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STRUCTURAL ANALYSIS OF SOME POTTERY FRAGMENTS BELONGING TO HAMANGIA (PHASE III) CULTURE

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Abstract. *The paper presents a structural analysis of two pottery fragments belonging to the Hamangia phase III Ceamurlia culture, discovered in a settlement with several living levels on the northern shore of Lake Techirghiol, at the Minerva – Paloda Hill. From two ceramic fragments, fired in a reducing atmosphere, samples were taken to perform X-ray diffraction (XRD) and wavelength-dispersive X-ray fluorescence spectra (WDXRF) analyzes to determine the crystalline structure and composition of the ceramic materials. Digital optical microscopy was used to observe the details of the fracture surfaces of these ceramic fragments. This work contributes to the knowledge of the techniques and materials used by the Hamangia civilization in the manufacture of ceramic vessels.*

Keywords: *Hamangia, pottery, archaeometry, oxides, WDXRF, XRD*

1. INTRODUCTION

In 2020, the archaeologists of the Museum of History and Archeology from Constanța carried out excavations on the northern shore of Lake Techirghiol which revealed several levels of habitation from different periods, of which the oldest level belongs to Hamangia third phase culture. The chronological framework would be between 4800 – 4650 BC [1], following the ^{14}C dating made on samples from the Hamangia III levels from Cheia 5212 – 4854 BC [2], 5020- 4797 BC [3] and Ceamurlia de Jos 4997 – 4770 BC [4].

The two ceramic fragments belong to the same vessel and were labeled H1.P.3.1. and H1.P.3.2., have different dimensions: 7.5 x 6.5 cm and 15 x 10 cm, the wall thickness of the former vessel being approximately 1 cm.

The outer surface of the vessel is polished, black-brown. It is very clear that the vessel from which the ceramic fragments come was covered with black slip, and contamination from this layer was avoided during the sampling.

The analysis of the slip layer is the subject of another study. The decoration is represented by impressions and excisions in oblique or parallel linear registers, filled with white paste.

2. EXPERIMENTAL

2.1. Materials

The two selected ceramic fragments that belonged to the same vessel are shown in the Figure 1 and Table 1. It can be seen that they have a thickness of approximately 1 cm, uneven. A coarse structure of the ceramic can be observed, which stands out through the dark black-brown core and the outer layers are brown in color. Numerous inclusions are also present, both crystalline and amorphous.

Table 1. Ceramic fragments, front and back view

Sample	*Front view*	*Back view*
H1.P.3.1.		
H1.P.3.2.		

Regarding the color of the samples in the section, the fact that the ceramic is brown on the outside and black-

brown on the inside is due to either incomplete firing or secondary firing. [5]



Figure 1. The ceramic fragments - side view

2.2. Analysis methods and devices

The purpose of this work is to present the results of the quantitative and qualitative analyzes on the ceramic material from which the vessel discovered by archaeologists was made. The experimental determinations were carried out at "Valahia" University from Târgoviște, at ICSTM and in the Laboratory of Multifunctional Materials and Microfluidics of the Faculty of Materials and Mechanics Engineering.

The microscopic study was carried out with the Bresser DST-1028 digital microscope, using 40x magnification. In addition, a cold corona-type light source was used, for a better degree of brightness on the areas of interest.

X-ray diffraction (XRD) analysis was performed using a Rigaku Ultima IV diffractometer (Cu-Kα radiation, λ = 0.15406 nm). ICDD cards were used to interpret the results.

Wavelength-dispersiveX-ray fluorescence spectra (WDXRF) were performed with a Rigaku Supermini200 X-ray fluorescence spectrometer, which is a benchtop sequential wavelength-dispersive spectrometer with Pd anode (power 200W, voltage 50kV, and intensity 4mA). The detection limit is 1ppm – 10ppb and the precision < 0.1-0.5%. The spectra are recorded and processed using ZSX software.

The powder samples were taken from areas with brown ceramic (marked with CB) and from areas with black ceramic (marked with CMN). The powders taken for XRD and WDXRF analyzes were mortared up to the limit size given by their hardness.

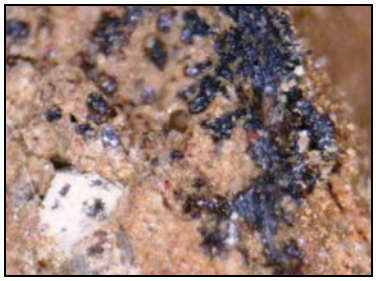
Contamination or phase changes were avoided as much as possible. For XRD analysis, the powders were deposited on glass slides.

For WDXRF analysis, powders were pelleted together with about 2 g of binder (Boreox – Fluxana) with the help of a laboratory press TestChemLPR-250.

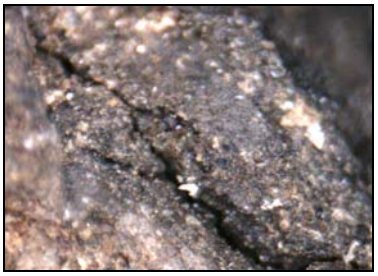
3. RESULTS AND DISCUSSIONS

3.1. Digital optical microscopy

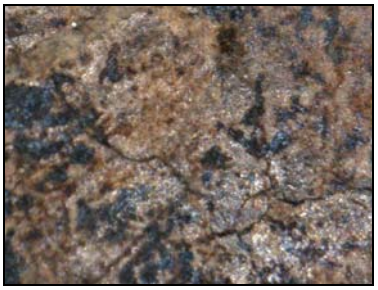
The microscopic images (Figure 2) were captured only on the irregular areas of the fractures, not on the surface of the samples. In these images, heterogeneity of the composition can be observed, noting the presence of inclusions but also a structural inhomogeneity. There are also areas with inclusions of white crystalline material, but also ceramic structures that seem to be made of quartz pigmented with iron ions (brown shade).



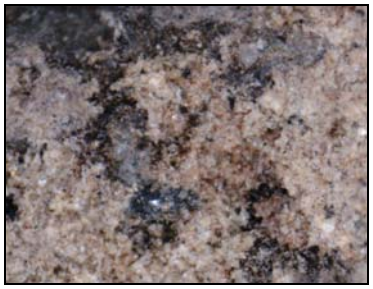
2.a. H1.P3.1.



2.b. H1.P3.1.



2.c. H1.P3.2.



2.d. H1.P3.2.

Figure 2. Images obtained by digital optical microscopy (x40 magnification)

3.2. Wavelength-dispersive X-ray fluorescence spectra (WDXRF)

The determinations by WDXRF reveal the massive presence of silicon accompanied by small amounts of elements like aluminium, sodium, iron, magnesium and others, which indicates the presence of minerals rich in these elements (Table 2).

Table 2. Wavelength-dispersiveX-rayfluorescence spectra (WDXRF) results: mineral composition of the pottery fragments

Oxid	*Content [mass %]*	
	H1.P3. middle black ceramic	***H1.P.3. exterior brown ceramic***
Na_2O	2.8589	3.3038
MgO	2.5966	2.7021
Al_2O_3	20.7228	20.9133
SiO_2	61.4097	60.3107
K_2O	2.5191	2.4517
CaO	1.2754	1.2489
MnO	0.0859	-
Fe_2O_3	6.5822	7.0299
ZnO	0.0217	-
BOREOX	1.9277	2.0396

3.3. X-ray diffraction

The main crystallographic phases and the degree of crystallinity were determined by X-ray diffraction, resulting in a complete qualitative and quantitative identification of the samples (Figures 3,4 and Tables 3,4). It is noted that the samples do not have a degree of crystallinity of 100% (H1.P3.CB with 98.8% and H1.P3.CMN with 98%), due to amorphous inclusions or incomplete structural transformations in the firing process of ceramic vessels.

The following crystalline compounds were identified: quartz* (mostly) accompanied by muscovite*, albite*, zinc oxalate, anorthite, minnesotaite, kalsilite, and windhoekite.

Table 3. XRD of black-brown ceramic in the middle

Phase name / Formula	*Content [%]*
Quartz* / SiO_2	45.6
Zinc Oxalate / $Zn(C_2O_4)$	6.9
Minnesotaite / $Fe_{2.3}Mg_{0.7}(OH)_2(Si_4O_{10})$	10.0
Albite* / $Na(AlSi_3O_8)$	5.3
Muscovite-2M2* / $K_{0.77}Al_{1.93}(Al_{0.5}Si_{3.5}O_{10})(OH)_2$	20.1
Kalsilite / $K(AlSiO_4)$	6.0
Windhoekite / $Ca_{1.68}Mn_{0.12}Fe_{2.96}^{+3}(Si_{7.87}Al_{0.08}O_{20})(OH)_4 \cdot 10H_2O$	6.1

*in both samples

Table 4. XRD of brown ceramic from the outer strat

Phase name / Formula	*Content [%]*
Quartz* / SiO_2	48
Muscovite-2M1 / $K(Al_{1.55}Mg_{0.24}Fe_{0.21})((Si_{3.38}Al_{0.62})O_{10}(OH)_2)$	13.2
Albite* / $Na(AlSi_3O_8)$	26
Anorthite / $(Ca_{0.96}Na_{0.04})$ $(Al_{1.96}Si_{0.04})Si_2O_8$	4
Muscovite-2M2* / $K_{0.5}Al_{2.5}Si_{3.5}O_{10}(OH)_2$	8.8

*in both samples

Both samples show a low Ca concentration, indicating the use of Ca-poor clay for the manufacture of these ceramics. In general, clay that has a CaO content of less than 5% (1.2754 %) is considered to be non-calcareous [6]. Regarding the concentration of hematite in the clay paste of the samples, it is about 7%.

It can be seen that no sample contains the phosphate group, so no hydroxyapatite (calcium phosphate). Iron is present in complex oxide structures.

The XRD results show that the main component of the analyzed ceramic material is quartz. Quartz (SiO_2) is a white or transparent mineral, but the presence of some impurities can give it new shades. Quartz cannot be found in these ceramic fragments in the form of tridymite or cristobalite due to the presence of muscovite, which indicates that the firing took place at a temperature lower than 800-850 °C. Quartz changes its structure with the increase in temperature to which it is subjected: at 870 °C it becomes tridymite, while at 1470 °C it becomes cristobalite, which are not found in the crystalline structures of the samples determined by XRD [7]. In the present case, it is clear that the vessels were fired up to 870 °C since the quartz did not transform into tridymite.

Anorthite belongs to the plagioclase group together with albite, appearing in volcanic and metamorphic rocks [8]. In addition, anorthite could have prevented vessels from breaking during firing through its ability to vitrify [9], as anorthite has resistance to thermal shock and high temperatures [10]. Albite is whitish plagioclase felspar found in metamorphic rocks and shale rocks [7], an obvious fact, because the geological substrate of Dobrogea is composed of the types of rocks mentioned above [11, 12]. Being feldspar, it is related to anorthite, albite having 10% of the composition of anorthite [7, 13].

Muscovite in two polymorphism type 2M1 and 2M2 is present in samples H1.P3.1 and H1.P3.2 (approximately 20% together in each sample). Muscovite is a hydrated phyllosilicate found in the form of translucent lamellae [14]. Being the most common mica, it is found in granites, schists, metamorphic rocks [15]. The presence of muscovite shows that the burning temperature did not exceed 800-850 °C [16].

Minnesotaite is an iron silicate found in metamorphic rocks [17] in association with muscovite, quartz, magnetite, hematite [18, 19, 20]. At 650 ºC, in the inert atmosphere, it transforms into ferrosilite, and at 700 ºC, in the oxidizing atmosphere, it transforms into oximinnesotaite [21], which proves that the firing of ceramics took place below this thermal threshold.

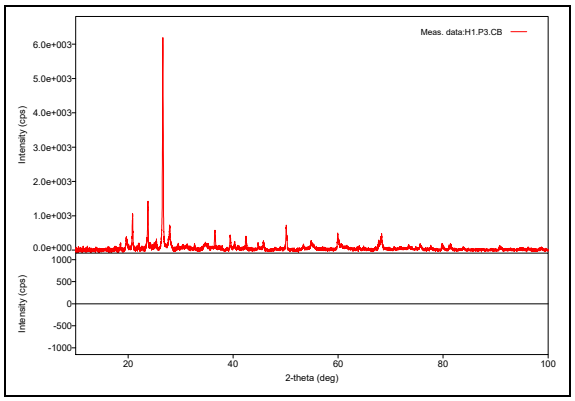


Figure 3. The diffractogram of the sample H1.P3.CB

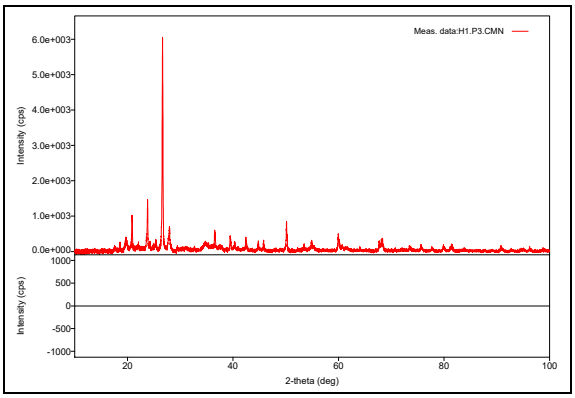


Figure 4. The diffractogram of the sample H1.P3.CMN

4. CONCLUSIONS

This work contributes to the knowledge of the techniques and materials used by the Hamangia civilization (third phase) in the manufacture of ceramic vessels.

The obtained results (XRD) show that the ceramic mass has a high content of quartz accompanied by various oxide compounds (muscovite*, albite*, zinc oxalate, anorthite, minnesotaite, kalsilite and windhoekite), low in calcium but rich in iron.

The fact that the crystalline oxide compounds identified by WDXRF and XRD in the outer brown ceramic and the black-brown inner ceramic, respectively, are almost similar, demonstrates that the color difference is only due to incomplete firings.

REFERENCES

[1] Voinea V, Băjenaru C, Lascu M, Nopcea C, Irimia A, Măiță M, Gheorghe A, Complexe Hamangia din situl Techirghiol Dealul Minerva – Paloda. Cercetări arheologice preventive 2020 (Raport preliminar). Pontica 2021; 54: 12-44.

[2] Balasse M, Tornero C, Bréhard S, Ughetto-Monfrin J, Voinea V, Bălășescu A, Cattle and Sheep Herding at Cheia, Romania, at the Turn of the Fifth Millennium cal BC. A View from Stable Isotope Analysis. Proceedings of the British Academy 2014; 198: 115–142.

[3] Voinea V, Neagu G, Ceramica Hamangia III. Pontica 2006; 42: 9-25.

[4] Carozza L, Micu C, Bălășescu A, Ailincăi S, Burens A, Gâza O, Mănăilescu C, Pour une relecture des collections archéologiques néolithiques et chalcolithiques dans la zone de Hamangia-Baia: nouvelles données chronologiques relatives aux recherches conduites par Dumitru Berciu. Cercetări Arheologice 2020; 27: 141-161.

[5] Nodari L, Maritan L, Mazzoli C, Russo U, Sandwich structures in the Etruscan-Padan type pottery. Applied Clay Science 2004; 27(1-2): 119–128.

[6] Tite, M.S. Ceramic production, provenance and use - A review. Archaeometry 2008, 50, 216–231.

[7] Estaugh N, Walsh V, Chaplin T, Siddall R. 2008. *Pigment Compendium A Dictionary and Optical Microscopy of Historical Pigments*. Elsevier, Amsterdam.

[8] Giuliani G, Groat L, Geology of corundum and emerald gem deposits: a review. *Gems & Gemology 2019*; 55(4): 464–489.

[9] Wei C, Liu X, Niu J, Feng L, Yue H, High temperature mechanical properties of laminated ZrB_2–SiC based ceramics. *Ceram Int*2016; 42:18148–18153.

[10] Harabi A, Zaiou S, Guechi A, Foughali L, Harabi E, Karboua NE, Zouai S, Mezahi FZ, Guerfa F, Mechanical properties of anorthite based ceramics prepared from kaolin DD2 and calcite. *Ceramica*2017; 63: 311-317.

[11] Săndulescu M. 1995, Dobrogea within the Carpathian foreland. In Grădinaru, E. (ed.) Field Guidebook. Central and North Dobrogea. IGCP Project No.369, Comparative Evolution of PeriTethyan Rift Basins, Romania, Oct.1-4, 1-4.

[12] Seghedi A, Oaie G, Aniţăi N, 2018. *Dobrogea – geological heritage*. GeoEcoMar Publ. House, București.

[13] Ferguson RB, Traill RJ, Taylor WH, The crystal structures of low-temperature and high-temperature albites. Acta Crystallographica 1958; 11: 331–348

[14] Shafei L, Adhikari P, Ching W, DFT Study of Electronic Structure and Optical Properties of Kaolinite, Muscovite, and Montmorillonite. *Crystals* 2021*; 11*, 618.

[15] Guidotti CV, Compositional variation of muscovite as a function of metamorphic grade and assemblage in metapelites from N.W. Maine. *Contr. Mineral. and Petrol.* 1973; 42: 33–42.

[16] Damjanović L, Holclajtner-Antunović I, Mioč UB, Bikić V, Milanović D, Evans IR, Archaeometric study of medieval pottery excavated at Stari (Old) Ras, Serbia. Journal of Archaeological Science 2011; 38(4): 818–828.

[17] Klein C, Some Precambrian banded iron-formations (BIFs) from around the world: Their age, geologic setting, mineralogy, metamorphism, geochemistry, and origin. Am. Mineral 2005; 90: 1473–1499.

[18] Gruner JW, The composition and structure of minnesotaite, a common iron silicate in iron formations. Amer. Mineral 1944; 29: 363-372.

[19] Klein C, 1983. Diagnesis and metamorphism of precambrian banded iron-formation., in: Iron-Formation Facts and Problems. Edited by A.F. Trendall, R.C. Morris. pp. 417–468.

[20] Konhauser KO, Planavsky NJ, Hardisty DS, Robbins LJ, Warchola TJ, Haugaard R, Lalonde SV, Partin CA, Oonk PBH, Tsikos H, Lyons TW, Bekker A, Johnson CM, Iron formations: A global record of Neoarchaeanto Palaeoproterozoic environmental history. Earth-Science Rev. 2017; 172: 140–177.

[21] Lempart-Drozd M, Błachowski A, GumsleyA, Ciesielska Z, Thermal decomposition of minnesotaiteand dehydrogenation during Fe_2^+ oxidation, with implications for redox reactions in Banded Iron Formations. Chemical Geology 2022; 601: 120867.