, this pilot project has been useful for identifying production patterns of both Early Classic and Late Classic ceramics. Because the data reflected the likely local production and consumption of Early Classic Aguila Orange pottery, it is expected that additional analyses of Early Classic types will better define the groupings as well as identify probable production locations. Additional Late Classic ceramic types will also be analyzed to determine whether the pattern of production for the Achote Black ceramics is mirrored in other ceramic groups across the broader region between Blue Creek and La Milpa. Supplementary tempering analysis (including thin-section analysis) will also be utilized to correct for any chemical variability that can be attributed to different tempering materials. There will also be an expansion of the sampling area, to determine whether similar production patterns are observed in areas west of Blue Creek during the Early and Late Classic periods.

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