

Results from Multi Technique Investigation of Pottery from Different Early Neolithic Sites in Albania

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Abstract

The archaeological excavations of the Neolithic sites in Albania show that this area has been the center of the confluence of different cultures with various levels of development and social organization. This is reflected in the pottery manufacturing, which during early Neolithic is classified in three major groups. The pottery from the Early Neolithic site at Kolsh, situated in north east, shows similarities with all the other cultures of central Balkans, the shards from the site Blaz in the north-west region show an Adriatic-Mediterranean character, while the south culture represented by Vashtemi and Podgorie sites appears to show cultural report with early Neolithic in the area of Thessaloniki. During the last years, the Institute of Applied Nuclear Physics of the University of Tirana and the Institute of Archaeology of the Center of Albanian Studies have initiated a cooperative study of the ceramic finds which aims at a better characterization and classification of the ceramic finds. In this context Optical Microscopy (OM), EDXRF, micro-XRF and XRD were used for the elemental and structural characterization of ceramic samples. Some data on the fabric texture, inclusions, decoration materials and elemental composition of the shards from pottery samples belonging to the mentioned Early Neolithic sites in Albania will be presented.

Keywords

Neolithic Ceramics, EDXRF, Micro-XRF, Albania

1. Introduction

Analysis of pottery from excavations involves two main lines of inquiry. The first,

termed typological analysis consists chiefly of detailed analysis of the rim forms and decorative features of vessels. The other line of inquiry involves the examination of pottery fabrics—the aim here being to determine the raw materials and processes used in the manufacture of pottery. The results of both fabric analysis and typological analysis can then be combined to establish definitive pottery styles which will help in the interpretation of archaeological excavation.

While the typological study of the pottery is widely used by the archaeologists in Albania, only a few studies related with pottery materials and their production technology are published [1] [2] [3]. The main objective of the present study is the collection of data for the materials (clay composition and pigments) and technology (tempers and firing conditions) used for the manufacture of pottery excavated at the different early Neolithic sites and based on them to find similarities and/or differences that can be useful for better archaeological classifications.

In this context different X-ray techniques EDXRF (Energy Dispersive X-ray Fluorescence), Micro-XRF (Micro X-ray fluorescence), XRD (X-ray diffraction), Optical Microscopy together with various multivariate techniques are being used for the characterization of the raw materials and investigation of the technologies used for the production of ceramic finds from different sites in Albania. EDXRF spectrometry was employed for the determination of the chemical composition of the pottery. The evaluation of the chemical data through simple elemental bip-*lots* and their treatment by means of multivariate statistical analysis (CA) led to the potential classification of the samples into distinctive groups and provided feedback for further discussion about their provenance. OM, XRD and μ -XRF were used for the investigation of the internal texture of the ceramic body and identification of the major types of inclusions as well as the materials used for the external decorations.

2. Archaeological Background

The geographical position of Albania, at the intersection of land routes that connect Anatolia, the Balkans and the Western Mediterranean on one side and its long Adriatic and Ionian coast on the other side, has determined the cultural features of its Neolithic civilization which combines elements of the Anatolian-Balkan and Adriatic-Mediterranean cultural complexes [4].

Pottery manufacturing during early Neolithic in Albania is classified in two major groups: north culture represented by Kolshi and Blazi sites and south culture represented by Vashtëmi-Podgorie sites (**Figure 1**).

The classic phase of Early Neolithic in south-eastern Albania is represented by the Vashtemi-Podgori culture, two sites situated in the Korça basin. The excavations of 1974 in Vashtemi revealed a deposit consisting of a single layer with three horizons, characterized more or less by similar types of pottery, namely red monochrome pottery in the main, pottery with white decoration on a red ground, and, very rarely, pottery with red decoration on white, ochre or light ground. All these features are equally evident in some huge deposits at the village of Podgorie, about eight kilometers northeast of Vashtemi. Strong typological

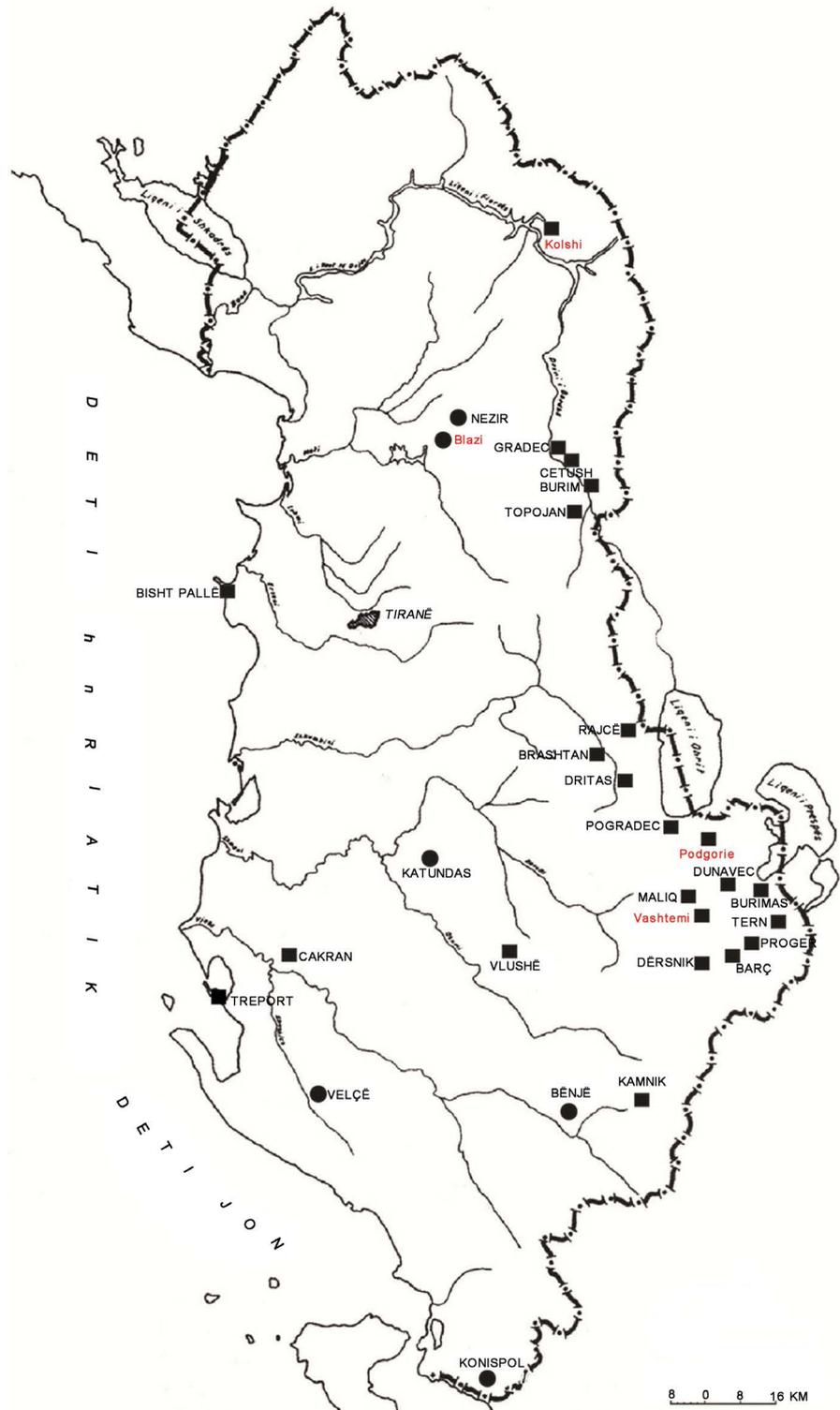


Figure 1. The distribution of Neolithic cultures in Albania.

similarities of the finds from this area with the finds from the Early Neolithic in the area of Thessaly indicate a direct cultural report between them. Pottery with 'impressed' decoration or Barbotine pottery was also found in minor quantity mainly in the upper horizons [4] [5]. The last excavations (2006-2013) and core

dates in Vashtëmi place it within the first wave of Early Neolithic settlements in the Korça basin. This recent study dates Vashtemi between 6470-6370 cal BC and Podgori between 6070-5970 cal BC [6].

The Blazi cave settlement, located in Mati river valley in northeast of Albania, was excavated by F. Prendi and Zh. Andrea from 1978 to 1979. Blazi early Neolithic culture shows special features that tie it with Adriatic group of Early Neolith. Blazi ceramics is characterized by coarse pottery, with grey, black or brown burnished exterior and predominantly Impresso type of decorations [4] [5].

Kolshi culture was excavated in 1974 due to some superficial findings from an expedition in Kukësi area. Kolsh ceramics is mainly with thick walls, with brown or reddish colour and barbotine decorations. The amount of fine ceramics is relatively small, and appears in carefully modeled shapes, with small dimensions and thin walls. The sherds from Kolsh are decorated with geometric motifs of red or dark brown colors on red background. The Kolsh culture shows similarities and connections with the culture of central Balkans [4] [5].

Although these cultures sprang from different origins, they were not isolated in their development but on the contrary entered into close contact with one another. This may be seen in the interchange of cultural elements, those of east Albania appearing in west Albania and vice versa; for example, the Barbotine pottery of Starcevo appearing in Blaz II, or “impress” pottery of Adriatic type at Vashtemi [4] [5].

3. Samples and Sample Preparation

We will consider here a small group of pottery shards from the collection of the excavations at four early Neolithic sites in Albania. The sites named Vashtemi and Podgori are situated in south east of Albania, while the sites named Kolsh and Blaz are situated respectively in the northeastern and northwestern part of the country. 20 - 30 shards from each site were selected by the archaeologists and we were allowed to cut small pieces and use them for the analysis. The shards from all the sites belong to pottery with thick and thin walls (**Figure 2**). Most of the shards show dark red and black color with black layers in the middle and some of them are painted on the surface.

Fresh cross sections of some of the shards were polished on successive grades of grinding paper (silicon carbide) and after cleaning and drying were used for optical microscopy and micro-XRF examinations. Standard thin sections have been prepared from the ceramic shards for the mineralogical and petrographic characterization.

The samples for EDXRF analysis were prepared in the form of thick pressed pellets. The shards were first cleaned from depositions (washed with distilled water) and dried overnight at 1050 C. Small pieces (5 - 6 g) were cut from the shards and were crushed and grinded in a mixer/mill for 15 min. The fine powder (<200 mesh) was converted to a pellet by pressing at 245 kN. The clay samples were treated and prepared in the same way. A portion of 1 - 2 grams

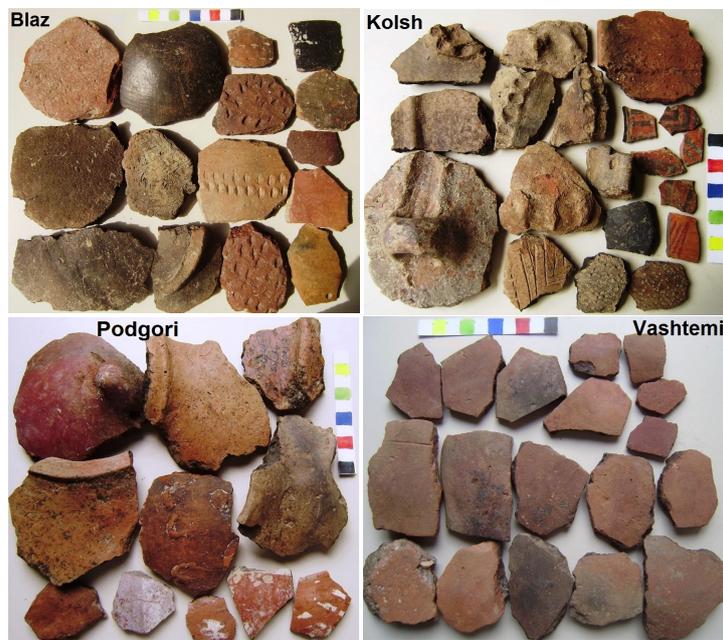


Figure 2. Ceramic shards from the studied sites.

from the same fine powder, placed in the sample holder with a flat surface, was used for XRD analysis in reflection mode.

4. Analytical Techniques

The microscopic petrographic investigations were carried out on a Leitz Laborlux 11 Pol S polarizing microscope.

The Micro-XRF spectrometer ARTAX 800 (Bruker) was used for the investigation of the ceramic cross sections and their surface decorations. The main parts of the spectrometer consist of an air cooled X-ray microfocus Rh-anode tube and a polycapillary X-ray lens (X-ray beam with spot size of 75 μm), an electrothermally cooled 10 mm² silicon drift detector (X-Flash) coupled with a digital signal processor and three stepping motors used for moving the measuring head in X, Y, Z directions. A colour CCD camera and a spot laser beam allow the reproducible positioning of the measuring head, as well as the visualization and documentation of the analyzed area. Helium atmosphere can be used to improve the excitation and detection efficiency of the low atomic number elements (Na, Mg, Al, Si). The spectrometer allows the collection of X-ray maps from the ceramic surface with a spatial resolution in the sub-mm range. In each pixel a spectrum was collected and the net characteristic peak areas of the detected elements were calculated. The X-ray maps, showing the variation of the element intensity over the measured area, were constructed using the three-dimensional matrix (X-pixels, Y-pixels, I-elements) and plotted in intensity readouts graphs. During the measurements the spectrometer was operated close to the maximum power (45 kV, 500 μA). The primary radiation was not filtered and the measuring time of 20 s per pixel allowed statistically significant intensities for most of

the elements in the spectra. Areas up to 10 mm² with spatial resolution of 0.1 mm were scanned in 5 - 6 hours.

The elemental composition of the samples was determined by EDXRF spectrometry. Two different EDXRF systems were used for the effective excitation of more than 20 elements in each sample. Elements from K to Zr were excited by a Mo secondary target and the 59.6 keV radiation of Am-241 source was used to excite the K lines of some heavier elements (Ba - Nd). The first system that uses the secondary target excitation mode, consists of a Philips 1729 X-ray generator equipped with Mo anode X-ray tube (max. 50 kV *40 mA); a 30 mm² Canberra Si(Li) detector, while the second system is based on 30 mCi Am-241 excitation source and 80 mm² PGT HpGe detector. Both systems use a 900 source-sample-detector geometry and similar pulse processing chains consisting of Canberra spectroscopy amplifier (Mod. 2024), ADC (Mod. 8706), S-100 and Accuspec B MCA cards installed on separate PC-s and Gennie 2000 software. Thin Mo and Pb foils were respectively used for filtering the scattered radiation and the low energy lines of the Am source in each of the systems. The operating conditions of each measurement are presented in **Table 1**.

The intensities of the analytes' line were calculated by the program AXIL [7]. An approximate sample composition, peak shape correction together with the other required parameters were included in the fitting model. The program COREX [8], which uses back scattered peaks and fundamental parameters, was used for the calculation of the concentrations of the elements excited by Mo secondary target. A set of about 40 "calibrators" prepared from pure elements and or compounds were measured in the same conditions and the results were used for the required experimental calibrations (Excitation-detection efficiency vs atomic number, mass absorption coefficient at Compton energy vs the intensity of Compton Peak and average atomic number of sample vs the ratio of the scattered peaks). The concentrations of Ba, La, Ce and Nd, excited by the Am-241 source, were calculated using the Compton scattered peak as internal standard [9]. As the composition of ceramic samples are generally similar to that of soils and sediments, a series of sediment reference materials (GSD1-12, Chinese stream sediment SRM-s [10], IAEA standards SL-1, Soil-5 and Soil-7 [11]) were used for calibration in this case.

In these conditions we could detect more than 20 elements in each ceramic sample. The calculated values of detection limits for the elements excited by the Mo secondary target vary from 150 - 100 mg/kg for K and Ca, 40 - 15 mg/kg for elements Ti - Fe and 4 - 12 mg/kg for Ni - Zr. The elements excited by Am-241

Table 1. Operating conditions of EDXRF measurements.

Elemental range	Source	Filter	kV/mA	Time (s)
K - Zr	Mo sec. target	Mo	35/20	1500
Sn - Nd	Am-241	Pb	-	2000

source show values of detection limits in the range 8 - 10 mg/kg. The precision of the procedure was evaluated by repeated measurements of the Standard Reference Material GSS-1 (Chinese soil SRM) [10], which was frequently measured together with the samples. From the data summarized in **Table 2** it can be seen that the relative standard deviations for major elements are better than 5%, while for minor elements it is generally within 15%, except for some elements that suffer line interferences, blank subtraction or have concentrations close to detection limit. The good agreement between the certified and the calculated concentrations for this standard is an indication of the good accuracy of the analytical procedure. Additional information about the EDXRF system and the analytical parameters of the procedure can be found elsewhere [12] [13].

PANALYTICAL XPERT-PRO MPD PW diffractometer was used for X-Ray diffraction analysis of some of the pottery samples. It is an X-ray computer controlled diffractometer system, having a fixed tube Cu target, secondary graphite

Table 2. Reproducibility of the determinations.

Element	GSS-1		Calculated	
	Certified	Average	St Dev	Rel St Dev (%)
K (%)	2.150	2.156	0.087	4.2
Ca (%)	1.230	1.181	0.045	4.0
Ti (%)	0.483	0.462	0.022	5.0
Fe (%)	3.630	3.675	0.053	1.5
V	86.0	102.7	25.7	26.3
Cr	62.0	66.7	11.9	18.7
Mn	1760.0	1750.7	48.2	2.9
Ni	20.4	23.4	4.4	19.7
Cu	20.9	24.5	5.5	22.7
Zn	680.1	672.8	15.8	2.5
Ga	19.3	17.8	1.9	11.4
As	33.5	32.7	5.5	17.7
Rb	140.0	143.7	1.8	1.3
Sr	155.0	162.7	2.3	1.5
Y	24.9	25.8	1.3	5.3
Zr	245.0	244.4	12.1	5.2
Pb	98.0	108.9	5.3	5.1
Th	11.6	11.2	1.2	11.7
Ba	590.0	585.5	7.4	1.3
La	34.0	30.4	4.5	14.5
Ce	70.0	67.1	2.1	3.3
Nd	28.0	27.9	2.5	9.5

monochromator, flat plate horizontal sample holder and X-Celerator for the faster acquisition of data. The diffractogram patterns were obtained by continuous scanning from 7.5° to 90° as 2θ angle. Angle step size is 0.013° and step time is 30 seconds. It was operated at 40 kV and 40 mA with a source of CuK α radiation of wavelength $\lambda = 1.5405 \text{ \AA}$.

The Windows based software package IDAS [14], which includes Hierarchical Cluster Analysis (HCA) and other multivariate methods, was used for data processing. HCA included in IDAS uses Euclidian distance as dissimilarity measure and minimum variance (Ward's method) as clustering strategy. Centered log ratio transformation was applied to the concentration data [15].

5. Results and Discussions

5.1. Mineralogical Composition

A small number of samples (3 - 4) from each site were investigated for their mineralogical composition using thin section petrography and X-ray diffraction. From each group we selected samples with different chemical composition.

The colour of the ceramic body varies from reddish-yellow to brown or reddish-brown. In cross section, the ceramic wall presents in general a bilayered texture, marked by an outer layer with lighter colour and an inner layer with darker colour (Figure 3). According to Rye [16], this type of structure can be due to firing in reducing conditions with an oxidizing cooling stage, or to firing organic matter-rich clays in oxidizing conditions. In either of these cases, it is difficult to judge the firing condition by naked eye observation of the paste colours.

The thin section petrographic examinations show that generally the fabric of the ceramic body is made of semifine clays with amorphous-microcrystalline structure and contains several voids with spherical and elliptical shape as well as different natural non-plastic inclusions, which belong either to the raw materials or were added as temper (Figure 4). The grains of the inclusions are generally angular to sub-angular and range from 1 - 3 mm in size. They constitute 10% - 15% of the volume in the shards from Kolsh and Blazi and about 5% in the sherds from Vashtemi and Podgorie.

In the shards from Kolsh and Blaz the non-plastic inclusions are mainly composed of quartz, plagioclase, mica (muscovite), clinopyroxene, calcite and opaque

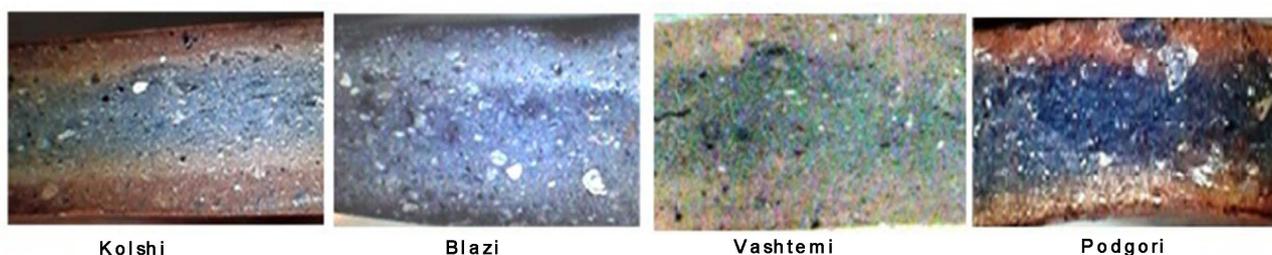


Figure 3. Cross sections of some shards.

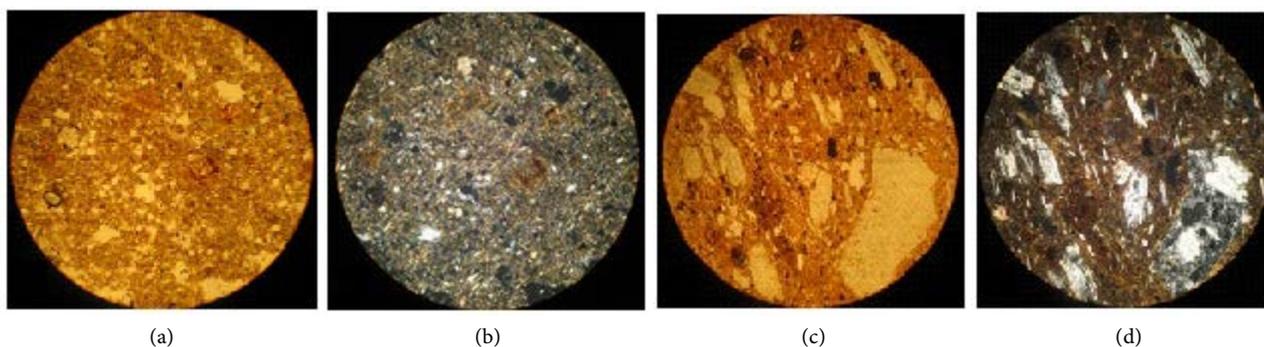


Figure 4. Thin section micrograph of Pod Nr. 813 (a), (b), Blaz Nr. 44 (c), (d). Images taken in plane polarized light and in cross-polarized light (PPL, XPL, $\times 10$).

minerals represented by hematite, while those from Vashtemi and Podgorie are mainly composed of quartz, plagioclase, mica (muscovite). Small potsherds and vegetal remnants (transformed into carbon) were also identified in some of the shards from each group.

X-ray maps obtained by micro-XRF spectrometer on a small area (10 - 15 mm²) of the cross section of some shards allow an approximate identification of some of the mineral inclusions in the respective clays. Intensity distribution maps (**Figure 5**) show the presence of Si, K, Ca and Fe rich particles, which can indicate the presence of the minerals rich in those elements, like silicates, calcite, K-feldspars, hematite, etc.

A limited number of samples from Vashtemi, Podgori, Blaz and Kolsh and the raw clays collected in the area of Vashtemi and Podgori were investigated with X-ray diffraction for the identification of main mineral phases (**Figure 6**).

The data collected are summarized in **Table 3**. These data show that quartz and albite are the main mineral phases observed in the shards for Vashtemi and Podgori, while in the shards from Blaz and Kolsh in addition to them calcite, diopside and hematite are also identified. This is in accordance with thin section petrographic results where clinopiroxene, calcite and hematite were observed among the non plastic inclusions of the shards from Blaz and Kolsh. This should be related with the different geological formations of the areas where the sites are located.

5.2. Elemental Composition

As was previously stated we have analyzed by EDXRF 96 ceramic shards from the Early Neolithic sites of Vashtemi, Podgori, Kolsh and Blaz. In each sample we have determined around 20 elements that include both major and minor elements.

The samples from each site were considered as a separate group and the range of concentrations for each element in the samples from each site are presented in **Table 4**.

Using the chemical data obtained by EDXRF for the body of all studied samples, bivariate graphs representing concentrations of Fe₂O₃ - CaO and Zr - Sr are plotted in **Figure 7(a)** and **Figure 7(b)**.

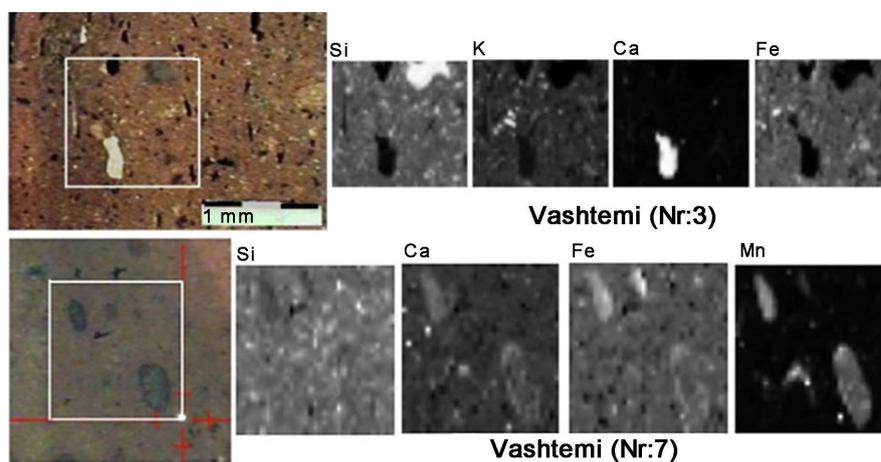


Figure 5. X-ray intensity distribution maps from the cross sections of some shards.

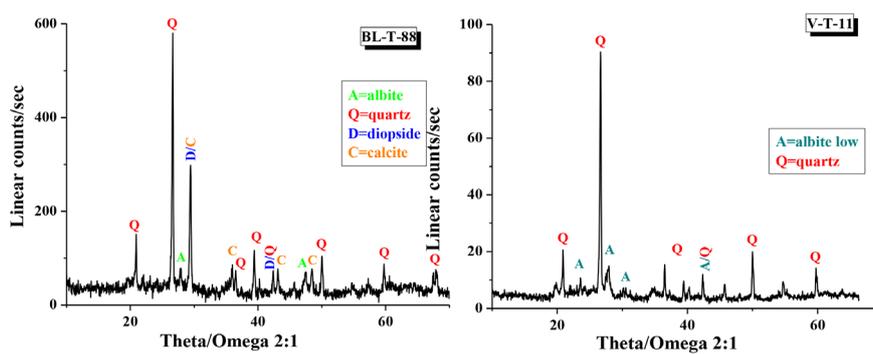


Figure 6. XRD spectra of two representative samples from Blaz and Vashtemi.

Table 3. The main mineral phases identified by XRD.

	Quartz	Calcite	Hematite	Albite	Diopside
P-CLAY	+	+		+	
Podgori T 1110	+			+	
Podgori T 700	+			+	
Podgori H 1230	+			+	
Podgori H 1343	+			+	
V-CLAY	+			+	
Vashtemi T 2	+			+	
Vashtemi T 11	+			+	
Blazi H 57	+				+
Blazi H 189	+				+
Blazi T 88	+	+		+	+
Blazi T 227	+		+	+	+
Kolsh T 427	+	+		+	
Kolsh T 1179	+		+	+	+
Kolsh H 887	+	+		+	

Table 4. The concentration range of the elements analyzed in the shards from each site. Concentrations in (mg/kg) unless otherwise indicated.

No. Samples	Vashtemi		Podgorie		Kolsh		Blazi	
	31		20		22		23	
	Min	Max	Min	Max	Min	Max	Min	Max
K ₂ O (%)	1.28	2.55	1.50	2.82	0.37	3.50	0.80	3.19
CaO (%)	1.72	3.73	1.95	5.14	1.19	8.39	0.66	17.85
TiO ₂ (%)	0.65	0.99	0.65	1.05	0.11	0.89	0.14	1.00
Fe ₂ O ₃ (%)	6.29	10.86	5.20	9.13	6.27	14.72	6.94	22.58
Cr	134	1351	81	495	83	1762	136	6334
Mn	592	1233	305	2441	685	1938	196	2946
Ni	96	476	47	477	163	1004	78	1074
Cu	13	36	6	37	33	199	7	97
Zn	95	146	64	148	63	146	63	169
Ga	7	26	13	28	4	29	4	32
Rb	75	130	81	188	15	131	24	118
Sr	170	278	107	402	46	236	14	95
Y	23	54	23	51	5	34	5	34
Zr	120	309	129	292	47	257	47	235
Ba	702	1153	439	942	148	1052	87	348
La	11	32	14	52	5	22	5	23
Ce	45	80	48	98	9	61	9	60
Nd	14	34	17	38	7	28	7	27

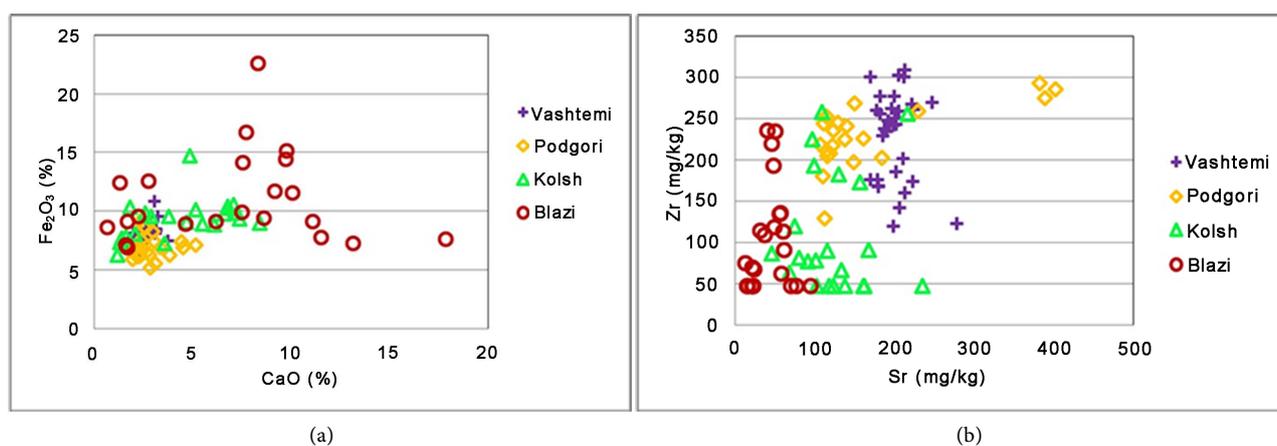


Figure 7. Bivariate plots of Fe - Ca and Zr - Sr of all the samples.

From **Figure 7(a)**, some initial conclusions can be derived regarding the raw materials employed for the production of the various pots, since they are directly connected to the chemical composition of the clay. The first indication obtained by the results is that almost all samples from Vashtemi and Podgorie exhibit low concentrations of Ca indicating the use of low calcareous raw materials (Ca-poor clays) for the manufacture of these wares. Generally, clays with CaO concentration less than 5% (Ca < 3.6%) are considered non-calcareous [17]. The situation

looks different for the shards from Kolsh and Blaz where respectively 45% and 60% of the shards are made of calcareous clays ($\text{CaO} > 5\%$).

Concerning the Fe_2O_3 concentration in the body paste of the samples, it is obvious from **Figure 7(a)** and **Table 4** that in the samples from Blaz it varies in a much wider range compared with the other groups. Its concentration is quite high in one sample from Kolsh and 5 samples from Blaz.

Bivariate plots of different major and minor elements indicate that most of the shards from Vashtemi and Podgori constitute rather compact groups although there are a few shards which can be considered as outliers from each group (**Figure 7**). It is worth noticing that in most of the cases the between group differences are not so large and the groups overlap but for some elements there exist observable differences of the concentration ranges of samples from different sites which can constitute evidence that different clay sources may have been used for these wares (**Figure 7(b)**). The situation appears different for the shards from Kolsh and especially Blaz where the concentrations of the elements vary in a wider range suggesting a quite frequent change of raw materials or different provenance of the pots.

A multidimensional data set consisting of 96 samples (rows) and 18 elements (columns) was created, demanding a multivariate statistical interpretation in order to extract the maximum useful archaeometric information. Hierarchical Cluster Analysis (HCA), specified earlier, was applied to the data matrix. It is worth mentioning that analytical variability, as presented in **Table 2**, doesn't influence the HCA results. In test runs of the HCA we included in the data set the results of one clay sample that was measured several times together with the samples and we found out that these artificial samples were always clustered together in the same cluster without affecting the general cluster structure.

HCA results with five clusters offers an acceptable resolution of the shards from different sites. The dendrogram in **Figure 8** shows that the maximum dissimilarity is observed between the majority of the shards grouped in clusters C3, C2 and C5 and the samples grouped in clusters C1 and C4.

The majority of the shards from Vashtemi, Podgorie and Kolsh are grouped in separate clusters with specific compositional profiles. In cluster 3 we have a group consisting mainly of the shards from Vashtemi (87% of them), 75% of the shards from Podgori are grouped in cluster 2, while in cluster 1 are grouped 73% of those from Kolsh. This is a strong indication of the local production activities at those sites. As it was previously mentioned, the shards from Blaz, showing a large variability of the elemental composition, are distributed between several clusters (C1, C2, C4 and C5). The clusters C4 and C5, with quite different compositional profiles, include mostly shards from Blaz (about 45% of them). The other shards from Blaz are distributed between the cluster C1 of Kolsh (8 shards) and the cluster C2 of Podgori (4 shards). Although there is clearly need for more research related with the shards from Blaz, based on these results both hypothesis of local production and import of pottery from other sides can be supported.

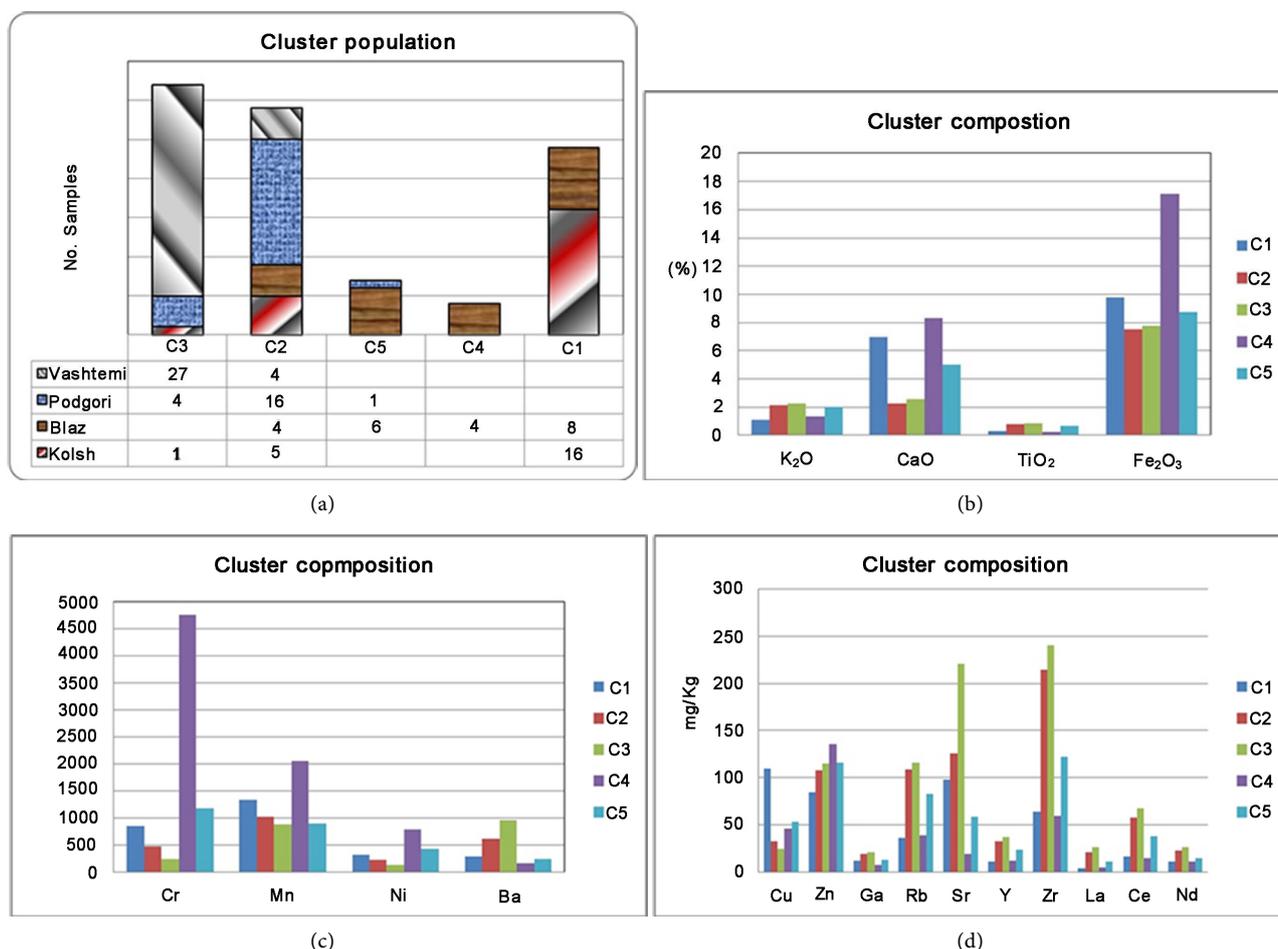


Figure 8. Results of the hierarchical cluster analysis; dendrogram, cluster population and cluster composition.

The presence of clusters C4 and C5 could indicate local production with different raw materials (clays and/or temper), while the similarities of a big number of shards with those from the sites of Kolsh and Podgorie could indicate commercial connections with those sites.

In conclusion we can state that separate clay deposits, close to each site, have been used for local ceramic production in the sites of Vashtemi, Podgorie and Kolsh. The variability of the chemical composition of the shards from Blaz supports both the local production and the import from other sites. We also observe that in each site the shards with thin and thick walls are clustered together, which means that they are manufactured using the same type of raw materials. The inclusion in the cluster C2 (group of Podgori) and C3 (group of Vashtemi) of a few shards from other sites could be an indication of the exchanges that could have been existing between the sites. However, more research is needed to fully support this hypothesis.

5.3. Decorations

Some of the investigated shards, especially those with thin walls from Podgori and Kolsh, have decorations with geometric motifs on the external surface. The

sherds from Podgori are mostly painted with white color on red background but one of the sherds is painted with bright red color, while the sherds from Kolsh are decorated with red or dark brown colors on red background. Generally the examined shards from Blaz and Vashtemi have not visible coloured decorations, although we have identified the remains of white colour on a shard from Blaz and those of brown colour on a shard from Vashtemi.

Initially the identification of the pigments used for the decorations were performed by comparing the micro-XRF spectra measured at the ceramic body with those from the colored areas, but later we thought that X-ray mapping of small areas from the decorated part of the ceramic could give better results. In this way we can clearly observe the variations of the intensity of different elements and connect the pigment with the respective “key elements”.

Some typical examples of the examined decorations are presented in **Figure 9**. In **Figure 9(a)** and **Figure 9(b)** are presented the results from the dark brown decorations of a shard from Kolsh and the remains of such a decoration of a shard from Vashtemi. The increased intensities of Mn and Fe in these decorations indicate the use of manganese rich pigments (some kind of brown earth). From **Figure 9(c)** it can clearly be observed that the white part of the decoration is rich in Ca while the red part is rich in Fe, which indicates the use of calcium white (probably calcite) and iron rich material (some kind of red ochre) for the white and red colours of the shards from Podgori. The increased Fe intensity of the red decorated area of the shard compared to the ceramic body indicates that the red colour is due to the application of a pigment and not any kind of red slip. In most of the shards we have found black spots or small areas with black colour which are rich in Ca and P. According to literature data they should be contaminations related with the environmental conditions of burial [18] [19].

Similar types of pigments were identified in studies of Neolithic ceramics from other areas in Balkans and Europe. Calcite, iron oxides and iron and manganese compounds (magnetite and jacobsite) were identified in the respective white, red and black pigments used to decorate Cucuteni Neolithic ceramics [20] as well as the Neolithic ceramics from North Greece [21]. Red ochre and soot were identified in the red and black decorations of the Neolithic ceramics from Slavonia, Croatia [22], while iron minerals haematite and maghemite were identified in the red decorations of the Neolithic ceramics from southern Spain, the later being an indicator of the firing conditions [23].

6. Conclusions

The investigation of ceramic finds from the Neolithic sites of South East Albania with different analytical techniques reveals interesting information regarding the materials and the technology used for their manufacture.

The results show that medium coarse, non-calcareous clays were used for the ceramic manufacture in the Early Neolithic sites in south-east Albania, while the situation looks different for the shards from Kolsh and Blaz where respectively 45% and 60% of the shards are made of calcareous clays ($\text{CaO} > 5\%$). Similar

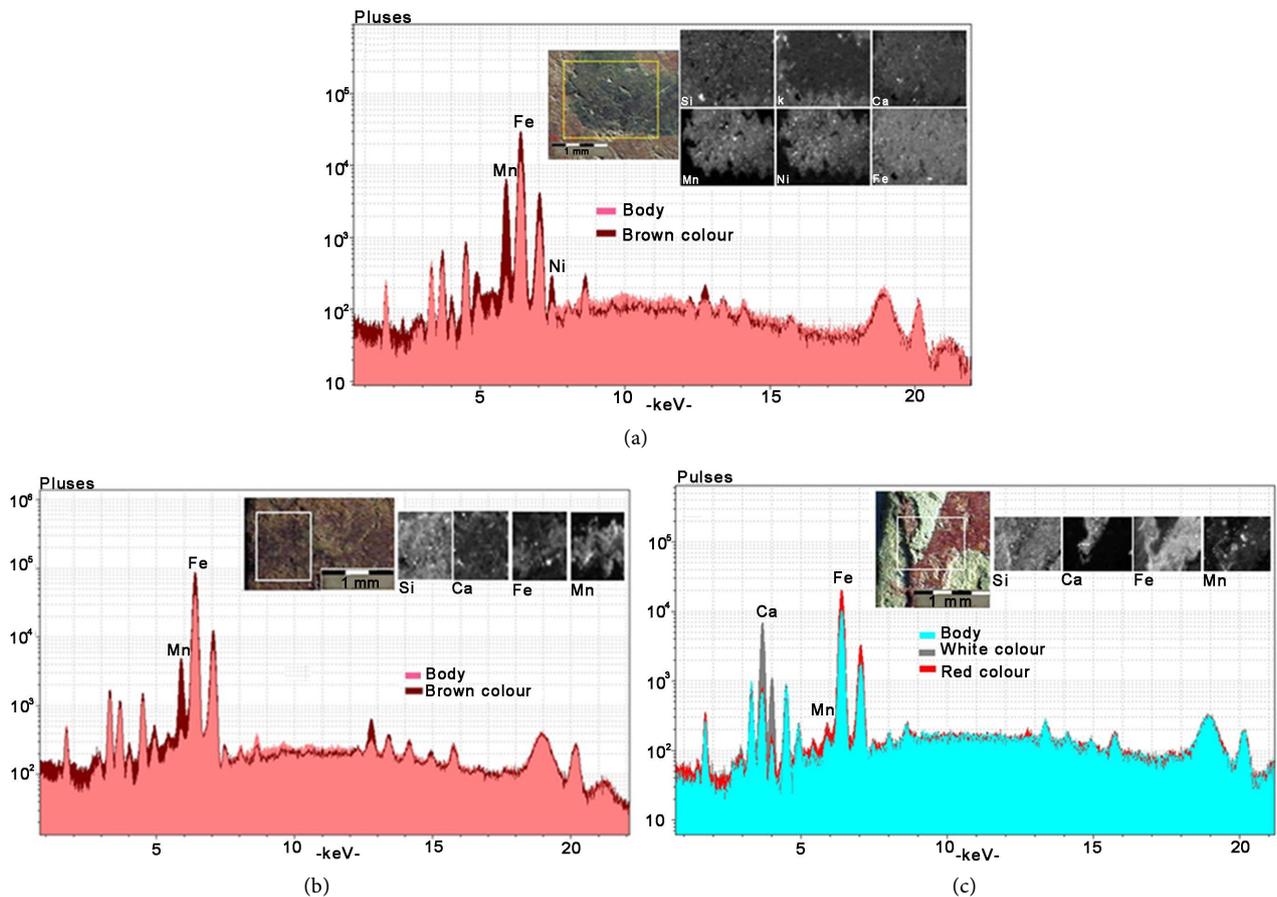


Figure 9. Comparison of X-ray spectra from the ceramic body and decorated areas and respective X-ray intensity distribution maps from the decorated surfaces of some shards from Kolsh (a), Vashtemi (b), Podgori (c).

differences, probably related with the geological formations of the respective areas, were observed in the mineralogical composition of the shards.

Separate clay deposits close to each site should have been used for ceramic production in Vashtemi, Podgori and Kolsh, while the variability of the chemical composition of the shards from Blaz supports both the local production and the import from other sites.

The examination of decorated sherds mostly from the sites of Kolsh and Podgori revealed that Ca-rich minerals (probably calcite), Fe-rich minerals (red ochre) and Mn-rich minerals (brown earth) were used respectively for the white, red and brown colours. It should be mentioned that similar types of pigments were found by other researchers on the Neolithic ceramics from different sites in Balkan and Europe.

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