Scientific Research Publishing

Journal of Materials Science and Chemical Engineering, 2017, 5, 71-89
http://www.scirp.org/journal/msce
ISSN Online: 2327-6053
ISSN Print: 2327-6045

Investigation of Pottery from Different Neolithic Sites in Southeast Albania Using Various Analytical Techniques

Erinda Ndreçka[1,2], Nikolla Civici[1], Ilir Gjipali[3], Filippo Niccolai[4], Stefano Ridolfi[5]

[1]Institute of Applied Nuclear Physics, University of Tirana, Tirana, Albania
[2]Department of Physics, Faculty of Natural Science, University of Tirana, Tirana, Albania
[3]Institute of Archaeology, Centre of Albanian Studies, Tirana, Albania
[4]Sinerlab S.r.l., Quarrata (PT), Italy
[5]Ars Mensurae, Rome, Italy

Email: erinda.ndrecka@hotmail.com

How to cite this paper: Ndreçka, E., Civici, N., Gjipali, I., Niccolai, F. and Ridolfi, S. (2017) Investigation of Pottery from Different Neolithic Sites in Southeast Albania Using Various Analytical Techniques. *Journal of Materials Science and Chemical Engineering*, **5**, 71-89.
https://doi.org/10.4236/msce.2017.57009

Received: May 23, 2017
Accepted: July 9, 2017
Published: July 13, 2017

Abstract

In this paper we will consider the results of the investigation of ceramic shards from four Neolithic sites located in the south-east of Albania using different analytical methods. The sites of Vashtëmi, Podgori, Dunavec and Maliq, situated at the plateau of Korça, represent the Neolithic culture at the different stages from Early Neolithic to Eneolithic. The application of EDXRF, micro-XRF, XRD and Optical Microscopy (OM) allowed us to collect data on the mineralogical and elemental composition of the ceramics and the materials used for the external decorations. The results indicate that coarse to medium coarse, non-calcareous clays were used for the ceramic manufacture in all the sites. Mineral inclusions rich in Si, Ca, K, and Fe were identified, some of which could have been intentionally added to the clays during the production process. The similarities of the elemental composition of the shards indicate that the ceramics in each site were prepared from different clay deposits that should have been close to each site. Minerals rich in Ca, Fe and Mn have been used respectively for the white, red and dark brown surface decorations, while bitumen has been applied after the firing in a black decoration.

Keywords

Neolithic Ceramics, EDXRF, Micro-XRF, Albania

1. Introduction

Potteries are the most abundant findings among the archeological artifacts. Pottery analysis reveals information regarding the daily life and cultural aspects of the society of the ancient period. The technical skills of the ancient potters have been the subject of active research for gaining a deep insight of forgone culture [1]. The Neolithic period is of great importance regarding pottery production, since the Neolithic civilizations brought in contact clay with fire to produce materials which are particularly hard and resistant to meet the requirements of the newly emerged needs for tools and resources at that time [2]. In addition, it is generally accepted that studies at several Neolithic sites lead to contradictory findings regarding the pottery distribution, thus, putting into question the role of pottery as an exchange item in this period [3].

From an archaeological point of view, the Neolithic sites discovered in the plateau of Korca, situated in south-east of Albania, are of great importance, since within a rather small territory you find different sites that have been inhabited from Early Neolithic to Eneolithic. The sites of Vashtëmi and Podgori belong to the Early Neolithic, and the site of Dunavec belongs to Middle Neolithic while in Maliq the different layers represent the Late Neolithic and the Eneolithic periods [4] [5]. The considerably large number of Neolithic ceramics of various types, styles and decorations discovered at these sites can give information on the materials and technologies used for their manufacture at different stages of social development within similar environmental conditions and resources. The analytical data on the materials and technologies used for the production and decoration of the ceramics can complement the archaeologists' observations of the local or imported character of the pottery and contribute for a better characterization and classification of the ceramic finds.

According to the literature, only a few archaeometric studies have been conducted concerning the chemical composition and/or provenance of the Neolithic pottery in Albania and especially for the ceramics from Early Neolithic sites of Podgori and Vashtëmi [6]. The author has observed differences in both the composition and the quality of the ceramics from both sides concluding that a direct connection between the sites cannot be demonstrated.

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 at the different sites and based on them to find similarities and/or differences that can be useful for better archaeological classifications. First we will investigate if the analytical data of the pottery from Vashtemi and Podgori can give clues of any kind of connection between the two sites and after that we will extend the comparison to the pottery from later Neolithic sites of Dunavec and Maliq. In addition to the chemical and mineralogical composition of the shards, we have investigated the materials used for their decoration, which constitutes the first attempt of such a study for the ancient pottery in Albania.

In this context different X-ray techniques (EDXRF, Micro-XRF, XRD), Optical Microscopy (OM) 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 Neolithic sites in southeast Albania. OM and XRD were used for the investigation of the internal texture of the ceramic body and their mineralogical composition while μ-XRF was used for the identification of the materials used for external decorations (paints and slips). EDXRF spectrometry was employed for the chemical composition determination of the pottery, since it is quite advantageous compared to other techniques due to the coexistence of three significant features; it is a non-destructive multi-elemental technique and the analysis requires less time and has a relatively lower cost than other similar techniques [1] [2]. The evaluation of the chemical data through simple elemental biplots 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.

2. Archaeological Background

The territory of present Albania was penetrated during the Neolithic period by cultural elements from various sources, which influenced its civilization. And in fact, at certain stages of this evolution, there grew up geographical units or groups which, as they developed, were oriented either towards the Aegean and the Central Balkans, or towards the Adriatic zone. The evolution of Neolithic civilization can be followed in Albania over three periods: Early, Middle and Late Neolithic. A separate cultural development, here called Eneolithic, took place as a transitory stage leading from the Neolithic Age to the Bronze Age [4].

The Korça region consists of a large plateau located in the mountainous south eastern part of the country, along the western shores of the lakes Ohrid, Prespa e Madhe and Prespa e Vogël (Mikri), which are shared with the Republic of Macedonia and Greece (**Figure 1**). The fertile plateau of this region together with the existence of the shallow Lake Maliq, now drained, offered suitable living conditions for the early farmers. Due to these conditions this region represents the most intensely occupied area in Albania, especially during the Neolithic, Copper and Bronze Ages [6]. All the studied sites have been located around Lake Maliq.

The classic phase of Early Neolithic in this region is represented by the Vashtemi culture. The site at Vashtemi is situated some eleven kilometers north of Korce. The excavations of 1974, 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. This layer also contained pottery with' impressed' decoration, made with the finger-nails or with a pointed tool. Barbotine pottery was also found, but only in the upper horizons. All these features are equally evident in some huge deposits at the village of Podgorie, about eight kilometers northeast of Vashtemi. Previous research relied mostly on stylistic similarities and rough typological frequencies of the ceramic finds, conclude that Vashtëmi and Podgori belong to the same cultural group [4]. Although, some visible differences es-

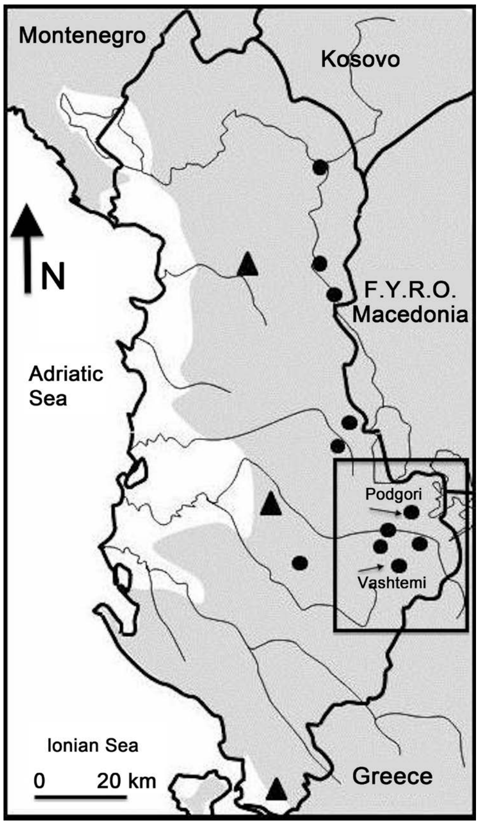


Figure 1. Map of Early Neolithic sites in Albania. Circles represent open-air sites; triangles represent cave sites. The rectangle in the SE is the focus of this study [6].

pecially in the quality of the white-on-red pottery, where the white paint is smoother and better-attached to the body of the pot in the Podgori ceramics than in Vashtëmi, point towards a differentiation between the two sites putting Vashtëmi as the earliest Neolithic site in that area [4] [5]. Differences in raw materials for ceramic productions between the two sites were also observed [6]. 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 Vashtëmi between 6470-6370 cal BC and Podgori between 6070-5970 cal BC [7]. Strong typological 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 [4] [5].

The most important sites of the Middle Neolithic period culture in Albania are those of Cakran (Central Albania) and Dunavec situated some five kilometers north of Korca. This period is mostly characterized by coarse impressed and Barbotine pottery, plain coloured ware, chiefly grey-black and black, and a finer pottery which differs from the two preceding types by more careful modelling and by its lustrous surface, generally dark grey or black [4] [5]. Amongst the different vase shapes, the most typical in this group are biconical cups with a variety of profiles and vases with four feet known as cult-rhytons. Ornamentation on both the common and the finer pottery shows knowledge of a number of decorative techniques. Incised geometric decoration and plastic decoration predominate; more rarely, one finds impressed decoration, encrustation in white, perforations, and designs painted in dark patterns on a light background.

Late Neolithic settlements have been found in a number of places in Albania, but the deposits discovered at Maliq in 1961 are considered the most representative. The deposits consist of different layers which extend from late Neolithic to the Eneolithic period. The Late Neolithic pottery is varied both in its shape and decoration. But what especially characterizes this level is a fairly fine pottery, with a polished grey-black surface; and also pottery painted before and after firing. One type of pottery predominates, with monochrome motifs applied directly on to the natural clay, or on to a glaze of various ochre, cream or light red tones. The main decorative colour is brown and other colours like grey, dark red, orange are found less frequently [4] [5].

The Eneolithic culture in Maliq is characterized by its pottery, especially the fine grey or grey-black pottery of various shapes and with fairly rich decoration of several kinds: painted, incised, encrusted, recessed, and in relief. For painted pottery grey is the predominant colour. Black paint is much less frequent, and when it occurs it is often combined with grey decoration [4] [5].

3. Samples and Sample Preparation

Representative groups of 20 - 30 shards from the four Neolithic sites of Vashtemi, Podgori, Dunavec and Maliq (**Figure 2**) were selected by the archaeologist 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. Most of them have dark red and black color and some of them are painted on the surface.

Figure 2. Ceramic shards from Vashtemi, Podgori, Dunavec and Maliq.

A total of six clay samples, collected from sources around Vashtëmi (4 samples), Podgori and Maliq (one sample each) during the excavation season, were included in the study with the purpose of comparing their composition with our ceramic shards. The clay is not used anymore for pottery making in the villages around Vashtëmi and Podgori, but in some areas is still used as a building material (this information was obtained by the local construction companies).

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 105˚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 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.

PANALYTICAL XPERT-PRO MPD PW diffractrometer 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 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˚ - 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 Cu Kα radiation of wavelength $\lambda = 1.5405$ Å.

The Micro-XRF spectrometer ARTAX 800 (Bruker) was used for the investigation of the ceramic surface decorations and their cross sections. An air cooled X-ray microfocus Rh-anode tube and a polycapillary X-ray lens are used to provide the X-ray beam with spot size of 75 μm for Mo Kα at the sample surface (measured experimentally). An electrothermally cooled 10 mm^2 silicon drift detector (X-Flash) coupled with a digital signal processor are used for the X-ray detection. Three stepping motors are used for moving the measuring head in X, Y, Z directions, while 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 analysed area. To improve the excitation detection efficiency of the low atomic number elements (Na, Mg, Al, Si) the spectrometer allows measurements in Helium atmosphere.

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 mm^2 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 mm^2 Canberra Si(Li) detector, while the second system is based on 30 mCi Am-241 excitation source and 80 mm^2 PGT HpGe detector. Both systems use a 90˚ 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 [8]. An approximate sample composition, peak shape correction together with the other required parameters were included in the fitting model. The program COREX [9], 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 [10]. As the composition of ceramic samples are generally similar to that of soils and sediments, a series of sediment reference materials (GSD1 - 12,

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

Chinese stream sediment SRM-s [11], IAEA standards SL-1, Soil-5 and Soil-7 [12]) 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 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 8%, 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 concen-

Table 2. Reproducibility of the determinations. Repeated measurements of SRM GSS-1.

SRM	GSS-1			
Element	Certified	Calculated		
		Average	St Dev (2 sigma)	Rel St Dev (%)
K (%)	2.15	2.156	0.156	7.2
Ca (%)	1.229	1.181	0.094	8.0
Ti (%)	0.485	0.462	0.035	7.7
Fe (%)	3.63	3.675	0.191	5.2
V	86	102.7	36.3	35.4
Cr	62	66.7	17.9	26.8
Mn	1781	1750.7	115.6	6.6
Ni	20.4	23.4	6.4	27.5
Cu	21	24.5	6.6	27.0
Zn	680	672.8	43.3	6.4
Ga	19.3	17.8	2.6	14.6
As	33.5	32.7	6.2	19.1
Rb	140	143.7	8.8	6.1
Sr	155	162.7	10.0	6.2
Y	25	25.8	2.4	9.5
Zr	245	244.4	19.0	7.8
Pb	98	108.9	11.1	10.2
Th	11.6	11.2	2.1	18.4
Ba	590	585.5	35.9	6.1
La	34	30.4	5.4	17.9
Ce	70	67.1	5.1	7.7
Nd	28	27.9	3.5	12.7

trations 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 [13] [14].

The Windows based software package IDAS [15], 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 logratio transformation was applied to the concentration data [16].

5. Results and Discussion

5.1. Mineralogical Composition and Internal Texture

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

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**). It is generally accepted that the existence of this layer can serve either as a sign of a non-uniform firing in the whole body of the ceramic (insufficient firing time for the organic material within the clay to have been burnt out) or it can be an indication of the firing of ceramics in a reducing atmosphere followed by a fast final oxidizing stage [1] [17].

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 5% - 10% of the volume in the shards. The non-plastic inclusions are mainly composed of quartz, plagioclase, mica (muscovite), calcite and opaque minerals represented by hematite. Small potsherds and vegetal remnants (**Figure 4(E)**) were also identified in some of the shards from each group

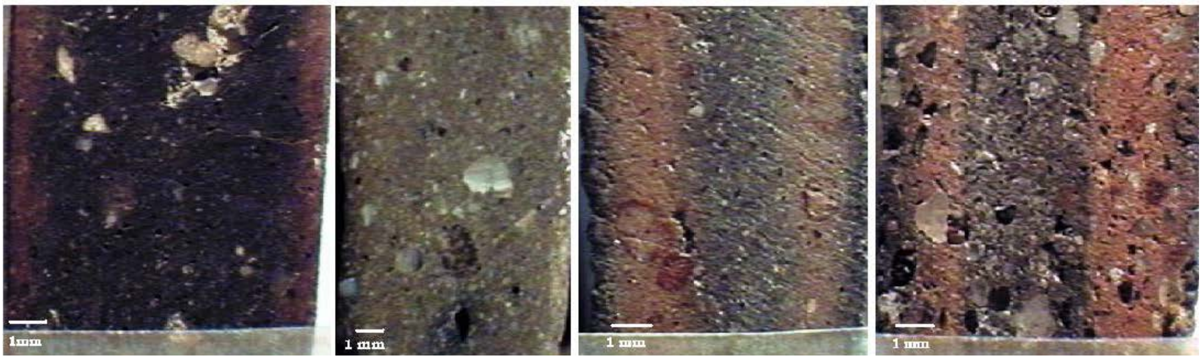


Figure 3. Photo of the cross sections of some shards from the sites (×13).

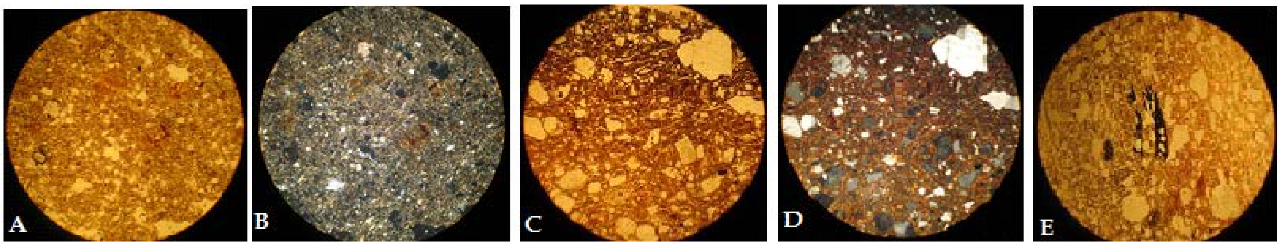


Figure 4. Thin section micrograph in plane polarized light and in cross-polarized light (PPL, XPL, x10) of Pod Nr. 813 ((A), (B)), Dun Nr. 75 ((C), (D)); Micrograph of a bioinclusion Dun Nr. 603 (E).

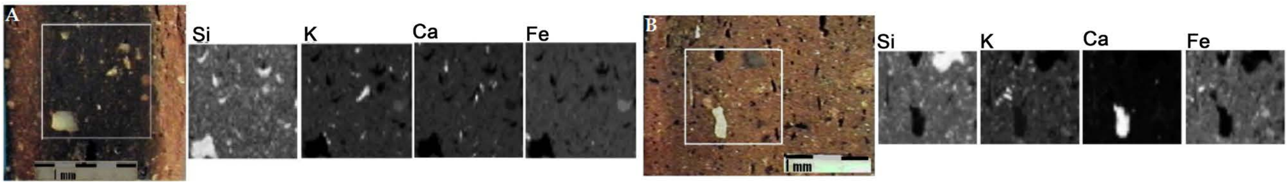


Figure 5. X-ray intensity distribution maps from the cross sections of some shards.

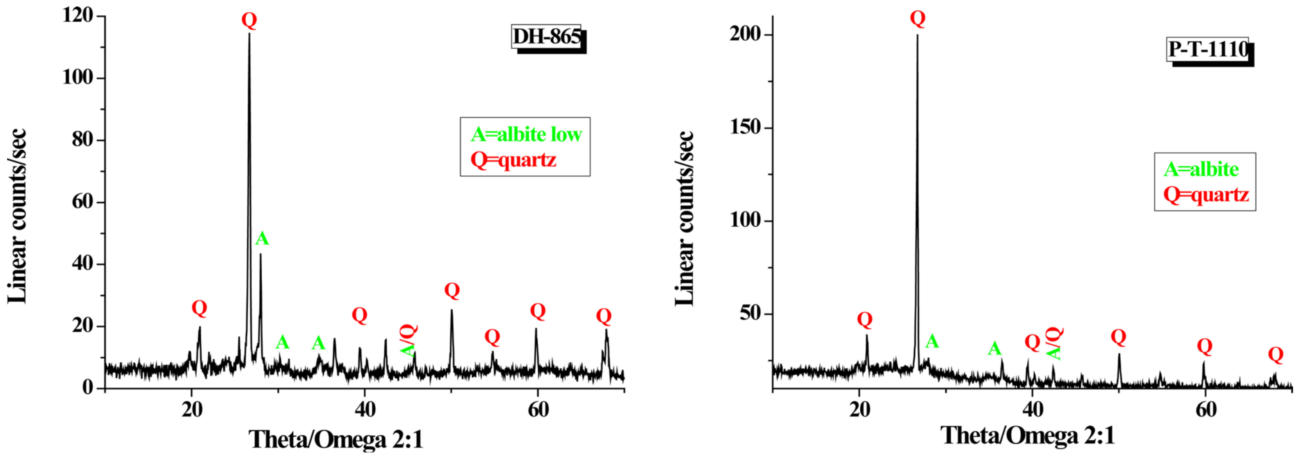


Figure 6. XRD spectra of two representative samples.

X-ray maps obtained by micro-XRF spectrometer on a small area (10 - 15 mm^2) 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 each site 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 Dunavec and Maliq in addition to them calcite, muscovite and orthoclase are also identified in different shards.

The mineralogical compositions show that the shards form all sides are made of similar raw materials. The clays used for the pottery reflect the Quaternary clays of the Korca basin and similar type of temper (clasts) were used for their

Table 3. The main mineral phases identified by XRD.

	Quartz	Albite	Calcite	Muscovite	Orthoclase
V-Clay	+	+	+		
Vashtemi T 2	+	+			
Vashtemi T 11	+	+			
P-Clay	+	+	+		
Podgori T 1110	+	+			
Podgori T 700	+	+			
Podgori H 1230	+	+			
Podgori H 1343	+	+			
Dunavec H 896	+	+		+	
Dunavec H 507	+	+			
Dunavec H 865	+	+			
Dunavec T 48	+	+		+	+
Maliq V H 1246	+	+			
Maliq V T 735	+	+	+	+	
Maliq Eneol H 1242	+	+		+	
Maliq Eneol T 450	+	+		+	

manufacture. The main observed differences are related with the grain sizes (mainly semifine but also fine and coarse) and the use of biological material, which is not observed in every shard.

5.2. Elemental Composition

As was previously stated we have analyzed by EDXRF about 120 ceramic shards from the Neolithic sites of Podgori, Vashtemi, Dunavec and Maliq as well as the six clay samples collected in the area. 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 minimum and maximum concentrations of the elements from each group are presented in Table 4, while the results obtained for the clay samples are presented in Table 5.

Using the chemical data obtained by EDXRF, bivariate graphs representing the concentrations of Fe-Ca and Zr-Sr respectively, for the clay body of all studied samples are plotted in Figure 7(A), Figure 7(B). From Figure 7(A), some initial conclusions can be derived regarding the raw materials employed for the production of the various wares, since they are directly connected to the chemical composition of the clay. The first indication obtained by the results is that almost all samples exhibit low concentration 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 [1] and this limit is exceeded in only 5 samples most of which are from the site of Maliq and two clays from Vashtemi that have Ca close to 10%. Concerning the Fe concentration in the clay paste of the samples, it is obvious from Figure 7(A) and Table 5 that in almost all samples it lies between 3% - 8%, with samples from Vashtemi and Podgori mostly in the upper part of the range and samples from Dunavec and Maliq in the lower part. The plot of Zr vs Sr presented in Figure 7(B) shows that the concentration range of Zr in the shards from Maliq is higher than in the other groups and it can be an indication of the specific clays deposits used for their manufacture.

Bivariate plots of different elements indicate that most of the shards from each site 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

Table 4. The minimum and maximum concentration values of the elements analyzed in the groups of shards from each site. Concentrations in (mg/kg) unless otherwise indicated.

Period	Early Neolithic				Middle Neolithic		Late Neolithic		Eneolithic	
Site	Vashtemi		Podgorie		Dunavec		Maliq V		Maliq E	
No. samples	31		20		25		22		24	
	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max
K_2O (%)	1.28	2.55	1.50	2.82	1.96	2.79	1.66	3.23	0.39	2.25
CaO (%)	1.72	3.73	1.95	5.14	1.06	3.41	0.74	9.39	1.01	6.54
TiO_2 (%)	0.65	0.99	0.65	1.05	0.83	1.02	0.71	1.17	0.72	1.08
Fe_2O_3 (%)	6.29	10.86	5.20	9.13	3.90	6.72	4.60	8.92	4.05	8.40
V	96	300	35	257	95	334	80	312	30	326
Cr	134	1351	81	495	17	255	76	569	53	885
Mn	592	1233	305	2441	442	853	480	1406	464	1058
Ni	96	476	47	477	82	189	35	284	78	473
Cu	13	36	6	37	11	28	9	32	5	34
Zn	95	146	64	148	72	142	78	132	75	127
Ga	7	26	13	28	12	22	13	23	12	21
Rb	75	130	81	188	91	153	80	170	96	137
Sr	170	278	107	402	119	596	69	573	89	203
Y	23	54	23	51	21	40	26	56	20	41
Zr	120	309	129	292	169	272	417	855	431	778
Pb	10	48	10	45	10	45	31	45	30	50
Th	6	21	12	22	9	19	7	12	5	12
Ba	702	1153	439	942	571	1369	400	1153	387	1253
La	11	32	14	52	13	42	27	60	22	42
Ce	45	80	48	98	48	91	50	110	49	104
Nd	14	34	17	38	18	36	23	49	18	39

Table 5. Elemental composition of the clay samples. Concentrations in (mg/kg) unless otherwise indicated.

	Podg 1	Vasht 1	Vasht 500	Vasht 501	Vasht 502	Maliq 503
K (%)	2.28	2.21	2.59	1.92	2.01	1.77
Ca (%)	1.96	1.01	10.06	0.74	9.20	0.44
Ti (%)	0.55	0.50	0.38	0.47	0.37	0.49
Fe (%)	4.95	4.03	3.62	5.78	4.22	4.35
V	321	328	318	455	209	327
Cr	656	597	255	926	575	506
Mn	1315	958	546	995	711	792
Ni	231	118	106	586	391	160
Cu	28	13	16	17	11	12
Zn	122	90	106	79	71	68
Ga	9	4	5	8	3	4
Rb	163	123	129	119	92	115
Sr	87	91	277	56	173	62
Y	41	31	27	31	24	34
Zr	293	279	232	198	184	264
Pb	47	39	41	43	30	40
Th	11	8	11	10	8	10
Ba	452	531	621	343	263	335
La	44	38	34	30	30	38
Ce	85	78	55	60	49	70
Nd	35	37	28	30	22	36

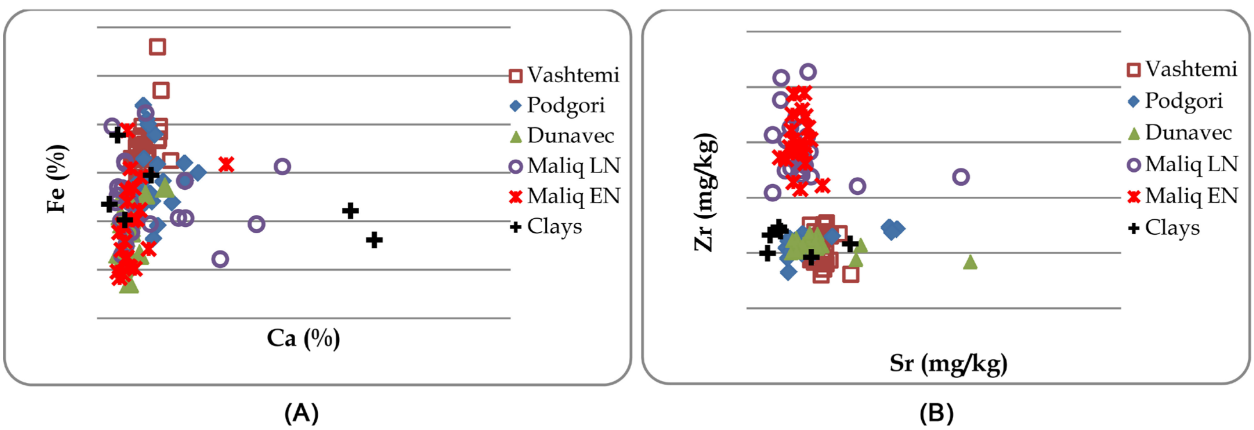


Figure 7. Bivariate plots of Fe-Ca and Zr-Sr of all the samples.

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 be used for these wares (Figure 7(B)).

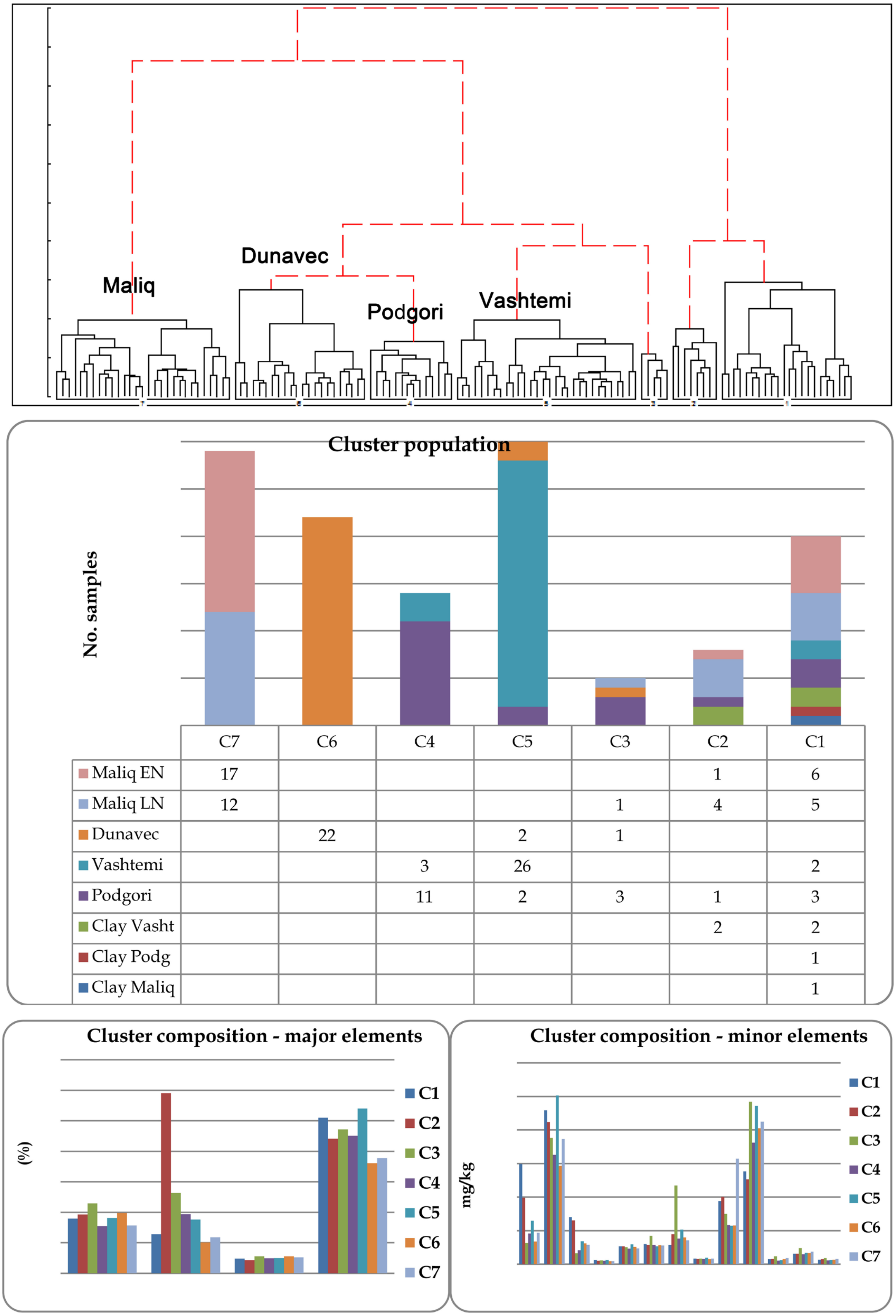
In order to extract the maximum useful archaeometric information Hierarchical Cluster Analysis (HCA), specified earlier, was applied to the data matrix, which consisted of 130 samples (rows) and 17 elements (columns). The elements with high uncertainty (V, Ga, Pb and Th) were excluded from the data base. 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 of the clays 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 seven 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 - C7 and the samples grouped in clusters C1 and C2 which include some shards from almost every site and the clay samples. So it appears that there is not a clear correspondence between the majority of the pottery and clays. This could be related with the fact that the collected clays represent soils from the surface or the excavated layers which could be easily found and used in the respective areas, while more and probably better clay deposits should have existed close to the now drained, shallow Lake Maliq, around which all the sites were situated. The compositional similarity of some shards with the collected clays can also indicate the existence at each site of different workshops or the same workshop used different raw materials depending on the purpose or quality of the pots. This can be an explanation especially for the shards from Maliq LN and EN which are distributed between clusters 1 and 7 in relatively big proportions. The majority of them (12 out of 22 LN and 17 out of 24 EN) form a quite definite separate group in cluster 7, while the rest of the shards show compositional similarities with the clays in clusters 1 and 2. It is, also, interesting to note that this practice should have been in use throughout the existence of the site from LN to EN. The majority of the shards from the other sites are also grouped in separate clusters with a specific compositional profile. 88% of the shards from Dunavec are grouped in cluster 6, in cluster 5 we have a group consisting mainly of the shards from Vashtemi (85% of them), while in cluster 4 are grouped 55% of those from Podgori.

In conclusion we can state that separate clay deposits, close to each site, have been used for ceramic production. This is what we expected because the sites were active in different periods of time, except Vashtemi and Podgori which could have coexisted at least for some time. The inclusion of a few shards from Podgori in the cluster of Vashtemi and vice versa can be a weak indication of the exchanges that could have been exiting between the two sites. More research is needed to fully support this hypothesis. In addition we 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.

5.3. Decorations

Some of the investigated shards, especially those with thin walls from Podgori



	C7	C6	C4	C5	C3	C2	C1
Maliq EN	17					1	6
Maliq LN	12				1	4	5
Dunavec		22		2	1		
Vashtemi			3	26			2
Podgori			11	2	3	1	3
Clay Vasht						2	2
Clay Podg							1
Clay Maliq							1

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

and Maliq (Late Neolithic), have signs of decorations with geometric motifs on the external surface. The shards 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 Maliq LN are decorated with red or dark brown colors on red background. Generally the examined shards from Dunavec and Maliq Eneolithic are not painted while in those from Vashtemi we could find traces of previously existing decorations in a few shards although they were not clearly visible.

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'. In **Figure 9** are compared the XRF spectra measured at the ceramic body and at the decorated area together with the X-ray distribution maps of the decorated areas from some shards.

Some typical examples of the examined decorations are presented in **Figure 9**. From **Figure 9(A)** 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. The red decoration of the shard from Maliq LN (**Figure 9(B)**) is also rich in Fe but in this case it is associated with Ni and Cr indicating a different type of red ochre, probably from the deposits of iron-nickel mineral situated in Pishkash, Albania, north of the Ohrid Lake. Similar composition of Fe associated with Ni is found at the shard from Maliq LN (**Figure 9(C)**) and the dark colour of the decoration should probably be related with the firing process (firing in reducing atmosphere) [16]. It should also be mentioned that the composition of the pigments could be influenced by the process of their application on the ceramic body. Several researchers suggest that the decoration of the pottery surface was produced by using mineral pigments mixed with a clay-water suspension and applied as a clay slip [18] [19]. The black decoration of the shard from Maliq EN (**Figure 9(D)**) should probably have been prepared after the firing using bitumen as the black area is rich in sulphur with traces of vanadium, while manganese rich pigments (some kind of brown earth) are used for the brown colour decoration of the shards from Maliq LN and Vashtemi (**Figure 9(E)**, **Figure 9(F)**). In most of the shards we have found black spots or small areas with black colour which are rich in Ca and P, similar to the ones in **Figure 9(B)**, **Figure 9(C)**. According to literature data they should be contaminations related with the environmental conditions of burial [20] [21].

It is interesting to notice that calcite, iron oxides and iron and manganese

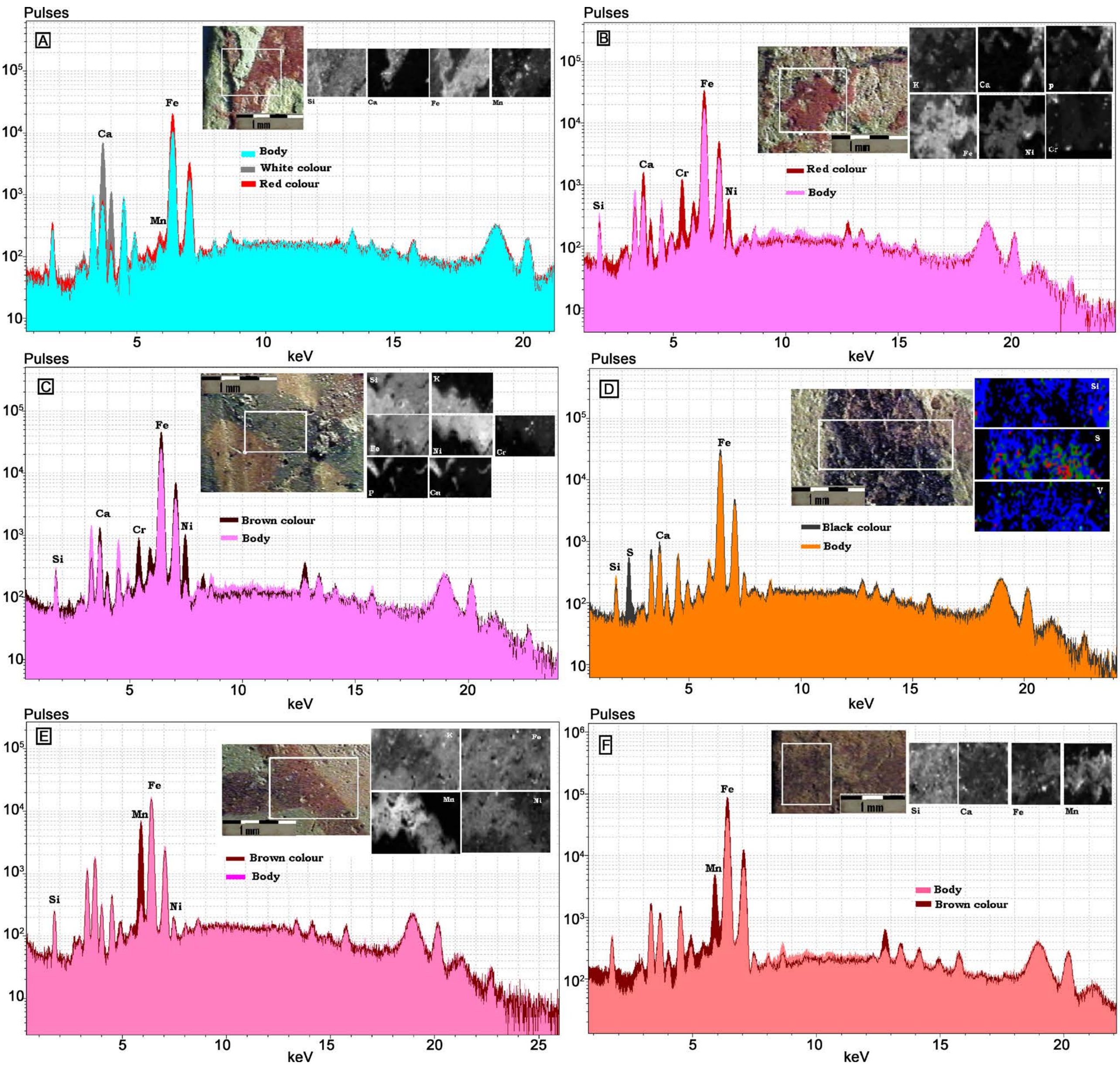


Figure 9. Comparison of the X-ray spectra from the body and decorated areas and X-ray intensity distribution maps from the decorated surfaces of some shards from Podgori (A), Maliq LN ((B), (C), (E)), Maliq EN (D) and Vashtemi (F).

compounds, such as magnetite and jacobsite, were identified in the respective white, red and black pigments used to decorate Cucuteni Neolithic ceramics [18] as well as the Neolithic ceramics from North Greece [19]. 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 reveal interesting information regarding the materials and the technology used for their manufacture.

The mineralogical compositions show that the shards from all sides are made of similar raw materials. The clays used for the pottery reflect the Quaternary clays of the Korca basin and similar type of temper consisting mostly of sand, crushed sherds and organic material in some cases were used for their manufacture. The main observed differences are related with the grain sizes (mainly semifine but also fine and coarse) and the use of biological material, which is not observed in every shard.

The elemental compositions of the shards show that mostly medium coarse, non-calcareous clays were used for the ceramic manufacture in all the sites that cover all the Neolithic period. Separate clay deposits close to each site have been used for ceramic production, although the data suggest the possibility that different clays could have been used for different types or quality of pots especially in Maliq. The same clay deposits close to Maliq should have been used for a quite long period from the Late Neolithic to Eneolithic. The data don't provide any significant clue that can indicate any connection between the Early Neolithic sites of Vashtemi and Podgori.

Micro-XRF spectroscopy was used for the examination of pigments on several decorated sherds mostly from the sites of Podgori and Maliq. The results show that Ca rich minerals (probably calcite) were used for the white colour, while different types of Fe rich minerals (ochre) were identified in the red colours. The dark brown colours were mostly prepared using Mn rich minerals but in one case we found the dark brown colour prepared with Fe rich minerals probably fired in reducing atmosphere. The black decoration of the shard from Maliq EN should probably have been prepared after the firing using bitumen as the black area is rich in sulphur with traces of vanadium. It should be mentioned that similar pigment types were found by other researchers on the Neolithic ceramics from different sites in Balkan and Europe.

References

[1] Tite, M.S. (2008) Ceramic Production, Provenance and Use—A Review. *Archaeometry*, **50**, 216-231. https://doi.org/10.1111/j.1475-4754.2008.00391.x

[2] Rice, P.M. (1987) Pottery Analysis: A Sourcebook. The University of Chicago Press, Chicago and London.

[3] Quinn, P., Day, P., Kilikoglou, V., Faber, E., Katsarou-Tzeveleki, S. and Sampson, A. (2010) Keeping an Eye on Your Pots: The Provenance of Neolithic Ceramics from the Cave of the Cyclops, Youra, Greece. *Journal of Archaeological Science*, **37**, 1042-1052. https://doi.org/10.1016/j.jas.2009.12.005

[4] (2008) The Prehistory of the Balkans, and the Middle East and the Aegean World, Tenth to Eighth Centuries B.C. In: Boardman, J., Edwards, I.E.S., Hammond, N.G.L. and Sollberger, E., Eds., *The Cambridge Ancient History*, 2nd Edition, Vol. III, Part I, Cambridge University Press, 187-207.

[5] Gjipali, I. (2012) Epoka e Gurit dhe Shqiperia. BOTART, Tirane (in Albanian).

[6] Ruzi, E. (2013) Investigating Compositional Variability among Early Neolithic Ceramics from Korça Region, Albania. *Chronika*, Institute for European and Mediterranean Archaeology, **3**, 1-15.

[7] Allen, S.E. and Gjipali, I. (2013) New Light on the Early Neolithic in Albania: the Southern Albania Neolithic Archaeological Project (SANAP) 2006-2013. *Proceedings of the International Congress of Albanian Archaeological Studies*, 65*th Anniversary of Albanian Archaeology*, 21-22 November, Tirana, 107-120.

[8] Van Espen, P., Nullens, H. and Adams, F. (1977) A Computer Analysis of X-Ray Fluorescence Spectra. *Nuclear Instruments and Methods*, **142**, 243-250. https://doi.org/10.1016/0029-554X(77)90834-5

[9] Orlic, I., Makjanic, J., Ross, J. and Valkovic, D. (1988) *X-Ray Spectrom*, **17**, 139-150.

[10] Anderman, G. and Kemp, J.W. (1958) Scattered X-Rays as Internal Standards in X-Ray Emission Spectroscopy. *Analytical Chemistry*, **30**, 1306. https://doi.org/10.1021/ac60140a001

[11] Potts, P.J., Tindle, A.G. and Webb, P.C. (1992) Geochemical Reference Materials Compositions. Whittles Publishing, London.

[12] IAEA AQCS, Reference Materials Catalogue, 2002-2003.

[13] Ndreçka, E., Vataj, E., Dilo, T., Gjipali, I. and Civici, N. (2014) Application of EDXRF Spectrometry for the Analysis of Ancient Ceramics. *Second International Conference on Radiation and Dosimetry in Various Fields of Research*, Nis, 24-26 May 2014.

[14] Civici, N. and Van Grieken, R. (1997) Energy Dispersive X-Ray Fluorescence Analysis in Geochemical Mapping. *X-Ray Spectrometry*, **26**, 147-152. https://doi.org/10.1002/(SICI)1097-4539(199707)26:4<147::AID-XRS193>3.0.CO;2-X

[15] Bondarenko, I., Treiger, B., Van Grieken, R. and Van Espen, P. (1996) Spectrochim. *Acta Electron*, **51B**, 441.

[16] Aitchison, J. (1986) The Statistical Analysis of Compositional Data. Chapman and Hall, London, 416 p. https://doi.org/10.1007/978-94-009-4109-0

[17] Sakalis, A.J., Kazakis, N.A., Merousis, N. and Tsirliganis, N.C. (2013) Study of Neolithic Pottery from Polyplatanos (Imathia) Using Micro X-Ray Fluorescence Spectroscopy, Stereoscopic Microscopy and Multivariate Statistical Analysis. *Journal of Cultural Heritage*, **14**, 485-498.

[18] Bugoi, R., Constantinescu, B., Pantos, E. and Popovici, D. (2008) Investigation of Neolithic Ceramic Pigments Using Synchrotron Radiation X-Ray Diffraction. *Powder Diffraction*, **23**, 195-199. https://doi.org/10.1154/1.2958068

[19] Papadopouloua, D., Sakalisa, A., Merousisc, N. and Tsirliganis, N.C. (2007) Study of Decorated Archeological Ceramics by Micro X-Ray Fluorescence Spectroscopy. *Nuclear Instruments and Methods in Physics Research A*, **580**, 743-746.

[20] Fabbri, B. and Gualtieri, S. (2008) Alterazione Postdeposizionale di ceramiche neolitiche con formazione di macropori e arricchimento di fosforo. *Rendiconti online Società Geologica Italiana*, **2**, 361-362.

[21] Maritan, L. and Mazzoli, C. (2004) Phosphate in Archaeological Finds: Implications for Environmental Conditions of Burial. *Archaeometry*, **46**, 673-683. https://doi.org/10.1111/j.1475-4754.2004.00182.x

[22] Lukačevića, I. and Rajković, D. (2015) Non-Invasive Analyses of Ancient Ceramics Colorants. *Croatica Chemica Acta*, **88**, 53-58. https://doi.org/10.5562/cca2516

[23] Capela, J., Huertas, F., Pozzuoli, A. and Linares, J. (2006) Red Ochre Decorations in Spanish Neolithic Ceramics: A Mineralogical and Technological Study. *Journal of Archaeological Science*, **33**, 1157-1166.