ORIGINAL PAPER

ARHAEOMETRIC INVESTIGATIONS ON CERAMIC MATERIALS FROM HUNEDOARA – THE COURT AREA

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Abstract. *A multidisciplinary study on the archaeological site located in Hunedoara – the Court area, developed in 2011 – 2012 have been analyzed in this paper. The ceramic samples were analyzed through spectral techniques: FTIR, Raman, microscopy techniques (SEM-EDS), colorimetric and porosimetry measurements, for determining the chemical, mineralogical and petrographic characteristics on the investigated ceramic samples discovered during the archaeological campaign from 2012; the results are presented in order to determine the raw material provenance and the production process. Some information on constructive history and degradation or damage status, are detailed.*

Keywords: *ceramic, Hunedoara - the Court area, microscopy, porosimetry.*

1. INTRODUCTION

The settlement from the Hunedoara – the Court area was discovered in the 70s by the priest Petre Govora, who, on the occasion of some public works, harvested a series of ceramic fragments that have been published [1]. The documented archaeological situation shows that the researched area was heavily inhabited by human communities at the beginning of the Eneolithic. The ceramics discovered in this area is mostly coarse and belong to the same the cultural horizon (Fig. 1), with colors ranging from brick or orange to brown and black. Sporadically, ceramic fragments were burnt in the black-topped technique. The ceramic paste is in addition to sand with different granularity, slime and many ocher granules, sometimes all of which are associated. Although the ceramic material was very fragmented, but from the technological point of view and that of the forms and decorative motifs, there are some similarities with analogies with the ceramics discovered in the settlements of Banat from Foeni and in Transylvania at Alba Iulia - Lumea Nouă [2, 3].

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The physical and chemical composition of archaeological ceramics is significantly altered by the life cycle of the artifacts, as follows:

- Thermal transformations in clay materials during firing help to estimate the firing temperature of the artefacts [4, 5]
- FTIR spectroscopy is considered as an important tool in the analysis of clay minerals revealing both the type of clay and the firing temperature [6, 7].
- Raman spectroscopy has been used for the characterization of ancient pottery, the identification of the pigments used on ceramic samples, puting into evidence some mineralogical phases and the transitions between them can act as "mineralogical thermometers" or give indications about the firing atmosphere, in the attempt to identify raw materials and/or manufacturing processes of prehistoric pottery [8, 9].
- SEM examination of the pottery provides information regarding not only the internal morphology that developed during the original firing in antiquity, but also the extent of the vitrification (the glassy phase) and the pore structure [10, 11].
- Porosimetry can provide information about archaeological manufacturing technologies, as firing temperature, the type of clay and tempering materials, and the manufacturing techniques [12, 13].

The archaeometric study of two ceramic samples, discovered during the archaeological campaign from 2012, at the Hunedoara-the Court, are presented in this paper; the identifying the provenance of the raw materials is important for collecting information about the exploitation of natural resources and to better understand the manufacturing and weathering / deterioration processes of these artifacts. Modern and performant analytical techniques, as FTIR, Raman, SEM-EDS, colorimetry, porosimetry, are used and the results are discussed too.

2. MATERIALS AND METHODS

2.1. MATERIALS

The tile samples discovered in the Hunedoara – the Court area, are shown in Fig. 1.

Figure 1. The ceramic samples from Hunedoara - the Court area.

2.2. METHODS

Fourier transformed infrared spectroscopy (ATR-FTIR) has been recorded with a Vertex 80 spectrometer (Bruker Optik GMBH, Germania) in the range of 4000–400 cm^{-1}, equipped with DRIFT accessory.

Raman spectra have been recorded with a FirstGuard Raman apparatus, BaySpec with two wavelengths (1064 and 785 nm).

The optical microscopy was performed with a Novex trinocular microscope (at different magnifications). Also, the optical microscopy has been recorded by a Primo Star ZEISS optical microscope that offers the possibility to investigate the samples in transmitted light at a magnification between 4X and 100X. The equipment had attached a digital video camera (Axiocam 105) which, by the microscope software, allowed real-time data acquisition. The obtained images could easily be converted from 2D in 3D format through its software for a better viewing.

The Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS) results were obtained by a SU-70 (Hitachi, Japan) microscope, used for characterization of micro- and nanomaterials qualitative and quantitative analysis of samples and composition of the structure for a sample surface, respectively.

Color measurements have been recorded with a CM-2600d spectrophotometer (KONICA MINOLTA) (Japan) under a D65 light source and an observer angle of 10°. The differences in L*, a*, and b* and the total color differences ΔE^*_{ab} were calculated using the equations from JIS 2008 [14]. The CIELab (CIE 1986) chromatic parameters were chosen for the study, i.e., lightness (L*), which ranges from 0 for black to 100 for white, and the chromatic coordinates a* and b*, coordinate a* ranges in value from +60 (magenta) to -60 (green) and b* from +60 (yellow) to -60 (blue).

The nitrogen adsorption/desorption isotherms were recorded at 77K in the relative pressure range p/p_o=0.005-1.0 using NOVA2200e Gas Sorption Analyzer (Quantachrome). Data processing was performed using NovaWin version 11.03 software. Prior to adsorption measurements, the samples were out gassed 4 hours at 300^oC under vacuum. The specific surface area was determined by the standard Brunauer-Emmett-Teller (BET) equation. The total pore volume was estimated from the volume adsorbed at a relative pressure p/p_o close to unity. The pore size distribution and mesopores volume were obtained from desorption branch of the isotherm by applying the Barrett-Joyner-Halenda (BJH) model. The t-plot method was used to estimate micropore surface area and external surface area.

3. RESULTS AND DISCUSSION

Hunedoara is located in the area of Southern Carpathians and Banat, in a very complex geological area, consisting of crystalline-mesozoic units belonging to the sediment-volcanic units that contribute to the Southern Carpathians [15, 16], recognized by mesozoic sedimentary formations (limestone, marl, clayey shale, conglomerate, sandstone) and magmatite (basalt), as well as neogene formations (basalt, andesite, pyroclastes) [17].

The stones found in majority in Romania are limestone (in various varieties) and siliceous (sandstone, granite, conglomerate). Depending on the geographical area and due to deficiencies in the processing of the raw material, clay, magnesium, calcium, manganese, limestone granules, sulphates can be present in the composition of clay used in the production of bricks, besides the aluminum hydrate as the main component and other substances, organic

substances, with various effects on the timing of the bricks. The main elements present in the analyzed samples have been determined by EDS technique (Fig. 2).

Elemental analysis using EDS with scanning electron microscopy provides material information correlated to structure for ceramic materials and the EDS maps well correlate phase morphology to composition for ceramic materials. The raw materials are clays with finely divided quartz (sand) (0.02–0.04 mm) and possibly feldspar, responsible for the rheology along the thermal processing. Clay minerals based on aluminosilicates, generated either by the weathering of igneous rocks under the influence of water, dissolved carbon dioxide, and organic acids, or from feldspar ($KAlSi_3O_8$) eroded from rocks such as granite and deposited in lake beds, which are aluminosilicates that contain sodium (Na), potassium (K), or calcium (Ca) with a composition from $NaAlSi_3O_8$ and $KAlSi_3O_8$ to $CaAl_2Si_2O_8$. Feldspar acts as fluxing agents to reduce the melting temperatures of the aluminosilicate phases where they are subsequently transformed into clay [18]. Except feldspar, silica, as the second major ingredient in refractories, is usually added as quartz sand, sandstone, or flint pebbles [19].

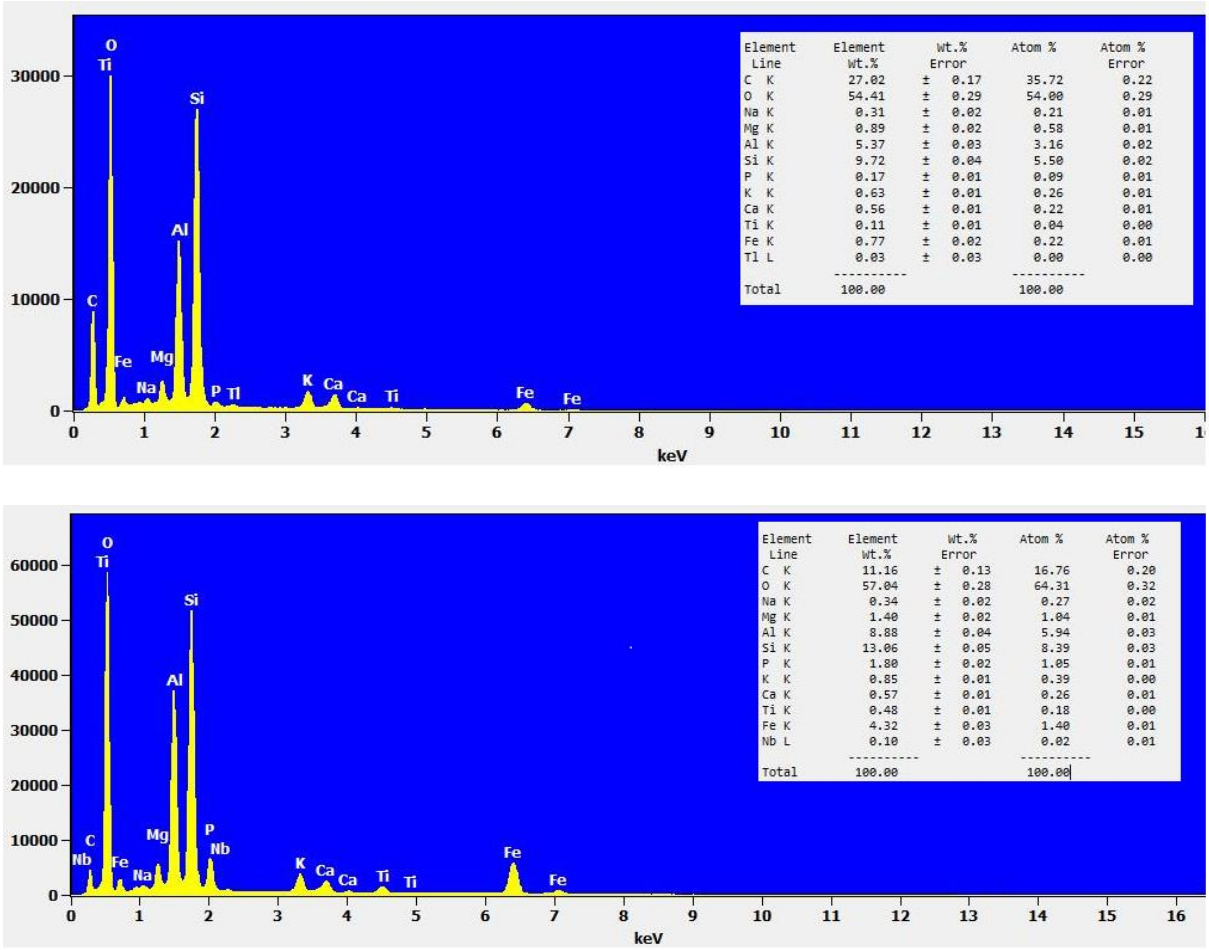


Figure 2. The EDS results of the black (up), and brown (down) samples.

Some clay materials used in ceramic production are characterized by the occurrence of pyrophyllite, from a few percent up to 80% wt. Since pyrophyllite has a different technological behavior with respect to kaolinite, it is convenient to classify as *Pyrophyllitic Clays* (PC) the raw materials with a significant amount of pyrophyllite (> 20%) as they present commonly lower loss on ignition, easier compaction, and lower refractoriness with respect to kaolin [15]. PC are usually claystones of different origin that, along with pyrophyllite, contain quartz, feldspars and often kaolinite and / or illite. The ceramic bodies

are distinguished in light-firing (from white to light brown) and dark-firing (from red to dark brown) on the basis of color after firing. Overall, clays used in light-firing and dark-firing bodies are fairly well discriminated by a Fe_2O_3 content of approximately 3% wt. (Fig. 2).

In order to determine the main chemical chromophores from the samples, FTIR analysis have been recorded, too, by using drift technique (Fig. 3).

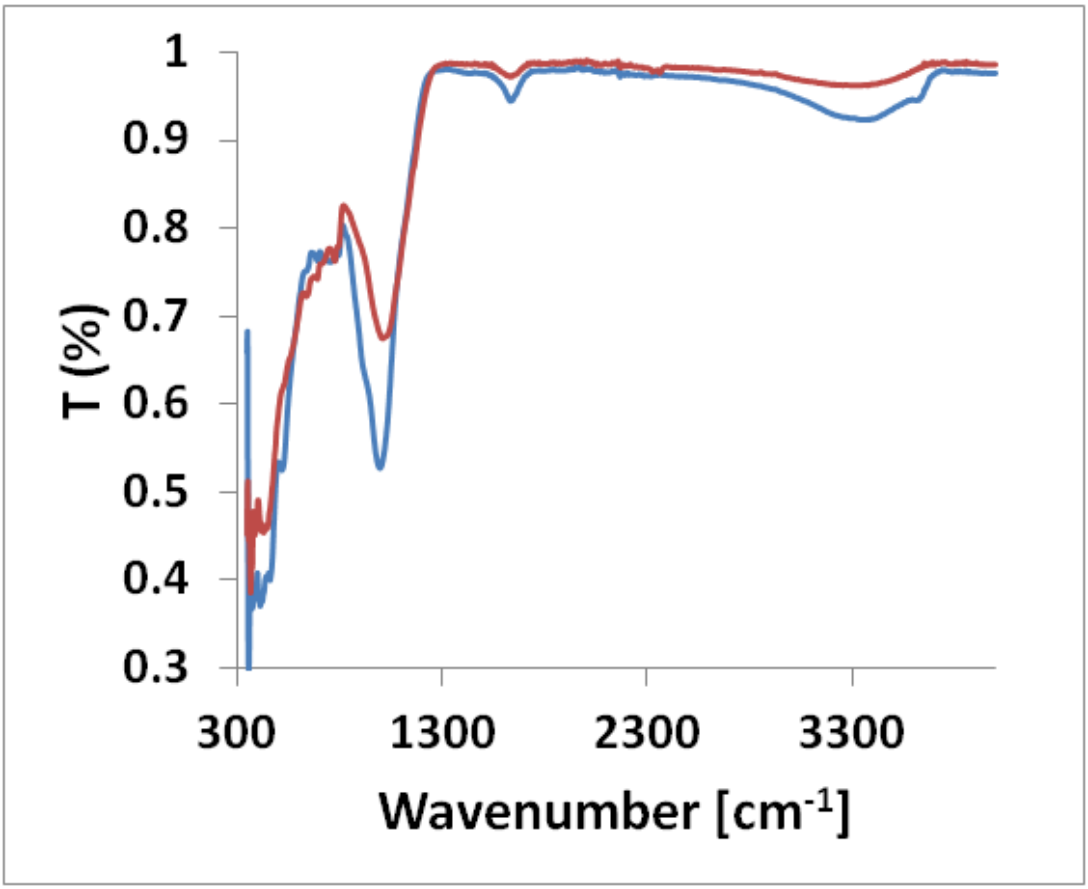


Figure 3. FTIR spectra of 1HD (blue line) and 2HD (red line).

Quartz is well detected in all the samples: 1088-1092 cm^{-1} due to Si-O stretching mode, the distinctive doublet at 796 and 777-783 cm^{-1} and the peak at 692-694 cm^{-1} due to Si-O symmetrical stretching and bending modes respectively [19]. The quartz intensity (band at 1083 cm^{-1}) was much lower than the calcite intensity although the quantity of both minerals is the same (mole). Muscovite, with three Si atoms (1026-1036, 1007 and 530 cm^{-1}) as well as feldspars (752-758, 646 and 465-471 cm^{-1}) and Pyroxenes at 519 cm^{-1} were also detected [20]. Silicate, phosphate, or sulfate spectra overlap each other in the region (900–1000 cm^{-1}).

Raman spectroscopy has been used for the characterization of ancient pottery for the identification of the minerals used on ceramic of different technological skills. The oxidising or reducing atmosphere implies the formation and therefore the presence of characteristic minerals, especially haematite α-Fe_2O_3, which is responsible for the reddish colour, and magnetite Fe_3O_4, which confers a dark shade on the ceramic material (Fig. 4). The Raman spectrum of hematite (α-Fe_2O_3) is here identified at 660 cm^{-1}, being different for different mineralogical composition and firing process of pottery productions [21]. The coloured iron-rich silicates that give rise to an intense band at 674 cm^{-1}. In the range 513–514 cm^{-1}, and 450–500 cm^{-1} region, the bands specific to alkali feldspar spectra, could be observed [22].

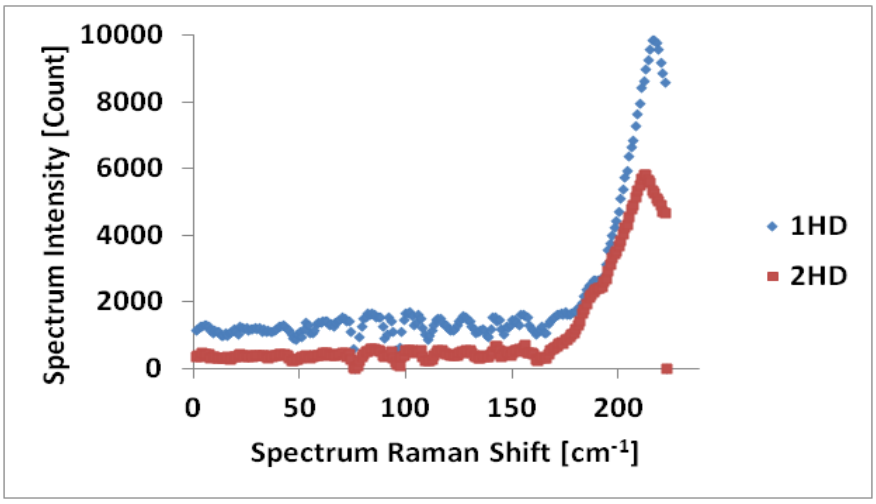
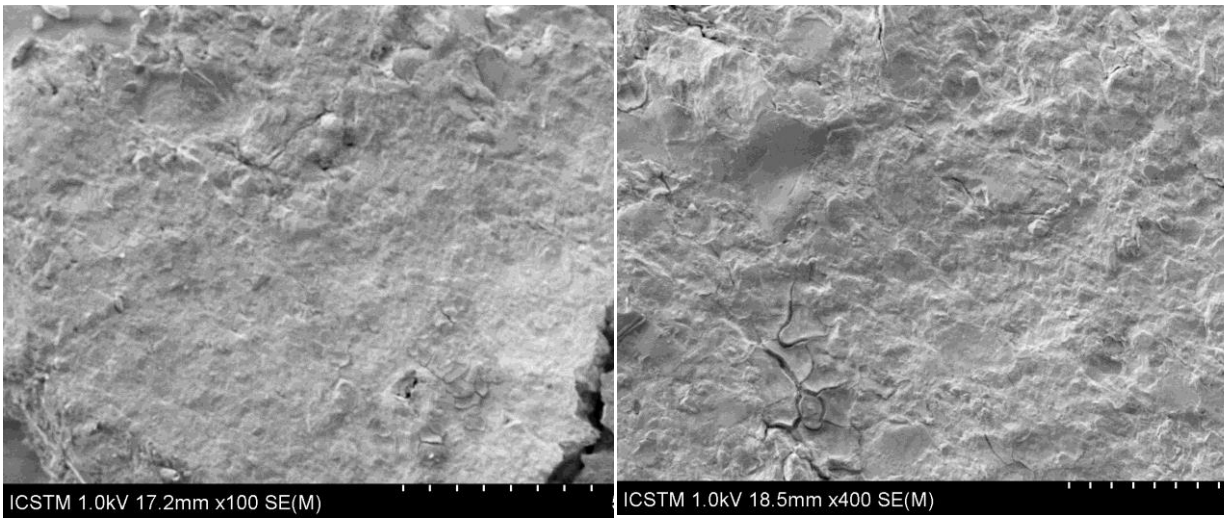
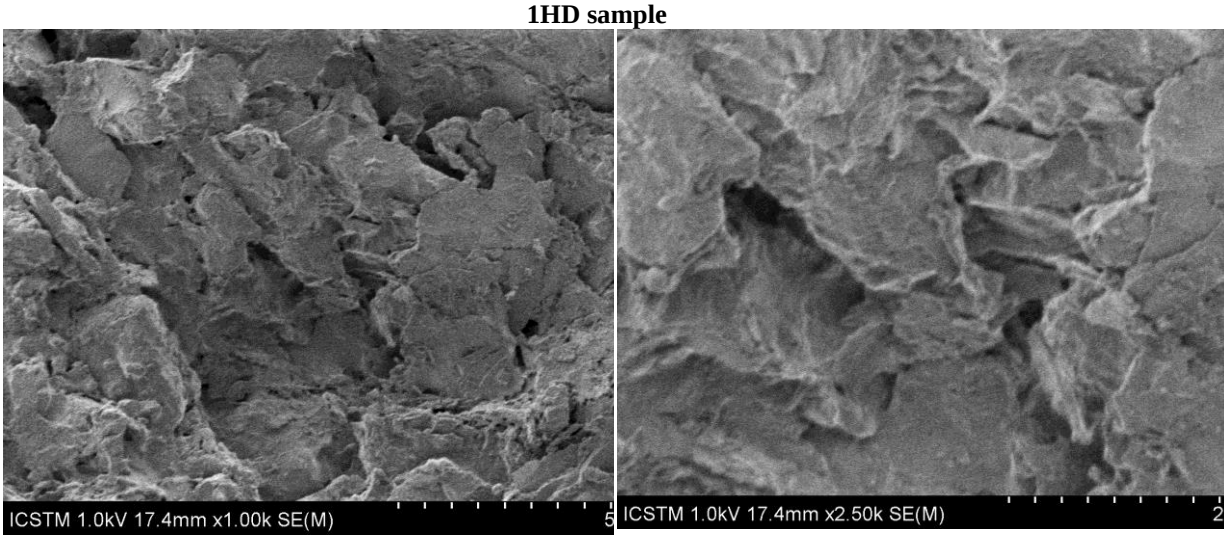


Figure 4. Raman spectra of the samples 1HD (blue) and 2HD (red).

The electron microscopy study of the ceramic body seems to indicate anorthite $CaAl_2Si_2O_8$, a high temperature feldspar mineral, as the main phase, although it was very difficult to verify this point by x-ray diffraction analysis. Anorthite grains contain potassium in significant quantity, thus confirming their lamellar crystallites cluster structure [23].



1HD sample



2HD sample

Figure 5. SEM images for the samples: 1HD and 2HD.

Sample 1 (up) shows large rounded white lump. The open and porous structure visible in the SEM images of 1HD, is a real proof for the firing treatment of the ceramic between 700 and 900 °C. In this temperature range, the sintering process is governed via solid state mechanism, especially surface diffusion. In addition, this sample underwent a series of phase transformations such as dehydration of hydroxides (gibbsite and goethite) and dehydroxylation of kaolinite to metakaolinite formation. This range of temperature is characterized by the decomposition of carbonates, which starts at around 650 °C and ends at around 800-850 °C. Calcite, the most common pure calcium carbonate ($CaCO_3$), decomposes in calcium oxide (CaO) and release CO_2 increasing the porosity. High-temperature crystalline phases (900-1000 °C) are the result of the reactions involving carbonates, calcium oxides and silicates as anorthite ($CaAl_2Si_2O_8$). The thermal analysis will be reported subsequently.

All these statements could be correlated with chromatic parameters and with Fe and O content (Fig. 6). High concentration of oxygen and small iron content are visible for 1HD, with a smaller lightness and clarity, as signs for burning that this sample supported [24].

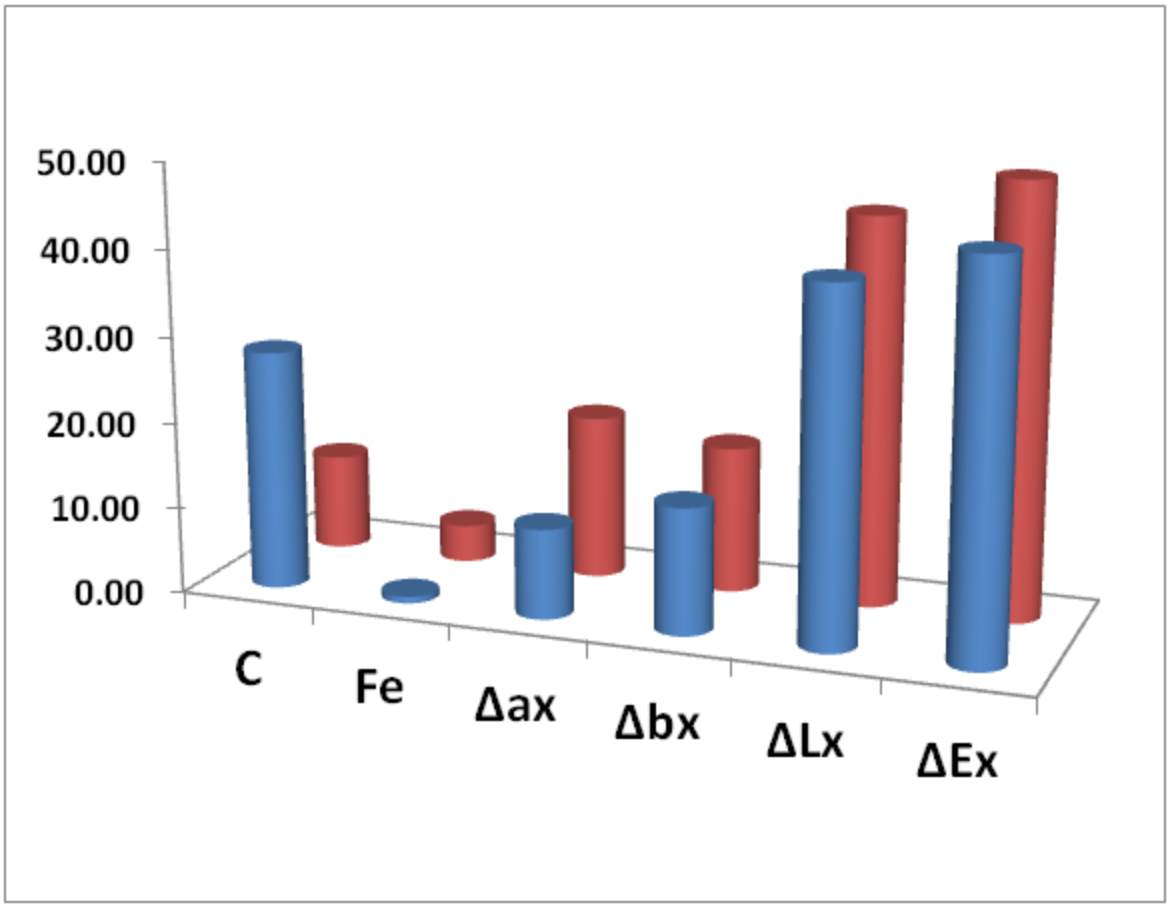


Figure 6. The chromatic parameters of the investigated tiles.

In this color space, which is presently one of the most widely used color spaces for measuring object color, *L** indicates lightness, and *a** and *b** are chromaticity coordinates [25]. The sample 1HD is black (L* =57.51, a*=8.17; b*=25.82), while the sample 2HD is red-brownish with high amounts of dark red putties (L*=53.55; a*=17.33; b*=27.47). The sample 1HD prove to be insufficiently pressed and show irregular chromatism, due to firing and time damages (Fig. 6).

Porosity has long been recognized as an important tool for study of ceramics: raw materials, clay processing and object fabrication methods, drying and firing regimes, and use, burial, or deterioration factors [26]. During clay processing and vessel fabrication, air bubbles can become trapped and the shrinkage during drying and firing can enlarge the pores, Table 1. As carbonates dissociate and organics burn out or char during firing, additional porosity can be created.

There are two types of pores:

- **Long linear pores** with parallel alignment, which can appear as a result of shrinkage of the clay as excess water is released during firing.
- **Less interconnected linear pores** which may appear at higher firing temperatures these than at lower firing temperatures [27]. If firing temperatures are high enough, porosity can decline if vitrification occurs [28], at it is visible in Fig.5.
- **Round secondary pores** can be produced by trapped gases as the clay matrix and silica minerals begin to melt, off-gas, and vitrify [28].
- **Bloated round pores** which appear visible at overfiring.

The bulk porosity analysis would not be as informative as being able to examine the variety in size, volume, and distribution of the pores (Table 1).

Table 1. The porosimetry parameters for the samples 1HD and 2HD.

Sample	Surface area (m^2/g)	Pore volume (cc/g)	Pore size (nm)
1 HD - black	17.73	0.026	4.287
2HD – red-brown	8.710	0.015	2.959

4. CONCLUSION

A multidisciplinary study on the archaeological site located in Hunedoara – the Court area, developed in 2011 – 2012 have been analyzed in this paper. The ceramic samples were analyzed through spectral techniques: FTIR, Raman, porosimetry, microscopy techniques (SEM-EDS), colorimetric measurements, for determining the chemical, mineralogical and petrographic characteristics on the investigated samples. Some information on the degradation or damage status, are detailed.

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