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DETERMINATION OF HELLENISTIC POTTERY AND WALL PLASTER MINERAL COMPOSITION

Zhivko Uzunov[1], Boyan Dumanov[1], Bilyana Kostova[1], Ventseslav Stoyanov[2,3], Ralitza Berberova[1], Boyka Zlateva[4]

[1]New Bulgarian University – Sofia
[2]University of Structural Engineering and Architecture (VSU) „Lyuben Karavelov"– Sofia
[3]MOI Academy - Sofia
[4]Sofia University "St. Kl. Ohridski" - Sofia
e-mail: zhuzunov@nbu.bg; bdumanov@nbu.bg; bkostova@nbu.bg; vensy.stoyanov@gmail.com; rberberova@nbu.bg; ahbz@chem.uni-sofia.bg

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Abstract: *Pottery and clay plaster is the first composite materials manufactured and developed by humans. They are the most abundant findings as archaeological artifacts due to their production in a wide time range, simple production process, high weather resistance, and low cost. The study of such materials aims to define the raw materials used and the temperature of the firing process. The present study investigated one wall plaster sample and five pottery fragments from Hellenistic settlement, located on a Harmanlaka summit by the Orizare village, Nessebar municipality, Bulgaria, and clay from the deposit, located near the archaeological site. The methods used were X-ray fluorescence analysis and powder X-ray diffraction measurements. The obtained results of samples mineral composition define: (i) studied clay as raw for potteries and plaster production; (ii) phase composition and firing temperature (three different temperatures of ceramic firing – 600 - 650°C; 600-800°C, and 950-1000°C; and (iii) temperature of wall plaster burning - 600 - 650°.*

МИНЕРАЛЕН СЪСТАВ НА БИТОВА КЕРАМИКА И ГЛИНЕНА СТЕННА МАЗИЛКА ОТ ЕЛИНИСТИЧЕСКАТА ЕПОХА

Живко Узунов[1], Боян Думанов[1], Биляна Костова[1], Венцеслав Стоянов[2,3], Ралица Берберова[1], Бойка Златева[4]

[1]Нов български университет – София
[2]Висшето строително училище "Любен Каравелов" – София
[3]Академия на МВР – София
[4]Софийски университет „Св. Кл. Охридски" - София
e-mail: zhuzunov@nbu.bg; bdumanov@nbu.bg; bkostova@nbu.bg; vensy.stoyanov@gmail.com; rberberova@nbu.bg; ahbz@chem.uni-sofia.bg

Ключови думи: *битова керамика, глинена стенна мазилка, Елинистическа епоха, минерален състав*

Резюме: *Керамиката и глинената стенна мазилка са първите композитни материали, произведени и разработени от хората. Те са най -разпространените археологически артефакти тъй като се произвеждат лесно и в широк времеви интервал, устойчиви са на изветряне и имат ниска себестойност. Тяхното изучаване цели да се определи изходната суровина от която са произведени, както и температурата ,при която са изпечени. Изследвани са една проба от глинена стенна мазилка и пет фрагмента от битова керамика от Елинистическо селище, разположено на вр. Харманлъка, близо до с. Оризаре, община Несебър, както и проби от глина от находище, разположено в близост до археологическия обект. За целта са използвани рентгенофлуоресцентен и прахов ренгенов анализи. Получените резултати доказват: (i) местно производство с местна изходна суровина; (ii) три различни температури на изпичане на керамиката - 600 - 650°C; 600-800°C и 950-1000°C и (iii) температура на изгаряне на глинената стенна мазилка - 600 - 650°.*

Introduction

Modern archeology uses non-destructive remote sensing methods (for studying/searching archaeological structures - drone, geophysical methods, etc.) and destructive methods (for artifacts investigations by X-ray fluorescence, powder X-ray diffraction measurements, thermal analysis, etc.). The study of artifacts' chemical and mineral composition and their comparison with raw materials provide information about people's knowledge of the ancient environment, the technology of manufacturing, and trade relations.

The study of ceramic artifacts is of importance for determining the raw materials of production and firing conditions. For this purpose, the examination of the mineral composition of ceramic and comparison with the mineral composition of raw material is of great importance. It is known that when firing ceramics under conditions of elevated temperature, the redox potential in the kiln, the chemical and structural composition of the clay change [1]. These changes are related to:

- destruction of raw minerals due to exceeding stability limit with increasing temperature. For example, clay minerals are resistant up to 550°C, calcite's decomposition occurs at 600°C - 660°C; potassium feldspars - around 1000°C; plagioclase and muscovite are resistant to temperatures close to 950°C [1,2]. In this regard, the determination of the starting clay mineral in annealed pottery is difficult [3];
- structural change of the raw minerals without changing the chemical composition under rising temperature in oxidation atmosphere - for example, quartz (SiO_2) is transformed and tridymite (SiO_2) started to form from 872°C up to 898°C, where the temperature can be shifted by the presence of alkali oxides above 1005°C [4].
- Formation of new minerals under elevated temperature – gehlenite $Ca_2Al[AlSiO_7]$ at 800 – 850°C, diopside $MgCaSi_2O_6$ – at a temperature above 800°C, hematite Fe_2O_3 – at 950°C, mullite $Al_6Si_2O_{13}$ - at temperatures above 950°C; wollastonite $CaSiO_3$ – above 1100°C, etc. [1,2].

The area of Nessebar is known for a couple of clay deposits. There are published investigations on ceramic focused on the building ceramic (roof tiles and architectural terracotta) and stamped amphorae to define the raw clay used for their preparation [5]. Similar studies have not been done on pottery. Such results will provide information about local manufacturing and its technology and/or pottery import and trade relations during that period. The technology of clay wall plaster preparation does not include firing. The clay plaster's macroscopic observation shows reddish coloration, supposing some degree of building burning.

The work aims to investigate: (i) the chemical composition of pottery fragments and clay plaster from the Hellenistic settlement and compare it with the potential raw material (clay), and (ii) mineral composition to define the pottery's firing temperature and clay plaster's burning temperature. The investigation was made by X-ray fluorescence analysis and powder X-ray diffraction measurements.

Samples and methods

Samples

Archaeological site for sampling: Hellenistic settlement located on a prominent summit named Harmanlaka, by the village of Orizare (Fig. 1). The archaeological data of the settlement was described in detailed elsewhere [6-8].

Fig. 1. Settlement site by the Orizare village, Bulgaria

Studied archaeological samples: №1 clay plaster; №2 wheel made monochrome pottery; №3 Fragment from the jug, №3 handmade pottery; №4 Lopas, plain pottery; №5 Cup, plain pottery; and №6 Bowl, red-gloss ware.
Studied raw material samples: two clay samples (A and B), sampling – two different levels of modern clay quarry (out of operation at the moment) with location Orizare village.

Methods

The X-ray fluorescence (XRF) analysis was performed by Micro-XRF Spectrometer M1 MISTRAL, Bruker (Rh-tube, Peltier cooling, 30 mm², Si-drift detector (SDD), <150 eV with Mn Ka, collimator 0.1 mm to 1.5 mm), calibrated with external standards. The samples were H_3BO_3 tableted (1 g sample + 0,5 g H_3BO_3). The XRF analysis was used for clay samples investigations.

The powder X-ray diffraction (PXRD) measurements were made by Empyrean Powder X-ray diffractometer (Malvern Panalytical, Netherlands) in the 3°- 100° 2θ range using Cu radiation (λ = 1.5406 Å) and PIXcel3D detector.

Results

Table 1 shows the XRF results from two clay samples' investigation.

Table 1. Results from the XRF analysis of clay samples (A and B)

№	wt %															
	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	Ti	V	Mn	Fe	Cu	Zn	Rb	Sr	Y	Zr	S
A	1.56	14.98	33.72	0.07	2.11	8.69	0.48	0.01	0.05	4.14	0.01	0.01	0.01	0.04	0.0014	0.01	0.15
B	2.73	25.68	48.26	0.12	2.39	8.33	0.38	0.01	0.04	3.65	0.01	0.01	0.01	0.03	0.0016	0.01	-

The results from the PXRD analysis are present in Fig. 2 and Table 2.

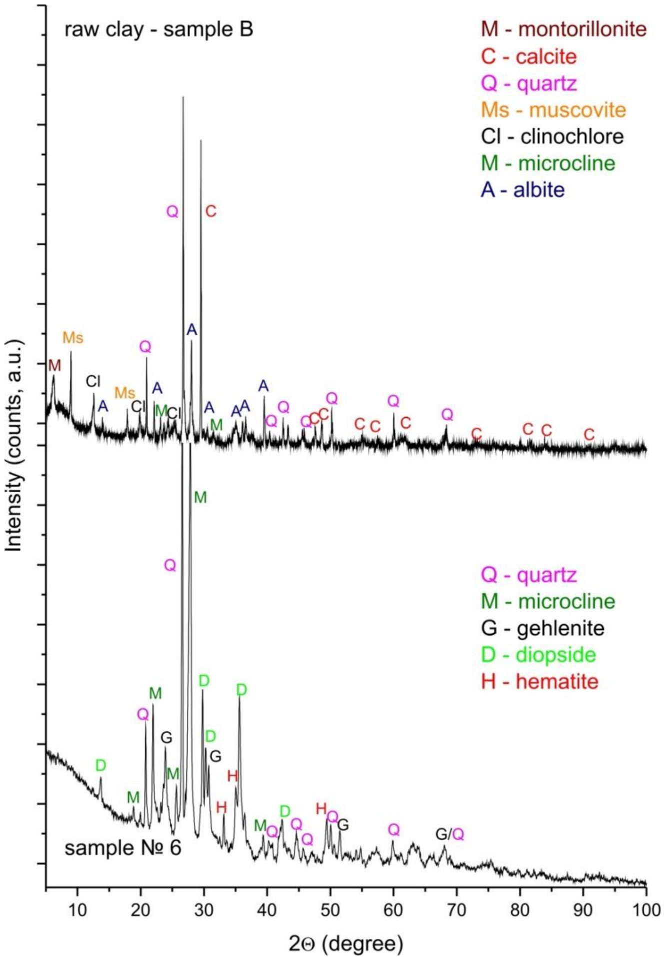

Fig. 2. PXRD patterns of raw clay (sample B) and pottery (Sample № 6)

Table 2. Results from the PXRD analysis

Sample	Mineral composition		References
raw clay – sample A and sample B	montmorillonite, clinochlore, quartz, muscovite, albite, microcline, calcite		montmorillonite [9] clinochlore [10] quartz, PDF # 06-1757 [11] muscovite [12] microcline - PDF #19-0926 [11] albite - PDF #89-6426 [11] calcite - PDF#06-6528 [11] gehlenite [13] diopside [14] hematite PDF# 33-0664 [11]
pottery	**raw minerals**	**newly-formed minerals**	
№1 clay plaster	quartz, muscovite, albite, microcline, calcite	-	
№2 Wheel made monochrome pottery	quartz, muscovite, albite, microcline, calcite	-	
№3 Jug, handmade pottery	quartz, muscovite, albite, microcline	-	
№4 Lopas, plain pottery	quartz, muscovite, albite, microcline	-	
№5 Cup, plain pottery	quartz, muscovite, albite, microcline, calcite	-	
№6 Bowl, red-gloss ware	quartz, microcline	gehlenite, diopside, hematite	

Discussion

The clay rocks usually are composed of three mineral groups: pelitic (minerals from clay, chlorite, and hydromica groups), authogenic (usually calcite, but also dolomite, siderite, pyrite, etc.), and clastic (quartz, feldspar, mica). Typically, the pelitic component is over 50%, with a highly variable ratio between pelitic and clastic minerals [15].

The XRF results (Table 1) of clay samples show differences in SiO_2 and Al_2O_3 concentration, which defines the altered ratio between pelitic and clastic minerals, even the same deposit. The results of CaO concentration coincide for both samples. The same stands for the amount of the other measured elements.

The PXRD investigations of both clay samples prove identical phase composition (Table 2):

- pelitic minerals: montmorillonite $(Na,Ca)_{0.33}(Al,Mg)_2(Si4O_{10})(OH)_2.nH_2O$ and clinochlore $Mg_5Al(AlSi_3O_{10})(OH)_8$;
- authogenic mineral: calcite $CaCO_3$;
- clastic minerals: quartz SiO_2, muscovite $KAl_2(AlSi_3O_{10})(OH)_2$, feldspar: potassium feldspar - microcline $K(AlSi_3O_8)$, and plagioclase - albite $Na(AlSi_3O_8)$.

The results obtained are partly following the literature data on clays from the Orizare region. The established phases: montmorillonite, calcite, and feldspar, coincide with the data from the others [5]. The detected muscovite (mica) and clinochlore (Mg-rich chlorite) were not reported in the previous studies [5]. Illite was not detected, which was proved by Kovatchev et al. [5].

The montmorillonite and clinochlore (raw clay pelitic minerals) were not found in studied ceramic samples. The decomposition temperature of 600°C for these two minerals [1,2] defines a minimum pottery firing temperature around 600°C. Same stands for the minimum burning temperature of sample №1 clay plaster.

The authogenic calcite was found only in samples №1, №2, and №5, which determines the firing temperature in the range 600 - 660°C for №2 and №5 samples and the burning temperature in the same interval for sample №1.

At samples №3 and №4, only the minerals quartz, muscovite, albite, and microcline were present. Autogenic calcite and newly formed minerals during the thermal treatment were not proven. That defines the firing temperature in the range of 600/660 - 800°C. The lower temperature boundary was defined by the calcite thermal stability, and the upper – by the lowest temperature of new minerals formation.

In sample №6, quartz and microcline only were detected from the raw clay. Newly formed minerals have been identified: gehlenite, diopside, and hematite. The formation of diopside is explained by the decomposition of calcite and Mg-chlorite (clinochlore) and the incorporation of Ca and Mg into the newly-formed diopside [2]. The gehlenite formation was associated with the decomposition of montmorillonite and the mobilization of Al in the newly-formed mineral. A sufficient amount of Fe has been detected in the raw clay (Table 1) to form the mineral hematite at high temperatures and oxidizing atmosphere in the kiln. Gehlenite and diopside were formed at temperatures above 800°C, hematite - at 950°C. The absence of muscovite marks a temperature above 950°C. The microcline thermal stability is up to 1000°C. That facts define the firing temperature of sample №6 at the interval 950 - 1000°C. Despite the specified high firing temperature, SiO_2 is established as quartz, not as tridymite. The shift of quartz resistance to higher temperatures is due to the presence of alkaline components in the system [4] (Table 1).

Conclusion

The chemical and phase composition study of clay samples from the area of the village of Orizare and the comparison with the phase composition of the studied Hellenistic pottery and clay plaster samples determined the studied clay as raw material and their local production, respectively.

The determined mineral composition of the raw clay, pottery samples, and clay plaster show:

- three different firing temperatures of the ceramics: 600 - 660°C, 600 - 800°C and 950 - 1000°C, proving three manufacturing technologies used;
- temperature of wall clay plaster burning and building burning at the fire, respectively - 600 - 660°C.

The obtained results are of importance for other archaeological sites from the region of Nessebar municipality.

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References:

1. El Ouahabi, M., L. Daoudi, F. Hatert, N. Fagel. Modified Mineral Phases During Clay Ceramic Firing. Clays Clay Miner. 63, 2015, 404–413. (https://doi.org/10.1346/CCMN.2015.0630506)
2. Heimann, R.,M. Maggetti. The struggle between thermodynamics and kinetics: Phase evolution of ancient and historical ceramics. In: The Contribution of Mineralogy to Cultural Heritage, EMU Notes in Mineralogy, 20, Ch. 6, 2019, 233–281. (10.1180/EMU-notes.20.6)
3. Jordán, M. M., A. Boix, T. Sanfeliu, C. de la Fuente. Firing transformations of Cretaceous clays used in the manufacturing of ceramic tiles. Applied Clay Science, 14, 1999, 225–234. (https://doi.org/10.1016/S0169-1317(98)00052-0)
4. Holmquist, S. B. Conversion of Quartz to Tridymite. Journal of the American ceramic society. 44, 2, 1961, 82–86. (https://doi.org/10.1111/j.1151-2916.1961.tb15355.x)
5. Kovatchev, V., T. Stoyanov, Ts. Stanimirova, D. Stoyanova, I. Lozanov, V. Mladenov. Archaeometric study of Hellenistic roof tiles and amphorae from Apollonia and Mesambri: an attempt at identifying local production. PATABS II. Production and trade of amphorae in Black sea. Acts of International round table held in Kiten, Nessebar and Sredetz. 2011, 203–243.
6. Uzunov, Z., Y. Tsvetanov, I. Arolska. Archaeological excavation of late Hellenistic site at Harmanluka, Orozare, Nessebar municipality. Archaeological discoveries and excavations in 2015. Bulgarian academy of sciences, National archaeological institute with museum. 2015. 281–283. (in Bulgarian with English abstract).
7. Karayotov, I. The Coinage of Mesambria. Vol II, Bronze coins of Mesambria, Burgas. 2009.
8. Bozkova, A., P. Kiyashkina, Z. Uzunov, V. Milcheva. The late Hellenistic period in mesambria pontica and its vicinity. Studia archaeologica universitatis serdicensis Supplementum VI (2018), Stephanos archaeologicos ad 80 annum professoris Ludmili Getov. 2018. 225–236. (in Bulgarian with English abstract).
9. Viani, A, A. Gualtieri, G. Artioli. The nature of disorder in montmorillonite by simulation of X-ray powder patterns. American Mineralogist, 87, 2002, 966–975 (database_code_amcsd 0002868). (10.2138/am-2002-0720)
10. Welch, M. D., W. G. Marshall. 2001. High-pressure behaviour of clinochlore P = 4.65 GPa. American Mineralogist, 86, 1380-1386 (_database_code_amcsd 0002742).
11. Powder Diffraction File (PDF), copyright by International Centre for Diffraction Data (ICDD) Newtown Square; 12 Campus Blvd., Newtown Square, PA 19073-3273.
12. Singha, M., L. Singh. Vibrational spectroscopic study of muscovite and biotite layered phyllosilicates. Indian Journal of Pure & Applied Physics, 54, 2016, 116–122.
13. Louisnathan, S. J. Refinement of the crystal structure of a natural gehlenite, $Ca_2Al(Al,Si)_2O_7$. The Canadian Mineralogist 10, 1971, 822–837. (_database_code_amcsd 0005090).
14. Raudsepp, M., F. C. Hawthorne, A. C. Turnock. Crystal chemistry of synthetic pyroxenes on the join $CaNiSi_2O_6$-$CaMgSi_2O_6$ (diopside): A Rietveld refinement study**.** American Mineralogist 75, 1990, 1274–1281**. (**_database_code_amcsd 0001333**).**
15. Kovatchev, V., Str. Dimitrov, P. Petrov 1991. Industrial minerals. MGU, Sofia, 1991. (in Bulgarian).