The University of Ioannina

A COMPOSITIONAL STUDY OF ANCIENT POTTERY BY MEANS OF X-RAY FLUORESCENCE AND MULTIVARIATE ANALYSIS

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Energy-dispersive X-ray fluorescence (XRF) was used to determine the composition of 64 potsherds dating to the Hellenistic period. Principal components analysis (PCA) of the XRF data revealed four distinct sherd clusters, originating from differences in major and trace elements concentrations. The PCA grouping, combined with archaeological criteria, allows conclusions related to the raw materials and paste recipes used in pottery manufacturing.

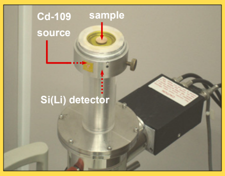

Fig. 1. The XRF irradiation setup.

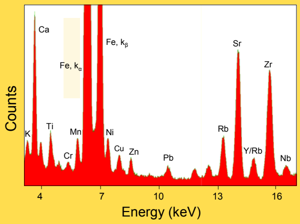

Fig. 2. XRF spectrum with elements' identification.

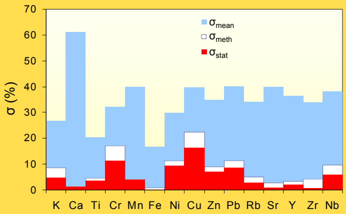

Fig. 3. The spread σ_{mean}, is significant, compared to the spreads due to method precision (σ_{meth}) and statistical error (σ_{stat}).

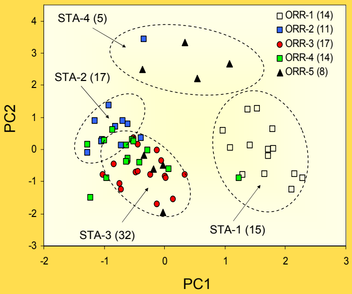

Fig. 4. Plot of the first two principal components (PC1-PC2) for potsherds assigned provisionally to groups ORR-1 through 5 (see Table 1). Four statistical groups, namely STA-1 through 4, are identified, ellipses indicating their 2σ boundaries.

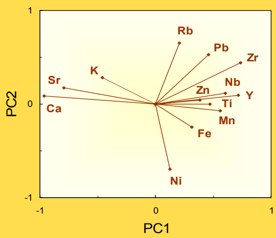

Fig. 5. A loadings' plot, showing the effect of the elemental variables on data scores projected along the first two PC axes.

Introduction

Compositional analyses of ancient pottery aim to classify ceramic products according to their chemical profile and address different aspects of ceramic production practices and distribution patterns. Various analytical methods, i.e. neutron activation analysis (NAA), X-ray fluorescence (XRF), inductively coupled plasma mass spectrometry (ICP-MS) etc. are typically employed in such studies. The interpretation of the compositional data is achieved by multivariate statistical methods, namely principal component analysis (PCA) or cluster analysis (CA). The goal of statistical handling is to allocate samples of similar composition and provide insight to the chemical boundaries of group separation.

This work reports XRF data and PCA results on 64 potsherds (see typological classification in Table 1). recovered from private houses at the Hellenistic settlement of Orraon, north western Greece. Orraon was founded at the beginning of the 4th century B.C. and held a strategic position in ancient Molossia. The excavations carried out by the University of Ioannina in collaboration with the Archaeological Institute of Berlin gave evidence that the settlement was rebuilt after its destruction by the Romans in 167 B.C, to be finally abandoned in 31 B.C. Orraon and the nearby Kassope are considered to be ideal models for studying the ancient city in NW Greece.

Materials & Methods

Elemental analyses were performed using a radioisotope-induced XRF spectroscopy arrangement, comprising an annular ^{109}Cd source and a Si(Li) detector in a 2π geometry (Fig. 1). Sample preparation involved cleaning and abrading the ceramic surface, extracting a 0.2 g piece, grounding and pressing to a 12 mm diameter pellet. The instrument and method precision were found to be below 10% for all elements except chromium and copper (Table 2), which were thus excluded from the statistical treatment.

XRF spectra (Fig. 2) were analyzed using standard reference soil samples. Quantitative data for 13 elements, normalized to log base 10 values, were submitted to a variance-covariance matrix PCA employing algorithms in the SPSS statistical package. The PCA method is applied to multivariate datasets (i.e. *N* observations, each characterized by *m* variables) in order to compress the original *m*-dimensional hyperspace into a new principal component (PC) space of reduced dimensionality. All the original data points can be projected to the PC space to get co-ordinate values called "scores". The magnitude (large or small correlation) and manner (positive or negative correlation) in which a variable contributes to the scores are expressed through the PC "loadings".

Results & Discussion

The XRF data reveal a considerable spread of elemental concentrations (see Table 2), which does not result from counting statistics or method precision (Fig. 3), but rather reflects the natural variability of raw materials used in pottery manufacturing. Despite the spread, chemical grouping is possible when a large set of elements is considered. As a first step in the classification procedure, potsherds were assigned to provisional groups suggested by the archaeologists on the basis of typological examination (Table 1). A scatterplot of the first two principal components, accounting for 50.1 and 10.6% of the total variability in the data set, respectively, is shown in Fig. 4. It is readily discernible that all ORR-1 samples form a clearly separated group (STA-1), whereas ORR-2, 3 and 4, together with some ORR-5 samples, appear as a diffuse cluster. Based on archaeological criteria and the fact that the ORR-2 members are clearly separated along the PC2 axis, two statistical groups (STA-2 and 3) have been identified. The well-defined STA-4 group is mainly populated by ORR-5 sherds.

Table 1. Archaeological grouping of potsherds.

Group	Type/use
ORR-1	Cooking pots
ORR-2	Storage and/or transportation pots
ORR-3	Black-painted pots for general use
ORR-4	Black-painted high quality tableware
ORR-5	Gray pots for general use

The effect of elemental variables on the first two PC axes may be inferred from the loadings' plot of Fig. 5. In particular: (a) group STA-1 is distinguished from the others mainly due to the considerable Ca deficiency of its members, (b) the core clustering of STA-2 and 3 points to uniform concentrations in all elements and (c) the location of STA-4 is dominated by high Rb and Pb and low Ni contents. To propose an archaeological interpretation, one should bear in mind that the elemental fingerprint of ceramics depends both on the source of raw materials and the recipe used for preparing the clay paste. Pottery-making involves mixing the clay fraction with temper, i.e. quartz, calcite and seawater, to improve the quality of the ceramic body. This refinement process is expected to induce deviations in the concentration of few major elements, i.e. Si, Ca or Na. On the other hand, significant variations in the content of trace elements hint to raw materials extracted from different clay beds.

Table 2. Elemental compositions given in μg/g, unless otherwise indicated.

Element	Min	Max	Mean	σ_{mean}(%)^a	σ_{instr} (%)^b	σ_{meth} (%)^c	σ_{stat} (%)^d
K (%)	0.36	1.97	1.19	26.8	8.2	8.5	4.8
Ca (%)	0.38	12.4	4.82	61.3	0.9	1.1	1.3
Ti (%)	0.37	1.09	0.67	20.5	4.5	4.7	3.5
Cr	136	879	410	32.1	16.8	17.2	11.2
Mn (%)	0.08	0.55	0.18	39.9	4.1	4.1	3.9
Fe (%)	4.99	11.6	7.39	16.8	0.4	0.8	0.2
Ni	41.5	392	226	29.8	10.5	11.3	9.4
Cu	18.8	133	45.5	39.7	20.7	22.4	16.3
Zn	66.4	341	151	35.0	8.0	8.9	7.1
Pb	12.6	75.2	34.6	40.2	10.6	11.2	8.6
Rb	35.2	150	88.3	34.1	3.8	5.0	2.8
Sr	82.9	514	229	39.9	1.9	2.7	0.8
Y	7.54	72.9	31.2	36.4	2.6	3.4	2.1
Zr	155	538	240	33.9	3.1	4.2	0.7
Nb	9.18	45.1	23.2	38.3	9.2	9.7	5.9

[a] Standard deviations from the mean.
[b] Instrument precision, determined by ten repetitive measurements of the same pellet.
[c] Method precision (i.e. error arising from sample preparation and inhomogeneity), evaluated by analyzing five replicate pellets prepared from the same sample.
[d] Average experimental error, resulting from counting statistics.

In this context, it may be concluded that cooking pots (STA-1) were manufactured without elaborate paste preparation, whereas addition of temper was practiced to produce higher quality tableware or pots intended for the transportation and storage of foodstuffs (STA-2 & 3). However, apart from the use of different recipes, all the above pots were produced from raw materials of similar composition, presumably originating from the same local deposits. The assumption that certain gray vessels (STA-4) were imported is based on their different trace elements profile.

An ongoing study of ceramics from ancient Kassope is expected to provide additional insight to pottery tradition and cultural exchange in the region.

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