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Study of medieval ceramics excavated at the monastery of Karaachteke (Varna, Bulgaria)

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The study of medieval ceramics is important in order to obtain information for development of ceramic production during this period. Various medieval unglazed and glazed ceramic artifacts discovered during archaeological excavations in the monastery of Karaachteke near Varna (Bulgaria) were chemically and structurally characterized by ICP-AES, XRD, SEM-EDS and Archimedes method to understand the technology of medieval ceramics production. Water absorption of unglazed artifacts is ranging from 10 to 15 wt.%, which indicates that the ceramics is good sintered and possibly is fired at a high temperature, around 950–1050 °C. The phase composition of the ceramic artifacts indicates the presence of crystalline phases of quartz and plagioclase, the amount of which varies in different samples. SEM proves the presence of coarse quartz grains having a size of 0.05 to 0.3 mm in the sintered ceramic body. This leads to the conclusion that it is used or highly sandy clay or ceramic body, consisting of red firing clay and coarse grain quartz sand.

The study of glazed artifacts proves that a transparent lead glaze with firing temperature about 950–1050 °C was widely used in the Middle Ages. Part of glazed artifacts is typical sgraffito pottery. Other part of glazed artifacts is of the type of the famous Preslav ceramics of a white ceramic body and transparent green glaze with the Seger formula $PbO.0,16Al_2O_3.2SiO_2$ and firing temperature above 1000 °C.

Key words: medieval ceramics, SEM, structure, glazes.

INTRODUCTION

The most common and significant material as volume found by archaeological excavation is the ceramics. With its forms and decoration, chemical and mineral composition it is among the main elements, that in multilateral study give information on the organization of production, business and trade relations, cultural influences and differences between ages and regions. The overall knowledge of a ceramic material and its properties requires knowing the relationship composition-structure-properties that are strictly dependent on the applied technology.

Subject of research are various unglazed and glazed ceramic artifacts found during archaeological excavations in the monastery Karaachteke by prof. Casimir Popkonstantinov (University of Veliko Tarnovo), assoc. prof. Rosina Kostova (University of Veliko Tarnovo) and Valentine Pletnyov (Regional Museum Varna) in the period from 2011 to 2013. Extensive excavation and research begin only in 1995, and with some interruptions, continue also today, as in a large scale they are in the recent years. The monastery of Karaachteke near Varna (Bulgaria) is one of the largest monasteries in the Balkans. The found ceramics is varied – without ornaments or decorated with relief and parallel or grid cross lines, with green transparent glaze, so called sgrafito ceramic of XII–XIV century and ceramic from the Ottoman period – XV–XVIII century. A sign of the intense life in the monastery is the found textured and painted pottery from white clay. Some of the dishes are imported from Byzantium, and others are in the style of "Preslav painted ceramics" from the end of IX and the beginning of the Xth century [1–2].

At present is interesting the study of medieval pottery in order to meet the level of development of ceramics during this period. The authors of this research have a big experience in the field of ceramic glazed and bodies, frits and decoration [3–10].

The aim of the present study is a chemical and structural characterization of unglazed and glazed

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medieval pottery found during archaeological excavations in Karaachteke monastery near Varna (Bulgaria).

EXPERIMENTAL PROCEDURE

Studied artifacts

Unglazed ceramic artifacts are shown in Fig. 1. The ceramic artifacts, indicated by UG1 are found at depth of 1.0 to 1.2 m. The ceramic artifacts, labeled UG2 are discovered at depth of 1 m, others ceramic artifacts, labeled UG3 and UG4 – at depth from 0.60 to 0.80 m. The glazed ceramic artifacts are found at depth of 1 m and are shown in Fig. 2, indicated by G1, G2, G3 and G4.

Analytical methods for study of the ceramic artifacts

– Chemical analysis – ICP – AES after alkali fusion and dissolved in acid and the classical silicate analysis.

– XRD – Diffractometer "TUR-M62", CoK_{α} radiation in the range of 2θ from 5 to 60°.

– SEM – Scanning electron microscopy SEM 525 M, Philips with Energy Dispersive Spectrometer EDS – EDAX 9900.

– Archimedes method for determination of water absorption of ceramic artifacts.

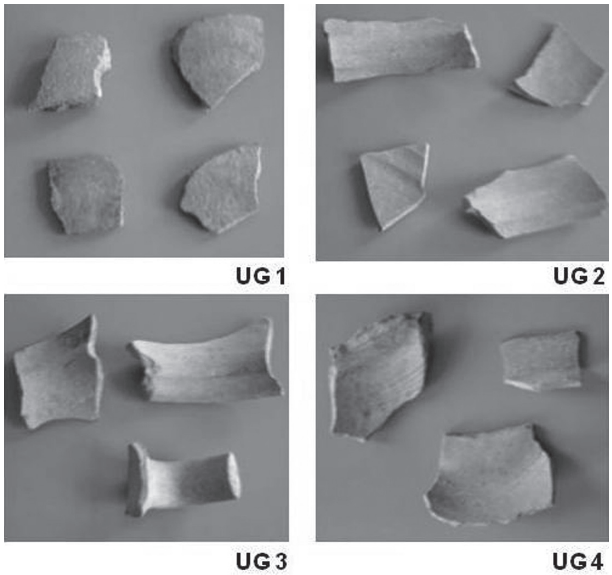

Fig. 1. Unglazed medieval ceramic artifacts from Monastery Karaachteke (Varna, Bulgaria)

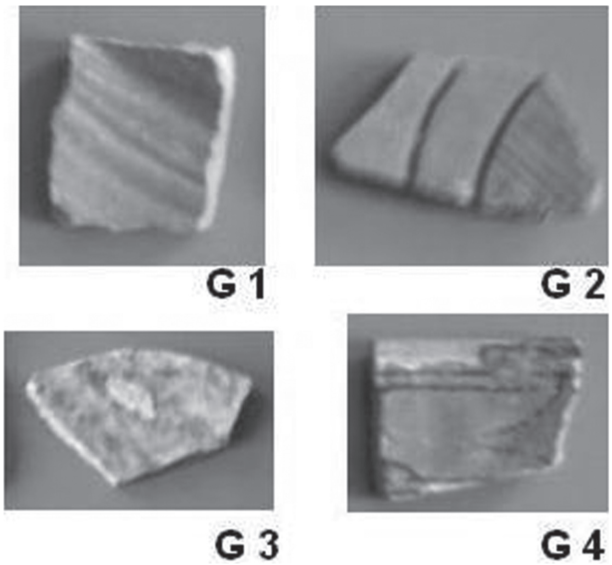

Fig. 2. Glazed medieval ceramic artifacts from Monastery Karaachteke (Varna, Bulgaria)

RESULTS AND DISCUSSION

The results from the chemical analysis of the composition of the unglazed artifacts are given in Table 1. SiO_2 and Al_2O_3 are the most important oxides in the ceramic body of unglazed ceramic artifacts. The coloring oxides (Fe_2O_3 + TiO_2) cause the slightly red color in the ceramic body of the unglazed artifacts. The artifacts contain more than 3 wt.% alkali oxides as K_2O and Na_2O. The water absorption of unglazed artifacts is varied from 10 to 15 wt.%, which gives reason to believe that the artifacts are well sintered probably at high temperature around 950–1050 °C. The phase composition of the ceramic artifacts, established by XRD and shown in Fig. 3, indicates the presence of crystalline phases of quartz and plagioclase, which amount is varied in the different samples.

The chemical composition and the microstructure of the glazed ceramic artifacts was characterized by SEM-EDS. Fig. 4 shows a scanning microscope photograph and local chemical analysis from EDS of glazed ceramic artifact denoted in Fig. 2 with G1. In the ceramic body are clearly visible coarse quartz grains having a size of 0.05 to 0.30 mm, immersed in a sintered ceramic matrix. The average chemical composition of the ceramic matrix surrounding the quartz grains is shown in Fig. 4. The presence of coloring oxides explains light red color of the ceramic body of the artifact G1. These results show that is used very sandy clay, which apparently was not digested, but only passed through a sieve of 0.5 mm or used in the form in

Table 1. Chemical compositions of unglazed ceramic artifacts

Artifacts	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	TiO_2	MnO	Na_2O	K_2O	SO_3	P_2O_5	LI
UG1	70.55	15.47	5.60	1.43	1.40	0.78	0.05	1.05	2.57	1.38	0.09	0.26
UG2	70.75	13.57	5.0	1.54	3.14	0.69	0.07	0.74	2.54	<0.03	0.11	1.06
UG3	66.41	17.54	5.91	1.38	1.65	0.74	0.05	0.73	3.54	<0.03	0.14	1.06
UG4	65.3	18.56	5.89	1.46	2.05	0.86	0.05	0.83	3.09	<0.03	0.06	1.28

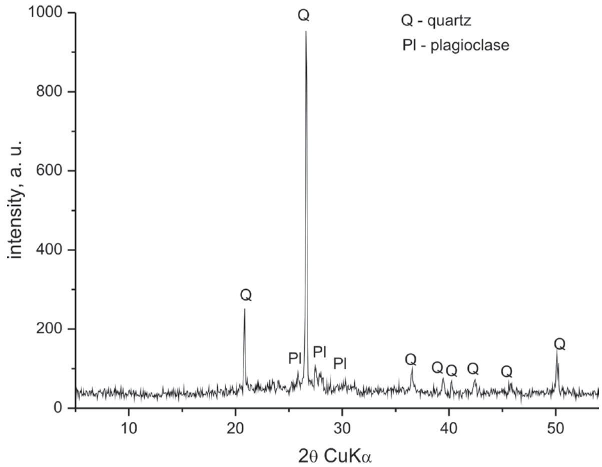

Fig. 3. XRD patterns of unglazed medieval ceramic artifact UG3

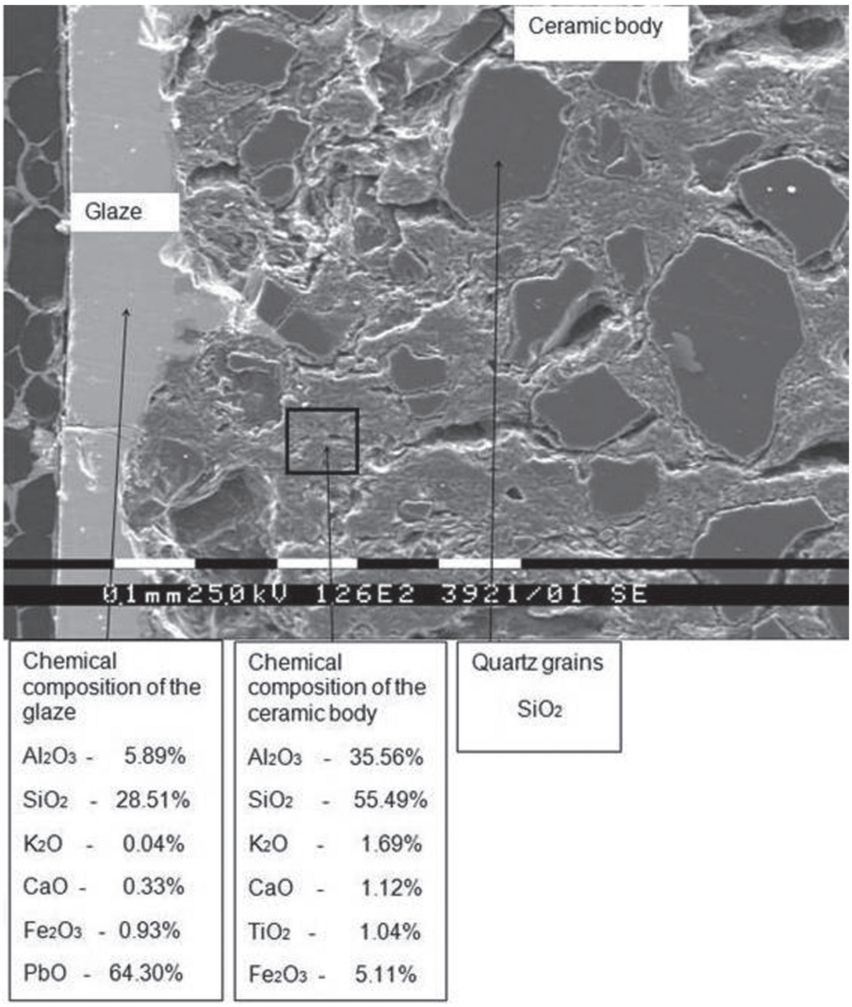

Fig. 4. SEM and local chemical analysis by EDS of the glaze and ceramic body of glazed ceramic denoted G1

which it is extracted. The content of grains of quartz sand is the ceramic body is needed from the presence of lead glaze having a high thermal expansion coefficient. The glaze on the ceramic body is a transparent lead glaze. This glaze probably is prepared by two raw materials: PbO – 70% and clay – 30%. The glaze is applied by dipping of the green ceramic body in the glaze following single firing or on a biscuit ceramic body on at double firing. Assumed, that the artifact is obtained by double firing, because it has relatively good water absorption, which shows good sintering of the ceramic body at about 950–1050 °C. The high percent of the lead oxide (64.30%) in the glaze notes that the temperature of the second glaze firing is lower with 50–100 °C and is done in a strongly oxidizing environment, otherwise the lead would be reduced. The oxidizing environment affects on the glaze color, which is yellowish-brown due to the lead glaze, to brick-red with an effect of bleed of the ceramic body through the glaze.

Fig. 5 shows a scanning microscope image and local chemical analysis of the glazed ceramic artifact marked on Fig. 2 with G2. SEM analysis shows the presence of two layers on the ceramic body – glaze and engobe. There is a relief decoration of dark red lines and the color of the artifact is yellowish brown. This artifact, visual and as a result of the carried out analyzes, can be referred as a typical sgraffito pottery. SEM of artifact G2 shows that the ceramic body comprises open pores and grains of quartz, which are smaller compared with the previous artifact G1. The ceramic body has a higher content of Fe_2O_3, compared with the engobe and glaze, which explains the dark red color of the relief ornaments, in which the engobe is removed at the manufacture of the product and there is direct contact between the reactive lead glaze and the ceramic

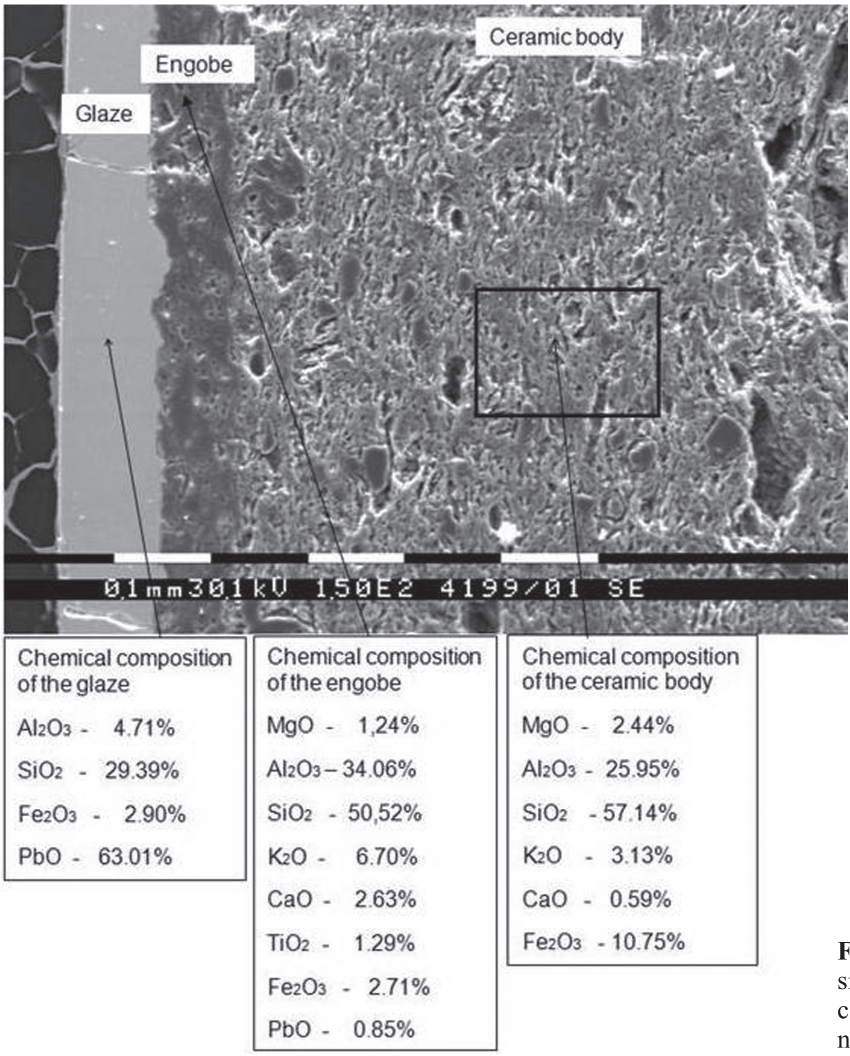

Fig. 5. SEM and local chemical analysis by EDS of the glaze, engobe and ceramic body of glazed ceramic denoted G2

body. This interaction leads to dark red coloration of the medium layer. Unlike the previous artifact G1, in this artefact is observed also the presence of engobe with chemical composition shown in Fig. 5, which relatively more sintered of the ceramic body. It can be argued that it is composed of fireclay, potassium feldspar, quartz sand and dolomite, i.e. during this period of ceramic development, ceramic bodies, glazes and glazes for recipe composition have been known and made. The role of the engobe is to cover the ceramic body and to prevent reaction between the glaze and the ceramic body or if such one exists it to be controlled only if it is necessary to obtain decoration ornaments with specific color. The lead glaze is transparent with Seger formula $PbO.0,13Al_2O_3.1,3SiO_2$ and firing temperature 940–960 °C. Such ceramics can be produced by a single firing or by double firing [9, 10].

SEM of glazed ceramic artifact G3 (Fig. 6) with white ceramic body and green transparent glaze shows that this artifact is glazed with also typical lead glaze. The composition of the ceramic body reveals that it is prepared from quite pure white fireclay – possibly washed, which requires high firing temperature. The ceramic body has closed pores and 15.0% water absorption. The lead glaze is transparent with Seger formula $PbO.0,16Al_2O_3.2SiO_2$ and firing temperature above 1000 °C. Apparently this ceramic artifact belongs to the famous Preslav ceramics.

SEM of the glazed ceramic artifact labeled as G4 shown in Fig. 2 with red ceramic body, green glaze and black lines ornaments is presented in Fig. 7. The picture also reveals that it contains glaze, engobe and ceramic body. Distinctively for this artifact is that these black decorative ornaments are made by engraving the body after the application of the engobe, so in the ornaments between the glaze and the body there is not engobe, which makes the thickness of the glaze larger. There is again a di-

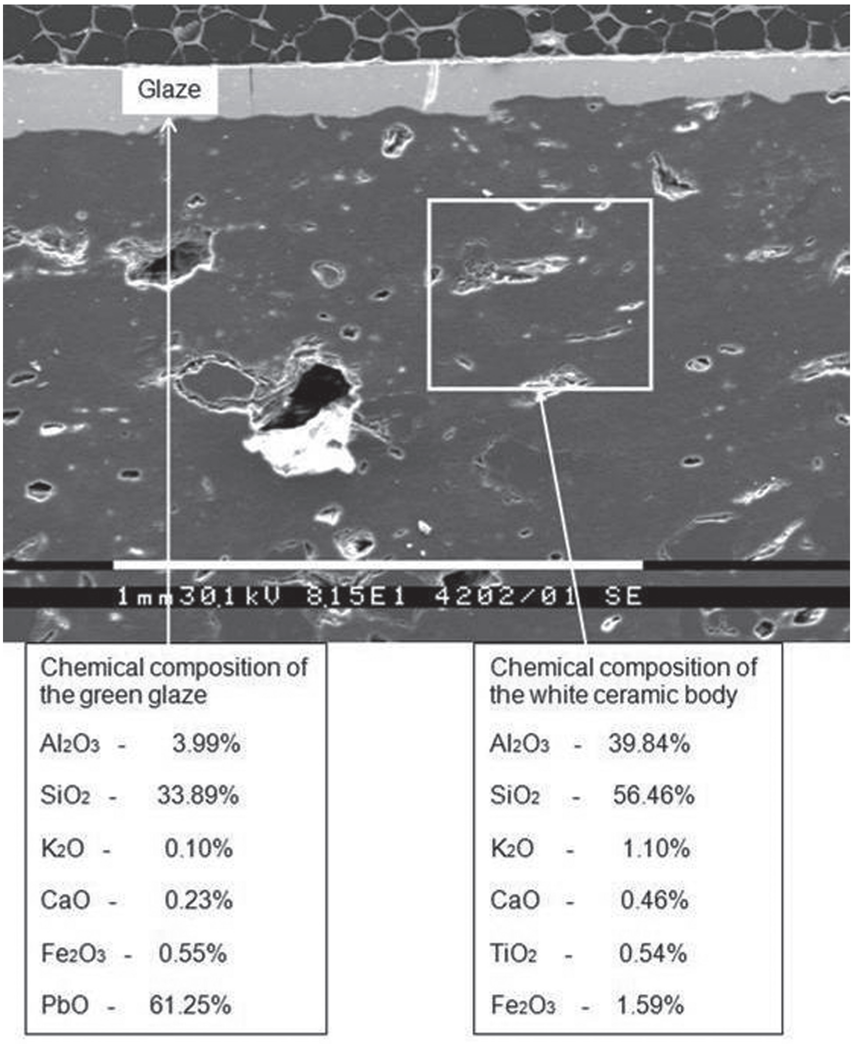

Fig. 6. SEM and local chemical analysis by EDS of the green transparent glaze, engobe and white ceramic body of glazed ceramic denoted G3

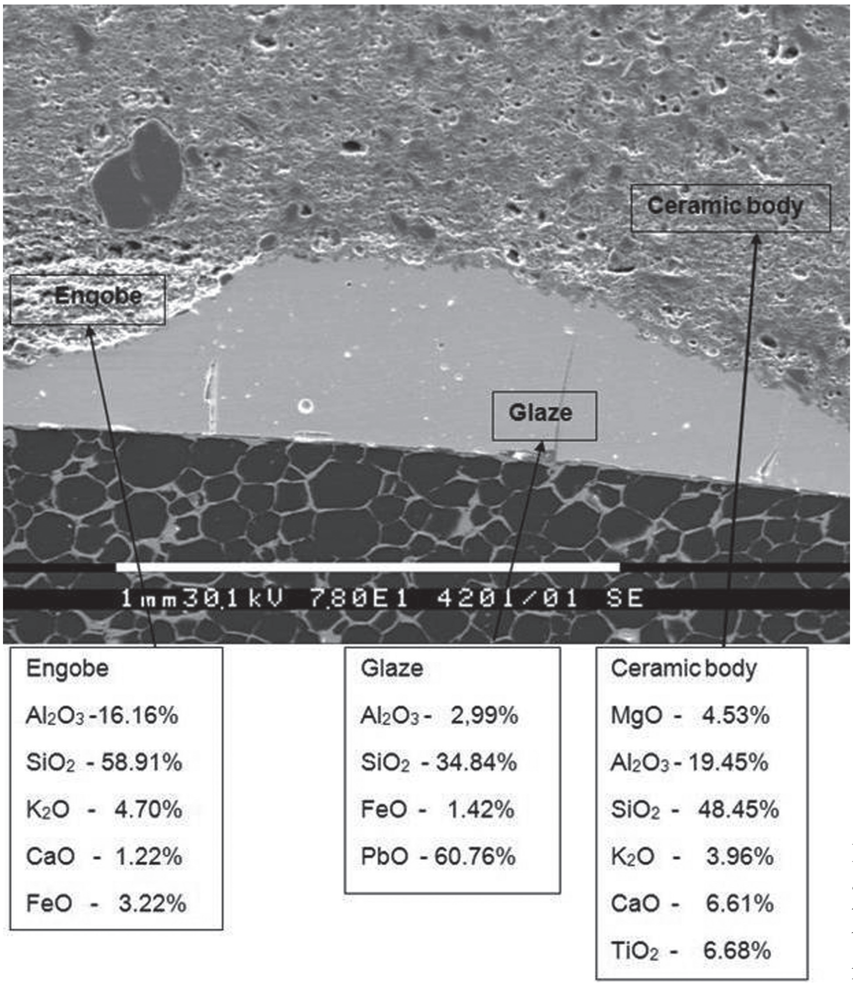

Fig. 7. SEM and local chemical analysis by EDS of the engobe, green transparent glaze and red ceramic body of glazed ceramic artifact denoted G4

rect contact between the reactive lead glaze and the ceramic body containing Fe_2O_3 – 10 wt.%, a concentration at which the carved ornament gets this black color. This is shown on Fig. 7. SEM observes more porous engobe compared to the ceramic body, which is more sintered. In recipe composition of the engobe, in addition to clay, quartz sand and potassium feldspar PbO is includes too, as probably the engobe is only homogenized without grinding. The reaction between the glaze and the engobe gives green color which can be obtained in reducing conditions at that content of Fe_2O_3. The glaze has a Seger formula $PbO.0,15Al_2O_3.1,9SiO_2$ and firing temperature 1000–1020 °C [9, 10].

Figure 8 shows the chemical composition of the boundary of the engobe and the glaze, the chemical composition in the black line, the chemical composition of the boundary between the black line and the ceramic body and the chemical composition of the glaze. Areas near the contact between the engobe and glaze, glaze and ceramic body were studied By SEM – EDS. It has been found that chemical components migrate in both directions. The lead from the glaze enters in the engobe and body, and K, Ca, and Fe dissolve in the reactive lead glaze.

CONCLUSION

It has been established that the main oxides in the ceramic body of the medieval pottery are SiO_2 and Al_2O_3. The artifacts contain also a certain amount of coloring oxides (Fe_2O_3 + TiO_2), which cause the slightly red color. The water absorption of the medieval pottery is in the range 10–15 wt.%, which gives reason to believe that the artifacts are well sintered, probably at high temperature around 950–1050 °C. The phase composition of the artifacts is represented by quartz and plagioclase, which amount varies by the samples. SEM proves the presence of coarse quartz grains having a size of 0.05 to 0.3 mm in a sintered ceramic body. This leads to the conclusion that it is used either highly sandy clay or ceramic body, consisting of red firing clay and quartz sand with dimensions of 0.05 to 0.3 mm, providing the high thermal expansion coefficient of the ceramic

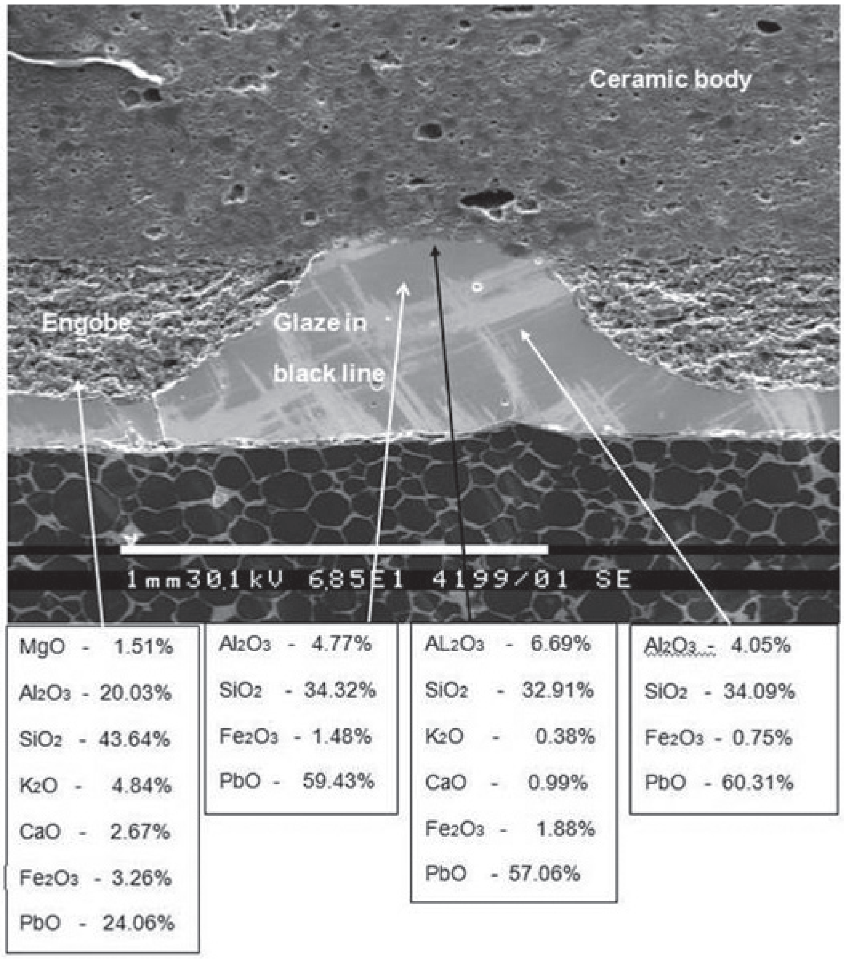

Fig. 8. Chemical composition of the boundary between engobe and glaze, of the black line, of the boundary between the black line and the ceramic body and of the glaze of glazed ceramic denoted G4

body after firing, necessary for the coordination of transparent lead glaze, also having a high thermal expansion coefficient.

The study of the glazed artifacts indicates that transparent lead glaze with firing temperature around 950–1050 °C is widely used in the Middle Ages. The sintered ceramic body of the glazed artifacts is obtained from ceramic body involving clay with a high content of Fe_2O_3, quartz sand and potassium feldspar. The conclusion is that the glazed artifacts G2 and G4 are typical sgraffito pottery, a fact indicating that during this period of ceramic development, when these products have been created (middle ages), the ceramic masters knew and made ceramic bodies, engobes and glazes in recipe composition from different raw materials.

It is proven that the artifact G4 is of the type of the famous Preslav ceramics with a white ceramic body and transparent green glaze, with the Seger formula $PbO.0,16Al_2O_3.2SiO_2$ and firing temperature above 1000 °C. It has been found that the chemical elements are migrating in both directions within the contact layers: engobe–glaze and glaze-ceramic body. The lead from the glaze enters in the engobe and body, and K, Ca, and Fe dissolve in the reactive lead glaze.

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ИЗСЛЕДВАНЕ НА СРЕДНОВЕКОВНА КЕРАМИКА ОТКРИТА В МАНАСТИРА КАРААЧТЕКЕ КРАЙ ВАРНА, БЪЛГАРИЯ

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(Резюме)

Изследването на средновековни керамики е важно, за да се получи информация за развитието на технологията на производство на керамиката през този период. Различни средновековни неглазирани и глазирани керамични артефакти, открити при археологически разкопки в манастира Караачтеке близо до Варна (България) са химически и структурно охарактеризирани с РФА и СЕМ за установяване на технологията на производство на средновековната керамика. Водопоглъщаемостта на неглазираните артефакти, определена по метода на Архимед, е в интервала от 10 до 15 тегл.%, което показва, че керамиката е добре спечена и вероятно е изпичана при висока температура около 950–1050 °С. Фазовият състав на керамичните артефакти показва наличието на кристални фази от кварц и плагиоклаз, количеството на които варира в различните проби. СЕМ доказва присъствието на едри кварцови зърна, имащи размер от 0,05 до 0,3 mm в спеченото керамично тяло. Това води до заключението, че за получаване на керамиката се е използвала или силно песъклива глина или керамична маса, състояща се от червено изпичаща се глина и едрозърнест кварцов пясък.

Изследването на глазираните керамични артефакти доказва, че през Средновековието широко е била използвана прозрачна оловна глазура и керамиката е изпичана при температура около 950–1050 °С. Част от глазираните артефакти са типична сграфито керамика. Друга част от глазираните артефакти е от типа на известната Преславска керамика, характеризираща се с бял керамичен череп и прозрачна зелена глазура с Зегерова формула $PbO.0,16Al_2O_3.2SiO_2$ и температурата изпичане над 1000 °С.