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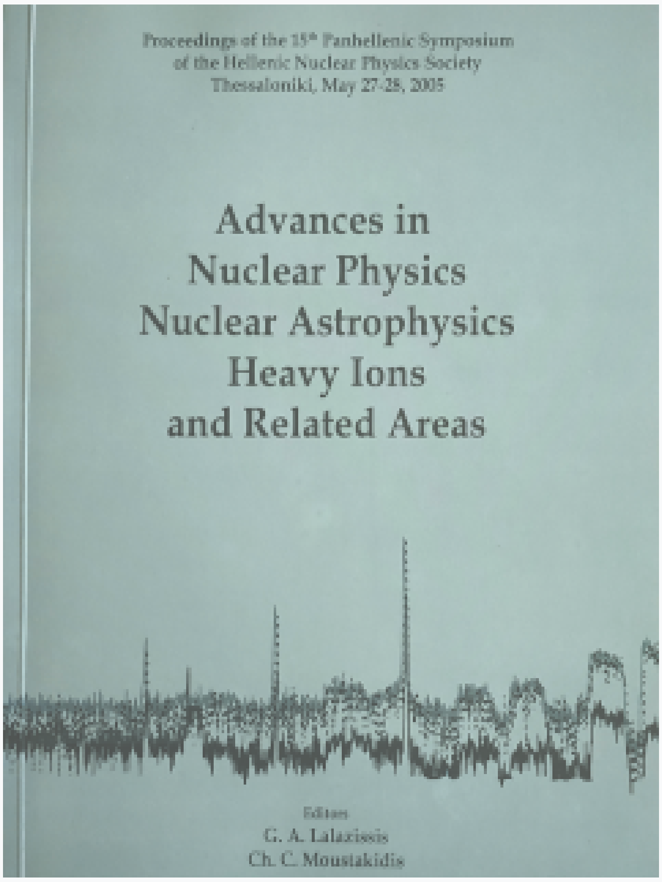

An X-Ray Fluorescence and Principal Component Analysis study of pottery from Orraon

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An X-Ray Fluorescence and Principal Component Analysis study of pottery from Orraon

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Abstract

Radioisotope-induced X-ray fluorescence XRF was used to determine the composition of 64 pottery sherds recovered from the settlement of ancient Orraon, northwestern Greece. The XRF data were submitted to Principal components analysis PCA and distinct sample clusters were identified, originating from differences in major and trace elements concentrations. The statistical classification, combined with archaeological criteria, allows conclusions related to the raw materials and paste recipes used in pottery manufacturing. Distinction between local production and imported pottery may also be inferred.

1 Introduction

Elemental analyses are considered to be a powerful tool, complementing archaeological investigations of ancient pottery. The aim of such studies is to isolate ceramic groups of similar chemical profiles, i.e. to find all members produced by the same clay mixtures, according to the same recipe and statistically test the validity of these groups [1,2]. Various analytical methods, such as neutron activation analysis (NAA), X-ray fluorescence (XRF) spectroscopy, inductively coupled plasma mass spectrometry (ICP-

MS) etc. are commonly employed in compositional studies of ancient ceramics. The interpretation of the data is achieved by statistical handling, which aims to identify samples of similar composition and provide insight to the chemical boundaries of group separation. Multivariate statistical methods, i.e. principal component analysis (PCA) or hierarchical cluster analysis (HCA), are typical methods of choice.

The present work reports XRF data and PCA results on 64 potsherds recovered during the excavations in the ancient settlement of Orraon (4th century B.C.), north western Greece.

2 Materials and Methods

2.1 Archaeological background

The ancient settlement of Orraon is located nearby Ammotopos village, 18 km north-west to the city of Arta, in Epirus prefecture. It was founded between 385 and 370 B.C., and held a strategic position in ancient Molossia. The archaeological 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. [3,4].

The potsherds examined in this work were recovered from Orraon House 1 and were classified according to typological examination into groups (1) ORR-1: cooking potsherds (coarseware), (2) ORR-2: sherds from storage pots, (3) ORR-3: sherds from black-painted pots for general use, (4) ORR-4: sherds from black-painted tableware and (5) ORR-5: sherds from gray pots for general use.

2.2 XRF measurements

The major, minor and trace element composition of the potsherds was determined using a radioisotope-induced XRF spectroscopy arrangement in a 2 pi source-detector geometry. An annular Cd-109 source was used for sample excitation. X-ray spectra were recorded with a Si(Li) detector (80 mm^2 crystal surface, 5 mm thick), having an energy resolution of 171 eV at the 5.9 keV Mn (Ka) peak. Data acquisition was performed through a PC card, controlled by the MAESTRO software, while the AXIL code was used for spectrum analysis.

Sample preparation involved cleaning the surface layer of sherds and severing a small piece, which was subsequently ground and homogenized. Thin pellets (12-mm in diameter) were prepared by mixing 300 mg of the sample powder with cellulose at a ratio of 10% w/w.

2.3 Statistical treatment of data

Compositional analyses generate a dataset containing N samples (observations), each characterized by m concentration values (variables). Principal components analysis (PCA) is a method aiming to compress the original, m-dimensional hyperspace into a new principal component (PC) space of reduced dimensionality. All the original data points are projected in the new PC space and their new co-ordinate values are called scores or principal components (PCs). The contribution of the initial variables the scores is expressed through the PC loadings.

Elemental compositions (in ppm), were normalized to log base 10 values [5,6] and submitted to PCA using SPSS (v. 10.1 for Windows). Out of the 15 measured elements, Cr and Cu were not included in statistical analysis because of low measurement precision.

3 Results and Discussion

3.1 Elemental analyses

The range of concentrations, their average values and spreads are listed in Fig. 1. The instrument and method precision, quantified by the coefficient of variation, as well as the average counting error are also indicated. The data reveal a considerable spread of elemental concentrations, reflecting the natural variability of raw materials used in pottery manufacturing.

Fig. 1. Elemental compositions determined by the XRF method. Values are given in ppm, unless otherwise indicated. Standard deviations from the mean and errors arising from instrument/method precision and counting statistics are also listed.

Element	Min	Max	Mean	σ (%)	$\sigma_{instrument}$ (%)[a]	σ_{method} (%)[b]	$\sigma_{experimental}$ (%)[c]
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
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
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] The instrument precision was determined by ten repetitive measurements of the same pellet

[b] The method precision was evaluated by analyzing five replicate pellets prepared from the same sample.

[c] Average experimental counting error.

3.2 Data classification

As a first step in the classification procedure, potsherds were assigned to provisional groups suggested by the archaeologists. A scatter-plot 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. 2. 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 typological examination 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 in this region. The well-defined STA-4 group mainly consists of ORR-5 sherds.

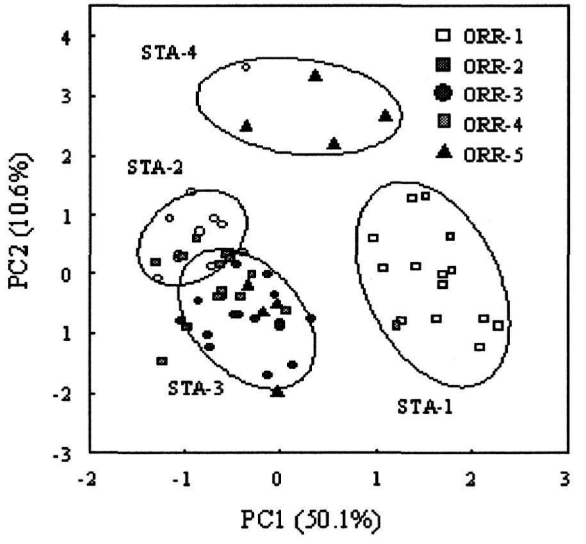

Fig. 2. A scatterplot of the first two principal components (PC1-PC2) for potsherds assigned provisionally to groups ORR-1 through 5 (see Table 1). Four statistical groups, namely STA-1 through 4, are identified, ellipses indicating their 2 sigma boundaries.

As may be inferred from the PC loadings' plot (not shown here), group STA-1 is distinguished from the others primarily due to the considerable Ca deficiency of its members. The core clustering of STA-2 and 3 points to uniform concentrations in all elements, while the PC coordinates of STA-4 are dominated by high Rb and Pb and low Ni contents. The elemental fingerprint of ceramics depends both on the raw clays and the non plastic tempers (such as quartz or calcite) used in pottery making. It may be assumed that calcite temper was added to prepare pots for storage of foodstuffs and for table use (STA-2, 3), whereas cooking pots (STA-1) were prepared without elaborate paste preparation.

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 different trace elements profile found in certain gray vessels (STA-4) supports the assumption that these items were imported.

4 Conclusions

The XRF data reported in this study will be the first input in a compositional data bank of ancient ceramics in the region of Epirus. Analysis by appropriate multivariate statistics led to the classification of potsherds in four groups, which fairly agree with the groups proposed by the archaeological examination. Group separation was found to originate from differences in clay sources and in paste preparation.

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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