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A NEUTRON ACTIVATION STUDY OF PLIO-PLEISTOCENE MARINE CLAYS FROM WEST CENTRAL ITALY: COMPOSITIONAL VARIABILITY AND IMPLICATIONS FOR THE PROVENIENCING OF ITALIAN FINEWARE POTTERY

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ABSTRACT

A program of NAA has been employed to examine chemical variability among a group of clay specimens from several outcrops of the Plio-Pleistocene marine transgression in various locales in west-central Italy. Results show that there is considerable compositional variability from source to source, while differences in maximum firing temperature between 750 and 900 degrees have no significant effect on composition. This suggests that NAA is a sufficiently powerful tool to permit the identification of production groups of archaeological pottery made with these materials and the matching of these groups with their source clays.

RIASSUNTO

Un programma di analisi mediante attivazione neutronica (NAA) è stato eseguito con lo scopo di esaminare la variabilità chimica all'interno di un gruppo di campioni di argille provenienti da diversi affioramenti della trasgressione marina Plio-Pleistocenica, in varie località dell'Italia Centro-Occidentale.

I risultati mostrano che c'è una considerevole variabilità composizionale nei diversi punti di prelievo, mentre differenze di temperature massime di cottura tra 750°C e 900°C non producono un effetto significativo sulla composizione. Questo suggerisce che la caratterizzazione chimica mediante NAA consentirà l'identificazione di gruppi di produzione di ceramica archeologica prodotta a partire da questi materiali e permetterà confronti tra questi gruppi e le argille di partenza.

1. INTRODUCTION

A considerable amount of archaeological, documentary, and ethnographic evidence indicates that workshops engaged in the production of fineware pottery in many parts of west-central Italy from Etruscan through modern times have made extensive use of the thick bed of calcareous clay laid down during the Plio-Pleistocene marine transgression. This clay has been particularly important in the manufacture of high quality tablewares, including red figure ware, black gloss ware and *terra sigillata* during the Classical period, and maiolica during the Medieval and post-Medieval periods. The authors here report on a neutron activation analysis (NAA) study of a selection of Plio-Pleistocene marine clays collected from sources in the regions of Lazio, Umbria and Tuscany. The aim of this work was to evaluate the potential that NAA holds for the identification of different production groups made with these clays and the matching of these groups with the specific source clays from which they were manufactured. The topics examined included 1) the degree of natural chemical variability from clay source to clay source and 2) the nature and extent of chemical variability introduced in pottery made with these clays by firing.

2. INVESTIGATION OF SOURCE TO SOURCE COMPOSITIONAL VARIABILITY

The project involved the analysis of 33 clay specimens collected from 14 sources. The sampling strategy was designed to achieve broad coverage of the several sources of Plio-Pleistocene marine clay present in west-central Italy so that it would be possible to obtain a first evaluation of gross compositional variability across the region. The sources from which clay was obtained are shown on the map in Figure 1. These include the following: Montelupo Fiorentino (specimen MLF01), Volterra Nord (specimens VTN01-02), Volterra Sud (specimens VTS01-05), Montaperti (specimen MAP01), Castelnuovo Berardenga Scalo (specimens CBS01-04), Orvieto/Sferracavallo (specimen OVS01), Orvieto/Le Crete (specimens OVC01-05), Orte Scalo (specimens OTS01-04), Civita Castellana (specimen CVC01), Narce (specimen NRC01), Mazzano Romano (specimens MZR01-02), Monterotondo Scalo (specimens MRS01-03) and Boccea/Fosso Galeria (specimen BFG01). Also included in the study were two specimens of calcareous lacustrine clay collected at Arezzo/Quarata (specimens ARQ01-02). The specimens, in the main cobble-sized lumps of consolidated clay, were obtained adventitiously through a variety of methods, with some collected from active or abandoned clay pits (CBS01-014, OTS01-03, MZR01-02, MRS01-03), some from road cuts, plowed fields, ditches and other exposures (VTN01-02, VTS01-05, OVC01-05, CVC01, NRC01, BCF01, ARQ01-02), and some from potters (MLF01, MAP01, OVS01, OTS04).

In order to examine compositional variability from source to source, circa 5 g of clay was removed from the interior of each specimen, crushed in an agate mortar, hydrated with de-ionized distilled water, formed into a pellet, and fired at 900 degrees C. for two hours in an electric kiln. A portion of the fired pellet was then crushed in an agate mortar, dried in an electric oven at 110 degrees C. for 24 hours, and 100 +/- 5 mg of this material weighed out into a precleaned microcentrifuge tube and sealed for analysis. The analytical work was performed at the Smithsonian Institution's activation analysis facility at the National Institute for Standards and Technology, Gaithersburg, Maryland, United States of America. The protocols employed for irradiation and counting have been detailed elsewhere by Blackman (Blackman et al. 1989). Concentration data were obtained for 31 elements, including Na K, Ca, Sc, Cr, Fe,

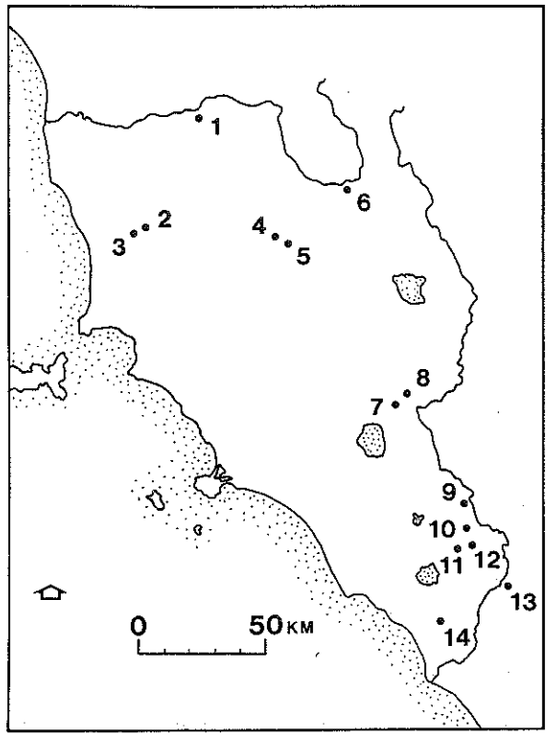

Figure 1. Map of west-central Italy showing locations of clay sources. 1. Montelupo Fiorentino 2. Volterra Nord 3. Volterra Sud 4. Montaperti 5. Castelnuovo Berardenga Scalo 6. Arezzao/ Quarata 7. Orvieto/Sferracavallo 8. Orvieto/Le Crete 9. Orte Scalo 10. Civita Castellana 11. Narce 12. Mazzano Romano 13. Monterotondo Scalo 14. Boccea Fosso Galeria

Co, Zn, As, Br, Rb, Sr, Zr, Mo, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Gd, Tb, Yb, Lu, Hf, Ta, Th, U, and W.

The resulting data were subjected to cluster analysis using a variety of distance measures and agglomeration procedures provided by the programs CONDIST and AGCLUS (Sayre 1980), respectively, with the clustering solutions evaluated to determine the extent to which they corresponded with the division of the specimens by source group. Excluded from use with this procedure were six elements considered to be problematic (As, Br, Zr, Mo, Ba, Gd, W).

A dendrogram generated with the clustering solution that most successfully replicates the division of the specimens by source group is shown in Figure 2. This was produced using raw concentration values, the squared Euclidean distance measure, and the so-called "Nature's Groups" agglomeration algorithm, which is a variation on the weighted, mean within-group linkage procedure. (Olivier 1973). By truncating this dendrogram at the 0.31-0.40 level of distance seven clusters are obtained, here identified by the letters A through G. The trace element data for one representative specimen from each of these clusters are presented in Table 1. Cluster A contains all six specimens from Mazzano Romano, Narce and Monterotondo Scalo, three neighboring sources in north-central Lazio. These materials are distinguished by

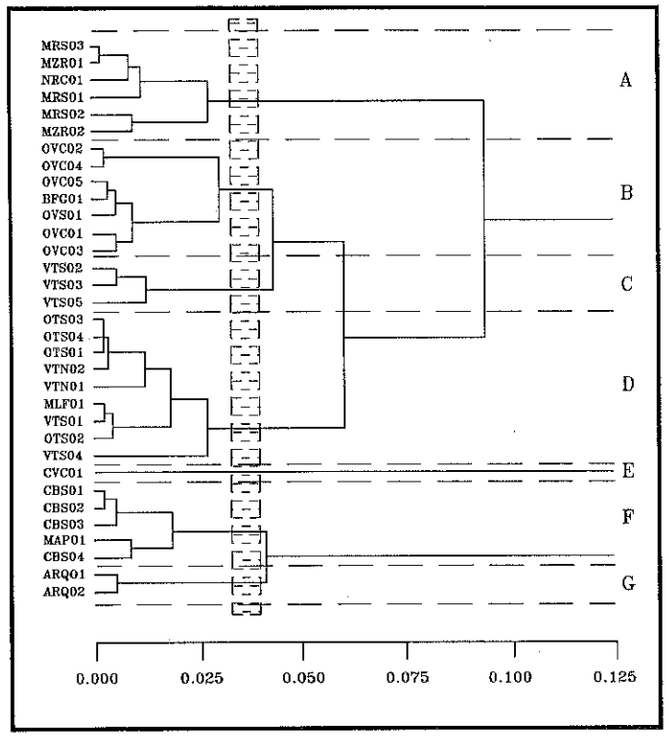

Figure 2. Dendrogram showing results of cluster analysis of 33 specimens of clay fired to 900 degrees C.

relatively high concentrations of Ca and Sr and depleted values for most of the other elements measured. Cluster B contains all six specimens from the Orvieto area in southwestern Umbria and the single specimen from the Boccea/Fosso Galeria source in west-central Lazio. These have high values for Ca and Sr, and moderate values for most of the other elements. Cluster C consists of three of the seven specimens from the area of Volterra in northwestern Tuscany. These specimens contain moderate to high values for most of the elements measured. Of the seven groups, Cluster D is the one that least well reflects a group of specimens from a well-defined source area. It includes all four specimens from Orte Scalo in north-central Lazio - three of which are grouped tightly at one side of the cluster - the remaining four specimens from the Volterra area, and the single specimen from Montelupo Fiorentino in north-central Tuscany. As with Cluster C, these materials are characterized by moderate to high values for most of the elements measured. Cluster E consists of the single specimen from Civita Castellana, in north-central Lazio. This has exceptionally high values not only for Ca, but for most of the other elements determined, with the exception of Cr, due to the presence of a substantial amount of alkaline volcanic sand. Cluster F contains all five specimens from the Le Crete area to the east of Siena in central Tuscany. These clays have low values for Ca and Sr and relatively high values for the other elements. Finally, Cluster G contains the two specimens of lacustrine clay from the Arezzo/Quarata source in northeastern Tuscany. These are generally similar to the materials in Cluster G, with low Ca and Sr concentrations and high concentrations of most of

the other elements. Several of the clustering solutions obtained using different groups of elements, normalized log score conversions of the data, and/or different combinations of distance measure and agglomeration procedure showed generally similar though marginally less satisfactory groupings of the materials.

Table 1. Elemental concentrations for seven representative clay specimens fired to 900 degrees C.

specimen		MRS01	OVC05	VTS03	OTS04	CVC01	CBS03	ARQ02
cluster		A	B	C	D	E	F	G
Na	(pct)	0.871	0.469	0.946	0.700	1.28	1.60	0.483
K	(pct)	1.59	2.02	2.33	2.17	2.65	2.47	2.29
Ca	(pct)	19.8	17.4	12.1	13.0	22.0	5.11	6.79
Sc	ppm)	9.9	13.6	17.4	14.4	8.9	17.2	19.1
Cr	(ppm)	96.2	132	214	141	65.0	199	193
Fe	(pct)	2.88	3.57	4.70	4.23	2.48	4.68	4.74
Co	(ppm)	8.5	16.1	21.7	15.6	16.2	21.5	19.4
Zn	(ppm)	73.8	108	111	113	89.1	125	130
As	(ppm)	8.75	9.55	11.3	8.20	29.1	18.8	4.23
Rb	(ppm)	112	144	147	148	508	173	158
Sr	(ppm)	710	693	653	615	1420	282	333
Sb	(ppm)	0.468	1.110	0.865	0.644	2.610	1.160	0.783
Cs	(ppm)	5.01	8.97	8.41	7.18	39.1	10.5	8.55
Ba	(ppm)	294	362	<101	265	1220	249	352
La	(ppm)	28.8	36.5	40.8	35.8	127	41.1	45.5
Ce	(ppm)	51.4	61.2	72.8	64.1	206	74.5	81.3
Nd	(ppm)	26.0	26.3	28.4	31.0	76.4	29.2	37.0
Sm	(ppm)	4.51	5.32	5.70	5.74	12.4	6.03	7.28
Eu	(ppm)	0.86	1.04	1.15	1.14	2.32	1.13	1.41
Tb	(ppm)	0.470	0.736	0.718	0.700	1.230	0.728	0.979
Yb	(ppm)	1.97	2.26	2.37	2.53	2.82	2.40	3.12
Lu	(ppm)	0.222	0.362	0.365	0.351	0.273	0.372	0.430
Hf	(ppm)	3.85	3.08	3.79	4.05	7.21	4.34	3.84
Ta	(ppm)	0.83	0.89	1.09	1.03	1.26	1.22	1.36
Th	(ppm)	8.8	10.2	11.7	11.3	54.1	13.2	13.8
U	(ppm)	1.36	2.18	3.53	1.43	3.98	1.33	1.97

The analysis of this small group of clay specimens suggests that there are general compositional profiles associated with specific sub-areas within the region and that some locales or individual clay sources may have diagnostic chemical fingerprints. At the same time, the nature of chemical variability across the region is not as clear cut as one would wish for in the best of circumstances. The composition of Cluster D, for example, demonstrates that clays from sources located as much as 200 km apart (i.e. Orte Scalo and Volterra) may have broadly similar chemical profiles. These presumably contain sediments of similar granulometry derived from compositionally similar parent materials. At the same time, some locales and even individual outcrops may yield specimens that display a significant degree of compositional dissimilarity. This was not unexpected, for example, in the case of the group of specimens from the Volterra area, since these were obtained from outcrops exposed over a roughly 350 meter segment of the local stratigraphic column. In other cases, however, such as the source at Orte

Scalo, relatively small outcrops yielded clay samples showing considerable compositional variability. The nature and extent of both of these phenomena can only be evaluated through a much more extensive and intensive program of analysis. Lastly, the specimen from Civita Castellana illustrates how the admixture to these clays of materials derived from formations belonging to the Central Italian Volcanic Province, either through natural processes or cultural intervention, will profoundly effect chemical composition.

3. INVESTIGATION OF EFFECTS OF FIRING ON COMPOSITION

A further set of analyses was carried out with these materials in order to evaluate the effects of firing on composition. Of specific interest in this connection was the question of the effects on composition resulting from the firing of these clays to different temperatures, since sizable thermal gradients can develop within updraft wood-burning kilns in the course of a single firing and different workshops presumably employed firing regimens with a wide variety of maximum and soaking temperatures. It was suspected that this might be a particularly important issue with regard to calcareous clays such as those of the Plio-Pleistocene marine transgression, since the range of maximum firing temperatures attained by traditional potters working in the region probably bracketed the calcination point. In order to examine this question analysis was carried out for raw specimens of all 33 clays and for material fired to 750 degrees from 20 of them, with the results of these analyses compared with the data obtained from the analysis of the specimens fired to 900 degrees.

Table 2 illustrates the general patterns of compositional change revealed by this program of analysis, presenting the data obtained for the three analyses of one representative specimen of a low (4.71 percent) Ca clay and one representative specimen of a high (17.2 percent) Ca clay. The differences in the values between the raw specimens and those fired to 750 degrees reflect the combined effects of counting error (indicated in Table 2 by figures for the absolute size of one standard deviation), inhomogeneity within the material, and compositional changes induced by firing. For those elements for which there are reasonably good counting statistics, the concentrations in the low Ca clay tend to be between 5 and 16 percent greater in the specimen fired to 750 degrees than in the raw specimen, with many values bunched in the 8 to 12 percent range. In the high Ca clay the scale of change is roughly twice as great, with most of these same elements 18 to 28 percent higher in the specimen fired to 750 degrees. In either case, a comparison of the values obtained for the specimen fired to 750 degrees and that fired to 900 degrees reveals no consistent trend in either elemental enrichment or depletion with increase in temperature. The differences in individual elemental values can in most instances be accounted for by the counting error alone. An exception is
Br, which apparently volatalizes with firing, dropping below the detection limit in both cases.

The fact that the high Ca clay, which has roughly four times the Ca content of the low Ca clay, experiences an enrichment in elemental values roughly two times the size of that attested for this other specimen, indicates that only about one half of the enrichment produced by firing can be accounted for by the loss of carbon dioxide resulting from the breakdown of calcite. The remainder presumably stems primarily from weight loss deriving from the combustion of organic matter and the driving off of bound and interlayer water from the clay mineral component. The absence of any significant differences between the clay specimens fired to 750 and 900 degrees indicates that whatever changes in chemical composition occur at temperatures up to 900 degrees have largely taken place by 750 degrees. Firing to maxium temperatures

specimen		CBS04 (low calcium)						MZR02 (high calcium)					
		raw	s.d.	750	s.d.	900	s.d.	raw	s.d.	750	s.d.	900	s.d.
Na	(pct)	1.39	0.01	1.55	0.01	1.52	0.01	0.555	0.016	0.690	0.023	0.701	0.019
K	(pct)	1.73	0.08	1.94	0.07	1.91	0.07	1.56	0.05	2.00	0.06	2.10	0.06
Ca	(pct)	4.71	0.45	5.57	0.61	5.11	0.51	17.2	1.3	17.2	1.5	24.4	1.9
Sc	(ppm)	11.3	0.1	12.6	0.2	12.6	0.2	10.1	0.1	12.7	0.2	12.8	0.2
Cr	(ppm)	135	1	153	1	155	1	95.3	0.7	118	1	122	1
Fe	(pct)	4.16	0.01	4.55	0.02	4.51	0.01	2.65	0.01	3.33	0.01	3.28	0.01
Co	(ppm)	15.1	0.1	16.6	0.1	16.4	0.1	9.1	0.1	11.4	0.1	11.5	0.1
Zn	(ppm)	89.3	1.5	94.8	1.7	76.9	2.1	93.5	1.4	97.5	2.0	97.4	2.1
As	(ppm)	23.9	0.4	21.7	0.4	22.4	0.4	6.40	0.22	8.28	0.28	8.09	0.26
Br	(ppm)	5.22	0.04	<0.71	-	<0.60	-	11.3	0.04	8.69	0.52	<0.49	-
Rb	(ppm)	114	4	126	5	141	6	113	4	135	5	136	6
Sr	(ppm)	248	28	301	32	157	30	569	34	778	45	893	55
Sb	(ppm)	0.708	0.068	0.979	0.074	0.759	0.069	0.570	0.050	0.665	0.068	0.762	0.050
Cs	(ppm)	5.38	0.09	6.24	0.11	6.17	0.13	6.21	0.10	8.04	0.14	7.45	0.20
Ba	(ppm)	329	43	308	54	282	52	173	30	<140	-	208	37
La	(ppm)	32.7	0.1	37.3	0.1	36.1	0.1	27.3	0.1	33.8	0.1	33.3	0.1
Ce	(ppm)	59.6	0.3	67.0	0.3	66.4	0.6	46.6	0.3	58.7	0.5	58.1	0.5
Nd	(ppm)	24.1	1.1	28.5	1.5	29.4	2.0	21.4	1.2	29.2	1.8	24.7	2.1
Sm	(ppm)	5.13	0.02	5.77	0.03	5.73	0.03	4.14	0.02	4.90	0.03	4.93	0.02
Eu	(ppm)	0.93	0.01	1.07	0.01	1.05	0.02	0.80	0.01	1.03	0.01	1.01	0.01
Tb	(ppm)	0.757	0.49	0.822	0.061	0.693	0.061	0.558	0.046	0.705	0.061	0.735	0.064
Yb	(ppm)	2.32	0.09	2.79	0.11	2.58	0.10	1.75	0.08	2.48	0.13	2.23	0.10
Lu	(ppm)	0.359	0.019	0.394	0.024	0.425	0.025	0.243	0.016	0.288	0.023	0.358	0.022
Hf	(ppm)	6.76	0.07	7.16	0.09	7.35	0.09	2.59	0.05	3.16	0.07	3.30	0.07
Ta	(ppm)	1.18	0.04	1.28	0.05	1.25	0.05	0.75	0.03	0.94	0.05	0.99	0.05
Th	(ppm)	10.4	0.1	11.7	0.1	11.6	0.1	7.8	0.1	9.9	0.1	9.7	0.1
U	(ppm)	2.49	0.20	1.91	0.21	1.47	0.18	2.28	0.18	5.19	0.46	4.42	0.27

s.d. = one standard deviation

Table 2. Changes in elemental concentrations induced by firing to 750 and 900 degrees C. in two representative clay specimens.

within this range would thus appear to have no significant effect on the composition of pottery manufactured with these clays, a conclusion that receives confirmation from the fact that the substitution of specimens fired to 750 degrees for those fired to 900 degrees produces no significant alterations in the clustering solutions discussed in the preceding section. The effects on composition produced by firing regimens of varying duration cannot at present be evaluated.

4. CONCLUSIONS

The results of this program of analysis are generally encouraging for those who aspire to employ NAA to discriminate between production groups of archaeological pottery manufactured with clays of the Plio-Pleistocene marine transgression obtained from different sources in west-central Italy and to match these groups with their source clays. The cluster analysis of the fired clay specimens indicates that there is significant chemical variation across the region and from one clay source to the next, while the comparison of specimens fired to 750 and 900 degrees shows that variations in maximum firing temperature over this range are unlikely to have produced compositional changes sufficiently large to obscure these distinctions. Trials have also been carried out to evaluate the effects of levigation on these materials, with preliminary results suggesting that short duration water separation of crushed clays produces no significant effects on the concentrations of most elements.

The authors are currently expanding this program of analysis to include outcrops of similar calcareous clays in areas of southern Lazio and Campania. Future work will focus on the analysis of greater numbers of specimens from sources of particular historical interest with a view toward developing a database sufficiently large to permit the calculation of the statistical probability that pottery of unknown provenience was manufactured with clay obtained from one or another of these outcrops. Some success has already been obtained on this score, with close non-statistical matches achieved for pairings of Plio-Pleistocene marine clays and groups of black gloss ware, *terra sigillata*, and Roman glazed pottery.

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