Arhaeometric Concepts and Methods of Intervention on Historical Monument Buildings. The Case of the Corvins’ Castle

R M Ion¹,²,*, L Iancu¹,², R M Grigorescu¹, D Carutiu-Turcanu³, S Tinca⁴, N Ion¹, I A Bucurica⁵, S Teodorescu⁵, I D Dulama⁵, R M Stirbescu⁵, A Gheboianu⁵ and M L Ion⁵
¹ Evaluation and conservation Cultural Heritage Team, ICECHIM, 202 Splaiul Independentei, Bucharest-060021, Romania
² Department of Engineering Doctoral Studies, Valahia University, 13 Aleea Sinaia, Targoviste, Romania
³ OVIDIUS University Constanta, Expertise Center for the Art of Science, Culture and Spirituality, Institute of Science, Culture and Spirituality, Constanta
⁴ Corvin’s Castle, Hunedoara, Romania
⁵ Valahia University of Targoviste, Institute of Multidisciplinary Research for Science and Technology, Targoviste, Romania
⁶ “Atelierul de Creatie” NGO, Bucharest

E-mail: rodica_ion2000@yahoo.co.uk

Abstract. A multidisciplinary study on the mortars from the Corvins’ Castle, Hunedoara, Romania has been carried out on two ceramic samples which were analyzed through spectral techniques (FTIR, Raman, X-ray powder diffraction) and diverse microscopy techniques (optical, scanning electron microscopy), for determining the chemical, mineralogical and petrographic characteristics on two ceramic tiles coming from the Corvins’ Castle discovered during the archaeological campaign from 2012, at the Administrator's House, inside of the castle yard; the results are presented in order to determine the raw material provenance and the production process. Some information on constructive details, construction history and degradation or damage status, are detailed. Also, the diagnosis results aim to determine the damaging causes, as well as the assessment of the safety or the way of intervention on the structure. The archaeometric study of two tiles, including the identifying of the raw materials provenance 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, SEM-EDS, XRD, colorimetric and gloss measurements, are used and the results are discussed too.

1. Introduction
Corvins’ or Hunyadi Castle located in Hunedoara, Transylvania, Romania (Figure 1), it was built in the 15th century on the site of an old fortress, on a cliff above the Zlasti River [1].

The story of the Corvins’ Castle (also known as the Hunyadi Castle) began in 1409 when the King of Hungary, Sigismund of Luxembourg (1384-1437), donated the royal possession of Hunedoara to Voicu and his family for outstanding military merits. The donation document also shows the name of
John, the future Iancu of Hunedoara, as the son of Voicu. Considered one of the most important military leaders in Central and Southeastern Europe in the fifteenth century, Iancu de Hunedoara is the one who started the construction of the castle around 1440, instead of the old fortress on a rock at whose feet it flows the Zlaști River.

The first documentary attestation of the castle appeared in 1443, in a document signed by Iancu de Hunedoara. At the beginning of the 17th century, the castle was in possession of the Bethlen family, and Gabriel, the Prince of Transylvania, was the one who brought the most important changes in the architecture of the monument, inspired by the late Renaissance fashion. Although impressive by military architecture elements such as the "Neboisa Tower" (which transforms the "don’t be afraid" tower) as the White Tower and the Artillery Terrace, the Corvins’ Castle also features highly refined civil architecture, represented by the Knights Hall or the Diete's Hall. In the seventeenth century the outer yard (the Hussars' Court) was built, a space that housed the dwellings of the administrator, the clerks, the house of the greyhounds, and the food and hatcheries. After the Austrians and Austro-Hungary's possession in the 18th-19th centuries, the castle was in the possession of the Romanian state from 1918. It has never been entirely rehabilitated, although such works have been carried out for many years, but even so it remains a unique monument that attracts and impresses tourists. The Hussars’ Yard was also built in the 17th century. It was a space that sheltered the houses of the administrator, of the clerk, greyhounds’ stable and storehouses for food and hay [2]. On 13 April 1854, a lightning caused a devastating fire that extensively damaged the castle. It was subsequently restored, but the restoration was carried out in several stages and some of these were not entirely successful.

Over the past few years, Corvins’ Castle underwent intense rehabilitation because the roof had been damaged due to moisture present in materials, cyclic, the influence of solar radiation, the temperatures, the water on the masonry, the influence of dissolved salts, the influence of frost and snow, the influence of wind and air currents, the influence of the particles of smoke, dust and sand, the influence of extreme natural phenomena, as floods or lightning, and the biological attacks by fungi and insects, birds or animals, which led to an excessive humidity [3]. Elimination of these problems should be solved by specialists in archeology and the restoration of historical monuments [4].

The raw materials are clays with finely divided quartz (sand) (0.02–0.04 mm) and feldspar, responsible for the rheology along the thermal processing. Clay minerals such as kaolinite (Al₂[Si₂O₅](OH)₄) generated either by the weathering of igneous rocks under the influence of water,
dissolved carbon dioxide, and organic acids, or from feldspar (KAlSi₃O₈) 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 NaAlSi₃O₈ and KAlSi₃O₈ to CaAl₂Si₂O₈. Feldspar acts as fluxing agents to reduce the melting temperatures of the aluminosilicate phases where they are subsequently transformed into clay [5]. Except feldspar, silica, as the second major ingredient in refractories, is usually added as quartz sand, sandstone, or flint pebbles [6]. The role of silica is either to maintain the shape during firing (as filler) or to improve the final mechanical properties.

The archaeometric study of two tiles, discovered during the archaeological campaign from 2012, at the Administrator's House, inside of the Corvins’ Castle yard, 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, SEM-EDS, XRD, colorimetric and gloss measurements, are used and the results are discussed too.

2. Materials and methods
2.1. Materials
The tile samples discovered in the Building House of the Administrator's House, Museum House of Bresles, situated in the Corvins’ Castel, Hunedoara, are shown in Figure 2.

2.2. Methods
2.2.1. Characterization 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.

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.

X-ray diffraction (XRD) diagrams have been registered with a X-ray diffractometer Rigaku Ultima IV, equipped with software for control, acquisition and data conversion. Several experimental configurations have been tested, as following: geometry in the Bragg - Brentano beam, anode voltage of 40 kV, anode current of 40 mA, scan at 1 degree / minute, at a 0.0200 step, angular scan range: 2q = 5-1500.
**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 following equations (JIS 2008 [7]): 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).

For **gloss parameters** a Specular GlossMeter was used, 3nh HG268, China instrument, which provided quantifiable gloss measurements, expressed as gloss units (GU) [8].

3. Results and discussions

Corvins’ Castle is located in the area of Southern Carpathians and Banat (Figure 4), in a very complex geological area, consisting of crystalline-mesozoic units belonging to the sediment-volcanic units that contribute to the Southern Carpathians [35]. The getic pavement is built mainly from crystalline shale, in which there are migmaitite, pegmatite, amphibolite, limestone and crystalline dolomites; over the crystalline formation are some sedimentation minerals, as: limestone, microconglomerate and sandstone. In these crystalline shale are important deposits of iron, being found as siderite deposits of variable lengths and thicknesses, which is transformed into limonite in the hematite, and pyrite, the ore being associated with the crystalline limestones. In the western part of Hunedoara there are talc of high quality. The sedimentary-eruptive zone of the Apuseni Carpathians is composed of mesozoic sedimentary formations (limestone, marl, clayey shale, conglomerate, sandstone) and magmatite (basalt), as well as neogene formations (basalt, andesite, pyroclastes) [9].

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. Depending on the content of the clay, in bricks can be found calcium sulphates and other soluble salts that produce efflorescences and disintegration phenomena [10, 11]. The concentration of iron-based components may change the coloration. The composition of the two tiles investigated in this paper is shown in Figure 3, a, b, c.

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. Enamels are composed primarily of silica, which forms the vitreous lattice, lead oxides, which lower the melting point [12]. The enamel was made with kaolin, zinc oxide, feldspar, calcite and lead base; copper and chromium oxides were added to provide green hue and it was glazed to attain a glossy finish; the enamel on the repair tiles had a lead, sodium and potassium base with lead oxide, silica and alumina [13]. The XRD analysis of the tile samples reveal that calcium carbonate is the main component of stone, the result of first sample of stone is quartz (73.8%), muscovite (15.7%), mica (6.2%) hematite (3.0%), gypsum (1.3%), the result of second sample is Pyrophyllite (69.7%), quartz (12.3%), Hercynite (5.6%), Anorthite (3%), Macrocline (5%), gypsum (1.5%), hematite (2.9%). Crystal structure analysis results and Indexing and quantitative analysis results are shown for both samples in the Tables 1 and 2.

Overall, clays used in light-firing and dark-firing bodies are fairly well discriminated by a Fe2O3 content of approximately 3% wt. During the reducing firing stage, the Fe3+ in the iron-rich slips, containing about 12 wt.% of iron as determined by EDX analysis [14], is converted to Fe2+ in a spinel phase of the magnetite–hercynite solid solution type. Some clay materials used in ceramic tile 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 or sericite.

Figure 3. The EDS results of the tile (a) up, (b) middle and (c) enamel (down).
Table 1. XRD results for tile C1.

| Phase name | Formula                  | DB card number | Content (%) |
|------------|--------------------------|----------------|-------------|
| Quartz     | SiO₂                     | 01-083-0539    | 73.8        |
| Muscovite  | (K₀.₈₂ Na₀.₁₈) (Fe₀.₀₃ Al₁.₉₇) (AlSi₃)O₁₀(OH)₂ | 01-080-0743    | 15.7        |
| Mica       | Rb₀.₉⁹ Fe₂.₀₃ (Fe₁.₀₄ Si₂.₉₆)O₁₀(O H)₂ | 01-075-4387    | 6.2         |

Table 2. XRD results for tile C2.

| Phase name                                      | Formula                  | DB card number | Content (%) |
|------------------------------------------------|--------------------------|----------------|-------------|
| Pyrophyllite                                    | Al (Si₂O₅) (OH)          | 01-083-1805    | 69.7        |
| Potassium tecto-alumino-trisilicate (macroline, | K (AlSi₃O₈)              | 01-087-1790    | 2.4         |
| potassium-rich alkali feldspar)                 |                          |                |             |
| Quartz                                          | SiO₂                     | 01-086-1630    | 12.3        |
| Anorthite, syn sodian (plagioclase feldspar)    | (Na₄₅Ca₅₅) (Al₁₅₅ Si₂₄₅O₈) | 01-085-1415    | 3.0         |
| Hercynite                                       | (Fe₀.₈⁶₇ Al₀.₁₃₃) (Fe₀.₂₃₅ Al₁.₇₆₅) O₄ | 01-070-9102    | 5.6         |

XRD analyses of the investigated tiles samples confirmed the presence of the minerals identified by optical microscopy.

The results of the microscopic examination indicate that most of the grains of the analyzed mortars, with the exception of C1 sample, revealed quartz, feldspars and rock fragments, indicating an origin from natural sands. Also, mica is present in this sample [16].

The ceramic bodies are distinguished in light-firing (from white to light brown) and dark-firing (from pink 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 Fe₂O₃ content of approximately 3% wt, Figure 4.

Sample C1 (up) shows large rounded white lump.

The open and porous structure visible in the SEM images of C2, 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, the green pieces on heating up to 900 °C 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 (CaCO₃), decomposes in calcium oxide (CaO) and release CO₂ increasing the porosity. High-temperature crystalline phases (900-1000 °C) are the result of the reactions involving carbonates, calcium oxides and silicates as anorthite (CaAl₂Si₂O₈).

The SEM images from Fig. 5 shows the morphology of the fine grained clay matrix and some rather large inclusions, but it is difficult to identify the nature of the latter because they exhibit no idiomorphic crystal faces [20].

These images evidenced a clay matrix, of an inclusion identified as quartz and sodium feldspar, as previously stated by XRD. The quartz (SiO₂) shows practically nothing else, while the inclusion identified as a feldspar additionally exhibits the lines of Na, Al, and very little K. Most probably, it is a sodium feldspar, Na[AlSi₃O₈] of the albite–orthoclase system. The clay matrix contains much aluminum, some potassium and a small quantity of iron.
Figure 4. Macroscopic pictures of the selected tile surfaces.

Figure 5. SEM images of the tile samples.

All these results could be argued by FTIR investigations, as it is shown in Figure 6. Silicate, phosphate, or sulfate spectra overlap each other in the region (900–1000 cm$^{-1}$). 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 (band at 979 cm$^{-1}$), has a main band approximately three times more intense. 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 [18].

Muscovite (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 [19].
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 [20]. The ceramic tile C1 is much reddish-brown (\(L^* = 56.18; a^* = 7.66; b^* = 19.86\)) in the points where there are high amounts of dark red putties than in the center (\(L^* = 55.13; a^* = 8.46; b^* = 20.41\)) or at the edge (\(L^* = 54.84; a^* = 8.08; b^* = 19.69\)). The sample prove to be insufficiently pressed and show irregular chromatism, Figure 7. The carefully manufactured and sized courtyard tiles C2 are highly compact. Their light yellow hue (\(L^* = 75.79; a^* = 1.56; b^* = 19.10\)) is speckled by the reddish putties uniformly distributed across their surface. The enamel on the original tiles C2 have reddish tone around the edges (\(L^* = 81.51; a^* = - 0.94; b^* = 25.79\)), lighter toward the center (\(L^* = 79.77; a^* = - 0.27; b^* = 25.78\)), and with bluish stains on the lines (\(L^* = 79.17; a^* = 0.06; b^* = 26.36\)).

![Figure 6. FTIR spectra of C1 (blue line) and C2 (red line).](image)

![Figure 7. The chromatic parameters of the investigated tiles.](image)

In correlation with color measurements, the gloss index could be used for measures the amount of light directed and reflected at a defined angle, by integrating the total scatter (reflected and diffused light). The most suitable geometry for general applications is 60°. The best optical geometry for
surface with very high and very low gloss is respectively 20° and 85°. Gloss is affected by the refractive power of the boundary between two materials when they have different refractive indices, when certain paints a binder layer containing no pigments is formed on the top surface of paint films, Figure 8.

![Figure 8. The gloss variation of the investigated tiles.](image)

Since the refractive index of this binder layer is generally different from those of both sides, air and pigmented phase, interference of light would occur resulting in a decrease in gloss, in good agreement with literature [21]. In our case, the gloss index strongly decrease after mica adding in ceramics (C1) and increase for enamel application (C2).

4. Conclusions
In conclusion, both ceramic samples taken from the Archaeological Site Administrator’s House from Courtyard of Corvins’ Castle are prepared in the same area with native natural materials as follows: the main minerals are quartz, muscovite, mica, hematite (at the first sample) and pyrophyllite, quartz, hercynite, anorthite, macrocline (at the second sample). Calcite is difficult to identify because of its decomposition as baking takes place at 900-1000 degrees without specific control, under these conditions calcite decomposes into CO₂ which contributes to the high porosity of the samples.

The color depends on the iron oxide content, and on other components (as TiO₂ and CaO), which may turn the color into yellowish or pinkish shades. Overall, clay used in light-firing and dark-firing bodies is fairly well discriminated by a Fe₂O₃ content of approximately 3% wt. During the reduction firing stage, the Fe³⁺ in the iron-rich slips is converted to Fe²⁺ in the spinel phase of the magnetite-hercynite solid solution type. Enamel is composed primarily of silica, which forms the vitreous lattice, kaolin, zinc oxide, feldspar, calcium and lead base which lower the melting point and alumina; copper oxides were added to provide green hue and it was glazed to achieve a glossy finish. Certainly should be mentioned the presence of Calcium sulphate generated during the ageing process, as at all the samples decoperted from archaeological sites.

5. References
[1] Bodochi I 2008 Castelul Corvinilor in secolul al XVII-lea (1) Corviniana XII 207-232
[2] Roman C C, Diaconescu D, Țiplic M 2004 Archaeological excavations at Hunedoara-The Corvins’ Castle - the sacristry of the chapel, Studii de istorie veche și arheologie. Omagiu profesorului Sabin Adrian Luca, BAHC IV 187-207
[3] Chefneux E 1967 Restaurarea Castelului Corvinilor de la Hunedoara, Dosar I.N.M.I. Arhiva monumentelor istorice 5473
[4] Roman C C, Tincu S 2009 Terra Sebus 1 153-172
[5] Maniatis Y 2009 The Emergence of Ceramic Technology and Its Evolution as Revealed with the use of Scientific Techniques, in: A.J. Shortland, I. Freestone, T. Rehren, From Mine to Microscope: Advances in the Study of Ancient Technology, Oxford: Oxbow Books, Chapter 2 11–28
[6] Bergaya F, Lagaly G 2000 General introduction: Clays, clay minerals and clay science, in: F. Bergaya, B.K.G. Theng, G. Lagaly (eds.), Handbook of Clay Science. Elsevier, Amsterdam, 1–18

[7] ASTM D 523-94 1999 Standard Test Method for Specular Gloss, 5.1. pp. 1

[8] Luca S A, Roman C, Diaconescu D, Suciu C 2005 Repertoriul arheologic al județului Hunedoara, Bibliotheca Septemcastrensis, XIV Alba Iulia

[9] Tite M S, Bimson M, Freestone I C 1982 Archaeometry 24 117–126

[10] Mukhopadhyay T K, Ghatak S, Maiti H S 2010 Ceram. Int. 36 909-916

[11] Bodochi I 2008 Castelul Corvinilor in secolul al XVII-lea (1), Corviniana, XII 207-232

[12] Ion R M, Iancu L, Carutiu-Turcanu D, Schroder V, Tincu S, Roman C, Ion N, Bucurica I A, Teodorescu S, Dulama I D, Stirbescu R M, Gheboianu A 2018 Traditional building materials and modern restoration products identified at the painted Matia-fresco Loggia, Corvins’ Castle, Romania, Geophysical Research Abstracts 20 EGU2018-5198

[13] Marcu D, Petrov G 1993 Ars Transsilvaniae 93-105

[14] Ion R M, Ion M L, Fierascu R C, Serban S, Dumitriu I, Radovici C, Bauman I, Cosulet St, Niculescu V I R 2010 J. Therm. Anal. Calorim. 102 393-398

[15] Ion R M, Dumitriu I, Fierascu R C et al. 2011 J. Therm. Anal. Calorim. 104 487-493

[16] Ion R M, Fierăscu R C, Teodorescu S, Fierăscu I, Bunghez I R, Țurcanu-Caruțiu D, Ion M L 2016 Ceramic Materials Based on Clay Minerals in Cultural Heritage Study, in: G. Morari Do Nascimento (Ed.), Clays, Clay Minerals and Ceramic Materials Based on Clay Minerals, InTech, DOI: 10.5772/61633

[17] Faria K C P and Holanda J N F 2012 Using SEM/EDS for characterization of clay ceramic bearing sugarcane bagasse ash waste, in: A. Méndez-Vilas (Ed.), Current Microscopy Contributions to Advances in Science and Technology 1085-1092

[18] Jordá J D, Jordán M M, Ibanco-Cañete R, Montero M A, Reyes-Labarta J A, Sánchez A, Cerdán M 2015 App. Clay Sci. 115 1–8

[19] Dondi M 2003 Technological and compositional requirements of clay materials for ceramic tiles; in: E.A. Domínguez, G.R. Mas, F. Cravero (Eds.), Proc. 12th Int. Clay Conf. 23-30

[20] JIS Z8729:2004. Color specification-CIELAB and CIELUV color spaces

[21] ISO 2813, 1997. Paints and varnishes: determination of specular gloss of nonmetallic paint films at 20/60/85 degrees

Acknowledgements
This work was supported by a grant of the Romanian Ministry of Research and Innovation, CCCDI – UEFISCDI, project number PN-III-P1-1.2-PCCDI-2017-0476, no.51PCCDI/2018 within PNCDI III.