

A study of ancient pottery by means of X-ray fluorescence spectroscopy, multivariate statistics and mineralogical analysis

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Abstract

Energy-dispersive X-ray fluorescence spectroscopy was used to determine the composition of 64 potsherds from the Hellenistic settlement of Orraon, in northwestern Greece. Data classification by principal components analysis revealed four distinct groups of pottery, pointing to different local production practices rather than different provenance. The interpretation of statistical grouping was corroborated by a complementary X-ray diffraction analysis. Compositional and mineralogical data, combined with archaeological and materials' science criteria, allowed addressing various aspects of pottery making, such as selection of raw clays, tempers and firing conditions.
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1. Introduction

Ancient ceramics are the most abundant artifacts that have been studied to improve our knowledge of past societies. Archaeological research based on the examination of ware shape, style, color, decoration and overall fabric, provide a wealth of information concerning typological and functional issues, chronology and provenance. To complement such taxonomy schemes, archaeologists often resort to an interdisciplinary approach involving physical and chemical sciences. Although a variety of techniques, investigating physical, optical, petrographic and chemical attributes are used to characterize ancient pottery, compositional analyses have met the greatest overall success. Elemental profiles are thought to be representative not only of a certain production region, but also of a particular workshop, thus allowing for meaningful pottery groups to be established [1–3]. Several methods are available to perform elemental analyses of archaeological materials. Instrumental neutron activation analysis (INAA) and X-ray fluorescence (XRF) have been widely exploited for a long time (see, e.g., [4–8]). The early opti-

cal emission spectrometry (OES) has been replaced by atomic absorption spectrometry (AAS) and later on by inductively coupled plasma (ICP) coupled to mass spectrometry (MS), atomic or optical emission (ICP-MS, ICP-AES or ICP-OES) [9–11]. Laser-induced breakdown spectroscopy (LIBS) and laser ablation ICP-MS have been proposed lately as promising, micro-destructive methods of analysis [12–14].

The interpretation of compositional data is achieved by methods of multivariate statistics, such as principal component analysis (PCA), cluster analysis or discriminant analysis. Statistical handling aims to identify groups of similar elemental fingerprint and to understand the chemical boundaries of group separation [15,16]. The emerging patterns, combined with archaeological input, illuminate questions on pottery provenance and distribution and give insight to production techniques. Technological issues are further probed by mineralogical studies aiming to determine the type of raw clays and tempering materials used, as well as the firing temperature and atmosphere to which they have been submitted.

In the present work, energy-dispersive X-ray fluorescence (XRF) spectroscopy was used to assess the elemental composition of 64 pottery sherds recovered from the ancient settlement of Orraon (4th century B.C.), in northwestern Greece. The com-

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positional data were treated by principal components analysis in order to identify chemical groups in the sample set. Evaluation of the results was further pursued in mineralogical data obtained through X-ray diffraction (XRD) measurements.

2. Archaeological context

2.1. The ancient Orraon

The ancient settlement of Orraon is located nearby Ammotopos village, 18 km northwest to the city of Arta, in Epirus prefecture (Fig. 1). Orraon was founded and fortified at the beginning of the 4th century B.C. by the Molossians, a tribe of central Epirus, during their expansion towards the sea. The settlement was destroyed by the Romans in 167 B.C., was subsequently rebuilt and was finally abandoned by its inhabitants who were obliged to settle in Nicopolis, a city founded by Augustus after his victory in the battle of Actium, in 31 B.C.

The settlement held a strategic position; it controlled the coastal zone occupied by the Molossians in the Amvrakikos bay, and at the same time it protected the main road connecting central Epirus with the bay and southern Greece. The private houses of Orraon, built with high quality local limestone, are exception-

Table 1
Archaeological grouping of sherds

Group	Codes (n ^a)	Type/use	Grain
ORR-1	1/1–1/19 (14)	Cooking vessels	Coarse
ORR-2	2/20–2/30 (11)	Storage and/or transport vessels	Medium–fine
ORR-3	3/31–3/54 (17)	Black-painted pottery for general use	Medium–fine
ORR-4	4/55–4/80 (14)	Black-painted tableware	Fine
ORR-5	5/85–5/95 (8)	Grayware	Fine

^a Number of analyzed sherds.

ally well preserved, sometimes even up to the upper storey (at a height of 5–7 m), where the windows and the doorjambs and frames are still visible.

Orraon and the nearby Cassope are considered to be the best models for studying the ancient private house in northwestern Greece.

2.2. The sample set

The potsherds analyzed in this study came from the excavations in House 1 of Orraon [17], initiated in 1975 and resumed in 1981 and 1986 by the University of Ioannina in collaboration with the German Archaeological Institute of Berlin [18]. A macroscopic examination of the sherds relevant to the fabric, glaze and type of the corresponding vessels, led to the archaeological classification given in Table 1. The sherds belong to various types of utensils, i.e. cooking pots, pots used for the storage and transport of foodstuffs and pots intended for general domestic use, including everyday serving vessels and fine tableware. The sherds' surface was either unpainted or black-painted and their color body ranged from orange-brown to creamy and light gray, according to Munsell's color chart.

A set of 95 sherds was handed for analysis, but destructive XRF measurements were permitted only for 64 sherds depending on their shape and size.

3. Methodology

3.1. XRF measurements

The major, minor and trace elements composition of the potsherds was determined with a home-built XRF spectroscopy assembly, operating in ambient air. Photons emitted from an annular ¹⁰⁹Cd source (12 mm diameter) were used to excite the characteristic X-rays of potassium (K), calcium (Ca), titanium (Ti), chromium (Cr), manganese (Mn), iron (Fe), nickel (Ni), copper (Cu), zinc (Zn), rubidium (Rb), strontium (Sr), yttrium (Y), zirconium (Zr), niobium (Nb) and lead (Pb). The source was housed in a cylindrical container, fixed coaxially above a CANBERRA SL80175 Si(Li) detector (5 mm crystal thickness, 80 mm² area), with a 25 µm-thick Be window and an energy resolution of 171 eV at the 5.9 keV Mn (K α) peak. Samples were placed on top of the assembly with their surface perpendicular

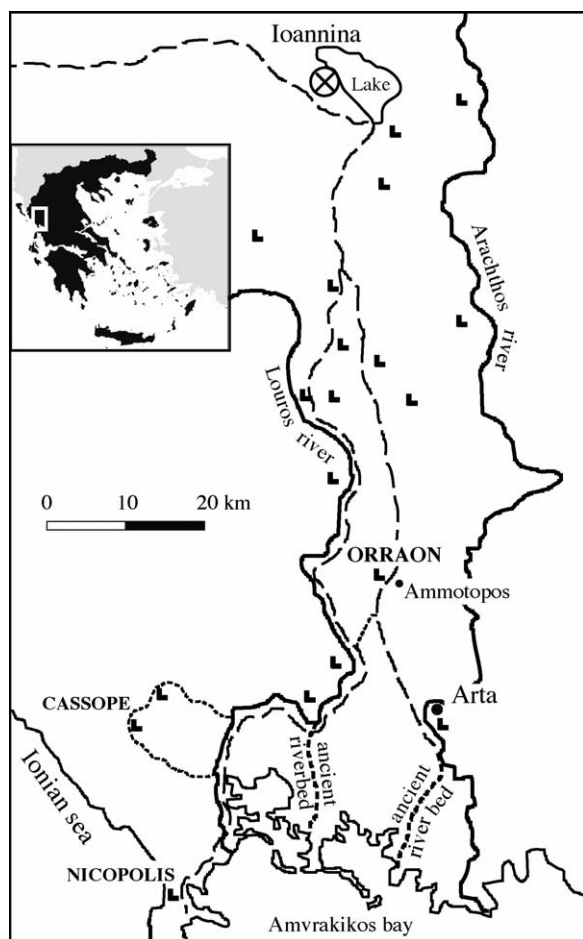


Fig. 1. Map showing the location of ancient Orraon, in Epirus, northwestern Greece. The two main roads connecting central Epirus with Amvrakikos are indicated with dashed lines.

to the detector axis. Data acquisition was performed through a PC card (ORTEC TRUMP-PCI), controlled by the MAESTRO-32 emulator. The AXIL software package was used for spectral analysis and elemental compositions were assessed with reference to the SOIL-7 standard material provided by the IAEA (International Atomic Energy Agency, Vienna, Austria).

Sampling was performed after cleaning and abrading the surface layer of potsherds. Portions of the ceramic body were subsequently removed, ground and homogenized in an agate mortar. Thin pellets, 12 mm in diameter, were prepared by mixing 300 mg of sample with cellulose at a ratio of 10% w/w.

3.2. XRD measurements

A mineralogical analysis of selected potsherds was carried out using a D8 Advance Brüker diffractometer operating with Cu K α ($\lambda = 1.5406 \text{ \AA}$) radiation and a secondary beam graphite monochromator. Powder samples, obtained as described above, were scanned over an angular 2θ range from 5° to 60° , in steps of 0.02° (2θ) at a rate of 2 s per step.

3.3. Statistical treatment of data

Compositional analyses generate a dataset containing N observations (samples), each characterized by m variables (concentration values). Following the common statistical description, the dataset may be displayed as N points in an m -dimensional hyperspace. The principal components analysis (PCA) aims to compress the original hyperspace into a new principal component (PC) space of reduced dimensionality, while retaining as much of the data variation as possible. Algebraically, PCA starts from the original correlated variables and uses eigenvalue–eigenvector matrix operations on the $N \times m$ data matrix to derive new uncorrelated variables. These new variables are called *scores* or *principal components* and are calculated as linear combinations of the original ones, weighted through the PC *loadings*. The loadings express the magnitude (large or small correlation) and manner (positive or negative correlation) in which the original variables contribute to the scores.

In general, the PC space contains a total of m principal axes, each one being progressively less important than the preceding one. In doing so, some degree of economy can be achieved by neglecting those PC axes that express little variation of the original dataset. Usually, the scatter plot of the first two principal components provides a most informative overview of the data and is sufficient to reveal groups of observations, trends and outliers.

Elemental compositions, expressed in parts per million, were submitted to PCA after “normalizing” to log base 10 values. This transformation is often applied to smooth out differences in magnitude between major and trace element concentrations [16,19]. Out of the 15 measured elements, Cr and Cu were not included in statistical analysis because of low measurement precision (see Fig. 3 below). PCA based on a variance–covariance matrix was carried out using algorithms in the STATISTICA software package (v.6.0 for Windows).

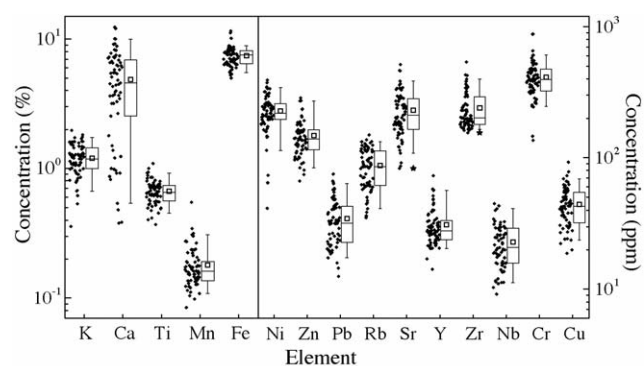


Fig. 2. The distributions of elemental concentrations (in % or ppm) in the entire set of the 64 samples. Boxes define lower and upper quartiles (25 and 75%) and median values, whiskers represent the 5–95% range of the distribution and open squares denote mean values.

4. Results and discussion

4.1. XRF results

The entire set of XRF data is illustrated in Fig. 2, together with descriptive statistics. For most of the analyzed elements, considerable spreads of concentrations are readily observed, which may due to different compositional patterns or to errors related to the analytical process. To estimate the contribution of the latter, the errors arising from counting statistics (σ_{counting}) were averaged throughout all measurements and are plotted in Fig. 3. In addition, the method precision – i.e. the error (σ_{method}) arising from sample preparation and inhomogeneity – was evaluated by analyzing five replicate pellets prepared from the same sample. Results are included in Fig. 3 as the percentage standard deviation of the mean of these five sets of measurements. Errors resulting from method precision were higher than 15% for chromium and copper, which were excluded from statistical analysis. Comparison of σ_{counting} and σ_{method} with the spreads (σ_{mean}) found in the 64 analyzed samples, points out that the overall elemental ranges actually originate from variations in

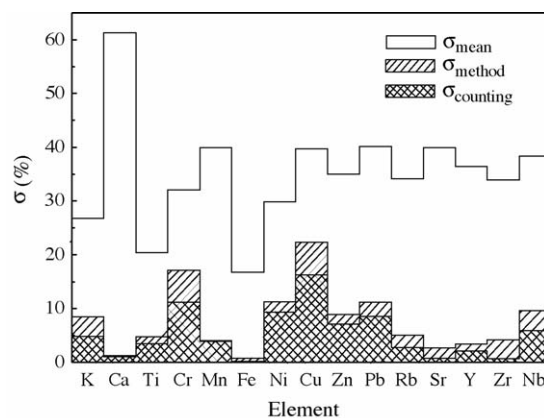


Fig. 3. Different kinds of spreads relevant to the XRF analysis. The spread of elemental concentrations (σ_{mean}) is calculated as the standard deviation of the mean (in % of mean) for the 64 samples. The errors arising from method precision (σ_{method}) and counting statistics (σ_{counting}) are given for comparison (see text).

the composition of potsherds. Such variations may either imply pottery from different production sites or reflect the natural inhomogeneity of local clay deposits and the application of different manufacture processes in local workshops. Inferences of this kind are discussed in the following sections.

4.2. Data classification

Principal components analysis on the 64×13 data matrix shows that the first two principal components account for 50.1 and 10.6%, respectively, of the total variance in the dataset. As a first step in the classification procedure, samples were assigned to the provisional groups suggested by the archaeologists (see Table 1). A score plot of the first two PCs for samples grouped as ORR-1 through 5 is shown in Fig. 4. The ellipses represent group membership assuming the 95% confidence limit (2σ) as the cut-off distance.

The effect of elemental variables on the first two PC axes may be inferred from the loadings' plot of Fig. 5. In such a plot, high positive correlations between elemental compositions are indicated by small angles between vectors, no correlation is indicated by right angles and inverse correlations are indicated by angles close to 180° [16]. Inspection of Fig. 5 shows that negative PC1 is dominated by Ca or, equally, a Ca deficiency results in positive PC1 values. A strong effect towards positive PC2 is caused primarily by Rb and Pb, while negative PC2 values are related to a high Ni content.

Three main clusters are identified in Fig. 4. A cluster, denoted as ORR-A, is clearly separated along the positive PC1 axis and contains all 14 samples from the ORR-1 group, as well as one sherd originally assigned to group ORR-4. Members of ORR-A vary considerably from the rest of the sample set due to particularly low concentrations of calcium. A small cluster (ORR-C), made up of one ORR-2 and four ORR-5 sherds, is well isolated along the PC2 axis. Its location is controlled by high rubidium and lead contents and a considerable nickel deficiency. The

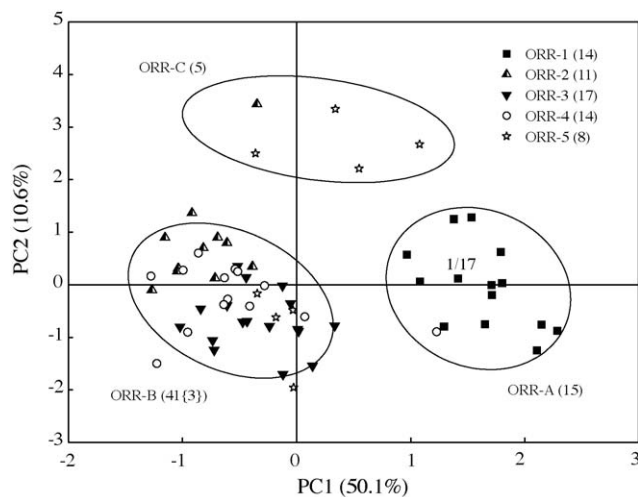


Fig. 4. Plots of the first two principal components for samples assigned provisionally to archaeological groups ORR-1 through 5 (see Table 1). Three statistical groups, ORR-A, ORR-B and ORR-C are established, ellipses indicating their 2σ boundaries. Sample 1/17 was analyzed by XRD.

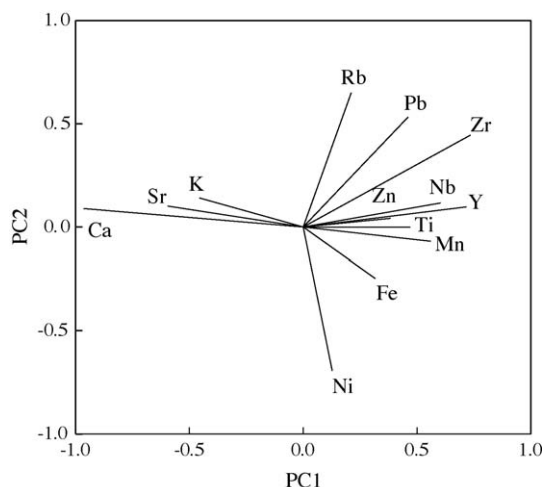


Fig. 5. A PCA loadings' plot showing the effect of elemental variables on PC1 and PC2 axes.

rest of the sherds appear as a diffuse cluster (ORR-B), mostly characterized by negative PC1 values. A closer examination of ORR-B discloses a clear distinction between ORR-2 and ORR-3 members along the PC1 axis, which prompted an attempt to identify meaningful sub-clusters within ORR-B. A cluster analysis based on the tree clustering method was performed, computing squared Euclidean distances between points in the PC space and applying the complete linkage rule to determine cluster distances. The resulting hierarchical tree, shown in Fig. 6, reveals two main branches denoted as ORR-B1 and ORR-B2, mainly composed of ORR-2 and ORR-3 members, respectively. Samples provisionally classified as ORR-4 are equally observed in both branches, whereas certain ORR-5 individuals are grouped in ORR-B2. Based on the cluster analysis, group boundaries in PC space were computed as shown in Fig. 7. The elemental compositions of the statistical groups specified in Figs. 5 and 7 are listed in Table 2.

Interesting implications may be proposed from the interpretation of these findings, bearing in mind various aspects of pottery making. The basic constituents of ceramics are clay minerals – mostly kaolinite, illite and montmorillonite – which are generally processed through crushing and sifting to remove coarse

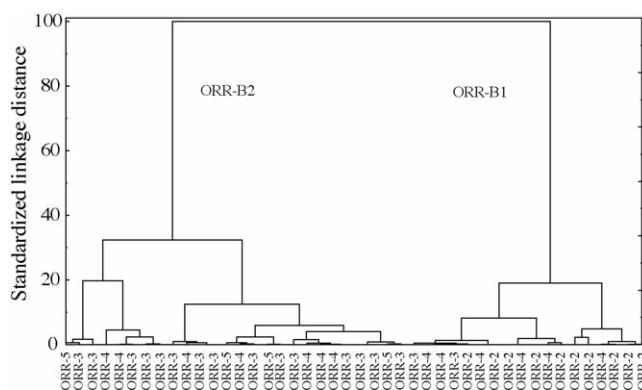


Fig. 6. Hierarchical tree clustering of the PC1 and PC2 coordinate values for the 44 samples grouped as ORR-B (see Fig. 4). Two subgroups emerge, marked as ORR-B1 and ORR-B2.

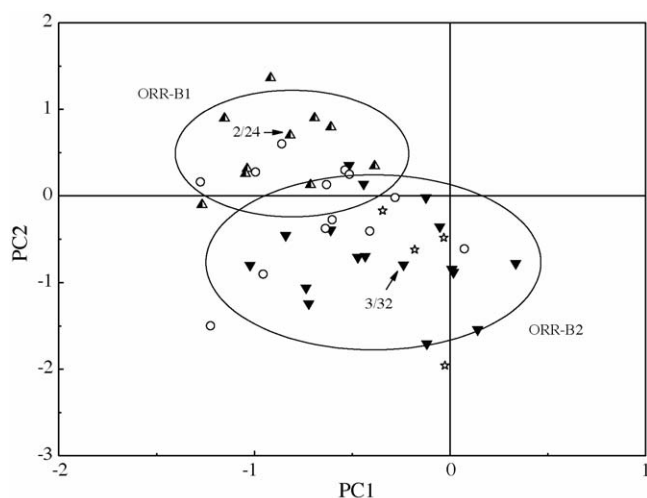


Fig. 7. The ORR-B cluster (see Fig. 4) is split in ORR-B1 and ORR-B2, based on the hierarchical tree clustering shown in Fig. 6. Data markers are explained in Fig. 4. The location of samples 2/24 and 3/32 analyzed by XRD is indicated.

materials and retain particular grain fractions. Clay minerals possess unique plastic properties and when kneaded with water, they can be worked to a form that retains its shape. After that shape is attained, the water of plasticity is removed by heating either in an open fire or in enclosed structures called *kilns*. Heating results in shrinkage that may lead to cracking or distortion of the final product. Adding non-plastic materials, known as *tempers*, to the raw clay improves its workability and allows water to evaporate more smoothly, minimizing shrinkage and preventing cracking. Potters have used a variety of tempers, including quartz, limestone, shells, volcanic ash or even crushed potsherds [1,20]. Note that, instead of adding tempers, mixing two or more different clays may be practiced in order to achieve the desired properties in the ceramic body [20,21]. In general, refinement with tempers is expected to induce large deviations in the concentration values of certain major elements, such as Si, Ca or Na

[1,22], while at the same time imposing a “dilution effect” on the compositional profile of minor and trace elements [20,22]. However, since the concentrations of these elements in tempers are much lower than in clays, large deviations may rather furnish arguments to distinguish between imported and locally produced pottery [7,23]. All facts considered, pottery composition will depend both on the clay source and the recipe used to prepare the clay paste. One basic working hypothesis in the study of pottery provenance is that the compositional variability within one clay source is smaller than the variability between different sources [2]. However, variability may also be evidenced within a single claybed, depending on geochemical processes and exploitation strategies, particularly when a long time period of exploitation is involved. Note that potters may select different locally available clays and even mix clays from two or more local deposits, when preparing different kinds of vessels. Ethnographically, it has been demonstrated that potters will exploit raw materials within a distance of 10 km from their residence [7,21,24].

In view of the above, the striking difference in calcium concentrations found between the two main data clouds (ORR-A and ORR-B1/B2) may imply either the use of clays from different deposits or the application of different production recipes. Given the utilitarian nature of these pots and the fact that most of the other elements exhibit rather uniform compositional profiles, it is reasonable to suggest that all pots were produced locally. In that case, ORR-B1 pots – i.e. mostly pots used for the storage and/or transport of foodstuffs – were prepared either by using calcareous clays or by adding calcite-temper to the clay paste or both. A similar production recipe may be postulated for ORR-B2 pots – i.e. unpainted or black-painted pots for general domestic use and fine tableware. By contrast, the calcium-deficiency of cooking pots (group ORR-A) indicates that the raw clays were extracted from a non-calcareous deposit and were not refined with calcite temper (see also Section 4.3). The remaining five sherds that stand out as group ORR-C belong mainly to gray pots for general domestic use. Their high content in Rb and Pb

Table 2
Elemental composition of the four pottery groups identified by PCA

Element	ORR-A (15 samples)		ORR-B1 (18 samples)		ORR-B2 (26 samples)		ORR-C (5 samples)		σ_{mean} (%)
	M	σ (%)	M	σ (%)	M	σ (%)	M	σ (%)	
K (%)	0.94	28.1	1.39	20.8	1.22	21.0	1.22	23.8	26.8
Ca (%)	1.01	30.1	7.38	27.6	4.94	32.9	3.99	39.4	61.3
Ti (%)	0.72	17.9	0.59	20.5	0.70	17.4	0.76	19.0	20.5
Cr	535	32.8	366	21.3	377	25.1	377	37.8	32.1
Mn (%)	0.24	43.5	0.15	26.0	0.17	25.3	0.17	38.6	39.9
Fe (%)	7.64	17.0	6.85	17.8	7.85	15.1	7.16	15.8	16.8
Ni	253	28.8	216	20.9	245	19.9	107	65.1	29.8
Cu	51.1	48.5	41.2	33.6	46.9	37.5	33.2	29.6	39.7
Zn	178	35.3	134	30.1	150	38.2	153	20.2	35.0
Pb	45.3	30.4	34.4	36.7	27.2	29.1	52.2	23.1	40.2
Rb	97.6	30.0	98.7	26.2	69.5	34.2	127	11.5	34.1
Sr	162	19.5	298	20.6	215	27.4	218	30.1	39.9
Y	46.6	26.2	25.3	25.1	26.8	17.6	32.2	19.3	36.4
Zr	340	22.9	210	13.7	185	11.2	356	13.8	33.9
Nb	30.3	24.4	16.9	29.4	21.9	37.4	32.7	23.5	38.3

The average concentrations M are given in $\mu\text{g g}^{-1}$ (ppm), unless otherwise indicated, and the spreads σ (standard deviations) in % of M. The spread σ_{mean} (%) in elemental concentrations throughout the whole data set is given in the last column.

is not related with paste preparation but rather with the use of different clays in the paste mixture. Note that Ni concentrations are not taken into account because of their pronounced spread in ORR-C (see Table 2). At this point, only tentative assumptions can be proposed that these pots were prepared at a different local workshop exploiting a different claybed or that they were imported items.

4.3. Mineralogical data

X-ray diffractograms are shown in Fig. 8 for selected samples, namely 1/17, 2/24 and 3/32, considered to be representative of the statistical clusters ORR-A, ORR-B1 and ORR-B2, respectively (see also Figs. 4 and 7). Recurring to typological taxonomy, sample 1/17 is a cooking potsherd, sample 2/24 is a sherd from a storage or transport pot and sample 3/32 comes from a black-painted tableware. The primary minerals identified in all samples are quartz (Q), illite–muscovite (I/M), plagioclase (P) and potassium feldspar (F). The varying intensity of these peaks, as well as the pronounced differences stemming from calcite (C), diopside (D) and hematite (H) may provide interesting insight to various aspects of production of these sherds.

The presence or lack of certain mineral phases allows advancing hypotheses on the firing conditions – both temperature and atmosphere – that have been used during pottery making. The thermal decomposition of calcite to lime starts at $\sim 600^\circ\text{C}$ and is completed around $800\text{--}850^\circ\text{C}$, giving rise to new “high temperature” calco-silicates and aluminocalco-silicates, such as members of the pyroxene group (i.e. diopside), certain plagioclase feldspars (i.e. anorthite), gehlenite and wollastonite [25–28]. However, secondary calcite may also occur in ceramics as a result of post-burial deposition processes due to recarbonation of lime [29]. Illite-muscovite minerals undergo

a decomposition process between 700 and 1000°C , although their (1 1 0) reflection at $19.8\ 2\theta$ is not essentially affected below $900\text{--}950^\circ\text{C}$ [30]. Depending on the composition of the ceramic body, the complete destruction of illite–muscovite between 950 and 1000°C normally ensues the development of diopside and gehlenite peaks and also gives increment to iron oxides, such as hematite [31,32]. Alkali feldspars and hematite persist to above 1000°C [27,33], while quartz decomposes at even higher temperatures.

Intense calcite peaks are observed in sample 2/24, in line with its high calcium content (9.2%) determined by elemental analysis. The absence of diopside indicates that calcite is of primary origin, allowing the conclusion that the sherd was submitted to a low firing temperature – i.e. below 800°C . The well-preserved illite–muscovite and the weak plagioclase peaks corroborate this assumption. Note that the pale creamy color of this sherd is typical for ceramics produced by firing calcareous clay pastes at low temperatures. Calcite is not detected in sample 3/32, despite its intermediate calcium concentration (3.7% Ca). However, a considerable development of diopside is evidenced, indicating that primary calcite was completely decomposed upon firing at a temperature of at least 850°C . The simultaneous increment in plagioclase (mainly anorthite) and decrease in the illite–muscovite peaks further suggest that even higher temperatures – i.e. up to 950°C could have been reached. The presence of hematite, associated with the vivid orange color of this sherd, implies an oxidizing firing atmosphere. Sample 1/17 shows no trace of either calcite or diopside peaks, in agreement with its low calcium content (0.82%). Firing temperatures in the range of $900\text{--}1000^\circ\text{C}$ under oxidizing conditions may be argued, due to the considerable decrease of illite–muscovite, the increase in plagioclase and the presence of hematite peaks. An important feature in the XRD pattern of this sample is the particularly pronounced quartz lines it exhibits (Fig. 8, inset). Quartz is often an indigenous inclusion found in clay deposits and thus its use as an intentionally added temper is not easy to determine. In either case, its abundance in sample 1/17 gives evidence for a different manufacturing process. It is possible that, when preparing cooking pots, Orraon potters preferred clays from particular local deposits for their physical and thermal properties. If the same deposits were exploited to produce all kinds of pots, the naturally occurring quartz phase could have been removed by fractionation before tempering with calcite to produce storage/transport vessels or various types of tableware.

The technological choices in the production of pottery depend on the performance characteristics desired for the final products. To prepare a wide range of vessel shapes, especially vessels having thin walls, calcite-temper is favored over quartz-temper, as it makes sticky clay easier to work. In addition, the thermal expansion rate of calcite is very similar to that of clay minerals, thus preventing the development of microcracks upon firing the clay paste. Note, however, that spalling may occur in the ceramic body unless firing conditions are carefully controlled, especially when preparing large vessels that require large calcite particles to support the vessel walls [34]. Quartz-temper is more likely to initiate cracks upon firing the clay paste, owing

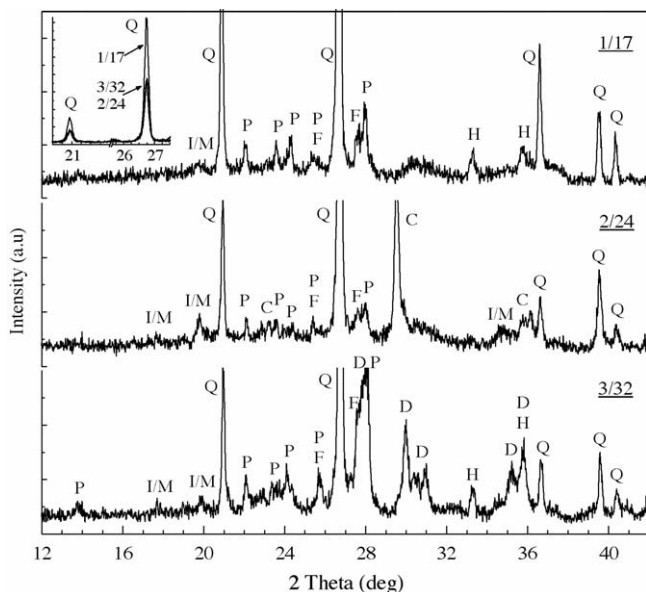


Fig. 8. XRD diagrams of samples allocated to clusters ORR-A (1/17), ORR-B1 (2/24) and ORR-B2 (3/32). The indicated mineral phases are illite/muscovite (I/M), quartz (Q), plagioclase (P), K-feldspar (F), calcite (C), diopside (D) and hematite (H).

to the higher expansion rate of the quartz crystal [34,35]. As a result, quartz-tempered pottery is less resistant to mechanical and thermal stresses during use, compared to calcite-tempered pottery.

It may be suggested that Orraon potters preferred tempering with calcite to impart higher mechanical strength to storage and transport pots. This property was presumably important as their products should be able to withstand accidental impacts during stacking or transit. Refinement with calcite was also favored when preparing various tableware, due to the flexibility it provided to manufacture smaller vessels of various shapes and wall thicknesses. A similar recipe might have been expected for cooking pots, as calcite-temper generally ensures a high thermal shock resistance possibly required for cooking pots to survive repeated heating and cooling during use [35]. However, Orraon cooking pots have a non-calcareous, quartz-tempered fabric, implying that they were treated as coarse utensils with a short period of life, probably produced and replaced on a frequent basis. It should be noted that the requirement for thermal shock resistance is considered to depend on cooking practices, such as the food being cooked, the duration of cooking episodes and the fuel used [36]. Evidence from around the world confirms that a wide range of temper types, as well as both calcareous and non-calcareous clays have been successfully used in the production of ancient cooking pots [35].

5. Conclusions

A set of 64 pottery sherds from ancient Orraon (4th century B.C., north-western Greece) was studied by means of XRF spectroscopy and mineralogical analysis, in order to extract information about pottery provenance and manufacture process. Multivariate statistical analysis of XRF data points to four compositional groups, in fair agreement with archaeological classification. Each group is mainly composed of pots intended for different use and group separation is related to the choice of specific production practices. In particular, pots used for cooking were non-calcareous and abundant in quartz inclusions; storage and transport pots were tempered with calcite and fired at low temperatures; various types of tableware were calcite-tempered and well fired. Apart from significant differences in calcium levels, the main body of sherds showed a quite uniform chemical profile, implying that all relevant pots were produced locally. Only a few individuals, rich in Rb and Pb, are separated from the main dataset. The reason for this separation cannot be firmly argued at this point.

No previous studies exist, investigating elemental patterns of ancient pottery from northwestern Greece. The data reported in the present work may contribute to developing a compositional databank and establishing reference groups of pottery from Epirus. An ongoing analysis of sherds from ancient Cassope (4th century B.C.) is expected to provide additional insight to pottery tradition, trade and cultural exchange in the region.

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