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# ARCHAEOMETRIC STUDIES AND CONSERVATION SOLUTIONS FOR CORVINS'CASTLE CIRCULAR TOWERS

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***Abstract* – For centuries, the architecture of the Romanian monuments reflected the highest standard of European architecture, many masonry buildings had used bricks, wood, roof tiles and various mortars. However, the characterization of the construction materials is prioritized for obtaining informations about the raw materials, building technology and the history of previous restorations. Under such context, in this paper, three types of materials were collected for analysis from the Corvins'Castle circular towers: Deserted Tower, Drummers Tower and Mace Tower. The structural, compositional and morphological aspects will be investigated, through physico-chemical properties of the towers'materials, by using FT-IR, Raman spectroscopy, XRD and EDXRF, ICP-MS, ion-chromatography, microscopic investigations (SEM-EDS, Optical microscopy)). Such techniques evidenced apatite compounds, that could justify the time resistence of these monument's towers as an explanation for their consolidation.**

## I. INTRODUCTION

The Corvins' Castle was built in 1446, in a Renaissance -Gothic style, by the orders of John Hunyadi (in Hungarian: Hunyadi János, in Romanian: Iancu or Ioan de Hunedoara) over the site of an older fortification on a rockabove the smaller Zlaşti River. The castle is one of the biggest and most impressive buildings in Eastern Europe [1]. The castle is built from dolomite limestone blocks, provided with crenelles at the top. The courtyard walls were flanked by circular and rectangular towers, the first being a novelty for the military architecture of the 15th century Transylvania [2,3]. The present archeometry studies are aimed at Deserted Tower (TP), Mace Tower (TT) and Drummers Tower (TB), Figure 1.

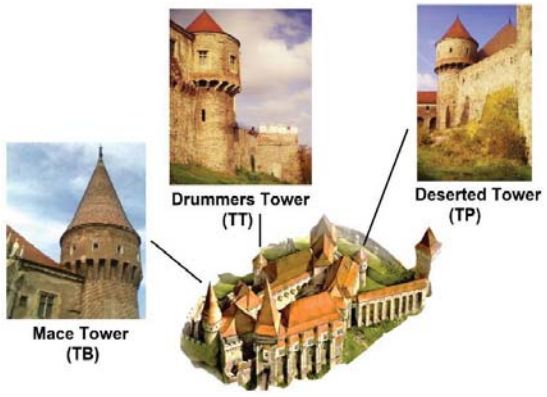


***Fig.1**. The position of the investigated towers.*

**The Deserted tower (the tower of the lily)** is provided with 2 defense levels, the diameter of which is 6 m.

**Mace tower**, a former observation tower in the time of John of Hunedoara, was named after thehemispherical form that its roof, it is considered the most impressive and massive construction in the northern area of the Corvin Castle.

**Tower of Drummers** is part of the circular tower system of the castle. The ground floor is made of full masonry, overlaid by a rifle chamber and a circular room with a Gothic motif decorated.

## II. MATERIALS

The samples received from archaeologists contain only stone samples, which are at different stages of degradation, as shown in Figure 3.

***Fig. 2****. The aspect of the investigated samples.*

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, and with a DRIFT accessory.

Raman spectra have been recorded with a portable dual wavelength Raman (Rigaku, USA) analyser equipped with a standard diode-pumped, air-cooled Nd:YAG laser source with power of 252 mW (785 nm and 1064 nm), with high sensitivity and a resolution of 4 cm-1.

The diffraction data (XRD) were recorded with a X-ray diffractometer Rigaku Ultima IV, with: high-resolution multimodal and multifunctional system, vertical goniometer θ / θ (285mm radius) in geometry G / 9, X-ray tube - Cu anode (2 kW) and Bragg-Brentano high-resolution geometry.

The wavelength dispersed X – Ray Fluorescence Spectrometry (WDXRF) was used for a qualitative and quantitative elementary composition (elements ranging from $^{8}$O to $^{92}$U). Detection limit: 1ppm - 10ppb; Accuracy <0.1-0.5%.

Induced Coupled plasma with mass spectrometry (ICP-MS) has been used for providing high performance elementary analysis, that allows qualitative and quantitative elemental analysis (in the $^{7}$Li and $^{238}$U range) in homogeneous liquid samples. The samples are processed with a TOP WAVE digestor, which assure a digestion under pressure with microwave.

The optical microscopy was performed with a Primo Star ZEISS optical microscope has been used to investigate the samples in transmitted light at a magnification between 4X and 100X. The is equipped with a digital video camera (Axiocam 105) and a microscope software, for a real-time data acquisition and to convert from 2D in 3D format.

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

The ion chromatography has been achieved by using an anion column Ion Pac AS14A Dionex with 8 mM $Na_2CO_3$/ 1 mM $NaHCO_3$ and 1ml/min flux, equipped with a ASRS-ULTRA Dionex suppressor Anion levels (mg/kg dry-weight of sample) were quantified using ion chromatography with a Dionex ICS-1000 and calibrated standards.

## III. RESULTS AND DISCUSSION

Hunedoara region is in the area of Southern Carpathians, in a very complex geological area, with sediment-volcanic units, predominantly formed by limestone, conglomerate, sandstone, magmatite (basalt) and granite [4].

Metamorphic rock, gneiss are generally quartz-feldspar rocks with various amounts of biotite, hornblende, diopside, hypersthene, garnet, Al-silicates, cordierite, zircon and opaque minerals [5]. From macroscopic point of view, the stone samples are brownish – yellow coloured, with grey grain aspects, and with visible weathering and significantly alterations and microcracks. Their colour varies from different shades of yellow grey to creamy and whitish-reddish because of deposits of ferruginous minerals, Figure 3.

The textures are medium to coarse, not defined grains, highlighting well-developed microcline and plagioclase crystals. A pink/purple translucent to opaque variety of quartz, possibly contain inclusions of a lithium-rich mineral such as lepidolite, could be a sample of coloured quartz.

Stretched and recrystallized quartz crystals were observed surrounding the plagioclase and microcline minerals.

The K-feldspar crystals (microcline) have varied sized (predominating larger sizes), and diffuse chess-board twinning due to the alteration in time [6].

An inductively coupled plasma - atomic emission spectrometry (ICP-AES) and ICP-MS analysis of a water sample has been analysed, gave (in mg/l) the following results: Al-0.13; Ca-32.92; Na-4.96; Mg-6.14; Si-2.75; Li-10.02; K-3.4. The other elements were under the detection limit. From this results could be predicted the lithium migration from the solid rock. Similar results have been obtained by EDS and EDXRF, well correlated with ICP-MS data.

For the first time, the presence of phosphate groups in the investigated samples, contributes to the argumentation of apatite presence idea. Gypsum crystals and halite inside the porous building stones induces the stone destruction due to the internal stresses, when the available space in the pores is limited. [$PO_4^{3-}$] is varying from 0.72 to 2.74 mg/l from TP to TB.


***Fig. 3.*** *Optical microscopy of the tower's materials.*

In order to achieve the composition of samples taken from these towers, the geologic composition should be evaluated. Hunedoara is located in the southern corner of the "Golden Quadrangle" of the Metaliferi Mountains [7].

The andesite identified in this area consists of plagioclase, green hornblende, biotite and quartz into felsitic or micrograined groundmass; frequent apatite, zircon, magnetite, ilmenite and, occasionally garnet, occur as accessory minerals, and evidenced deposits of hydroxylapatite on the cave floor (carbonate). These deposits, have been generated due to phosphoric acid solutions from the b at droppings on the carbonate substrate [8]. Calcium phosphates (i.e., hydroxylapatite, carbonatehydroxylapatite, brushite and ardealite) are the most representative mineral species, but the associated minerals also include calcite, gypsum, alpha (low) quartz, illite and interstratified kaolinite-illite species in this area [9].

On the investigated samples, the SEM examination shows that both the crusts and the mounds are composed by thick beds of crystalline aggregates whose morphology varies from random disposed hexagonal laths to post colloidal, rosette like, deposits, Figure 4.

Except these results, FTIR data and Raman the infrared spectrum of the same sample gave, however, a pattern typical for carbonate d hydroxylapatite, characterized by OH stretching (3570 $cm^{-1}$) and vibrational (635 $cm^{-1}$) bands, $CO_3$ (1466 $cm^{-1}$, 1435 $cm^{-1}$ , 872 $cm^{-1}$) bands, and $PO_4$ (1086 $cm^{-1}$, 1042 $cm^{-1}$, 955 $cm^{-1}$, 604 $cm^{-1}$, 564 $cm^{-1}$ , 472 $cm^{-1}$) bands.

Specific Raman active bands could be identified for analyzed samples: carbonate groups at 704 and 1081 $cm^{-1}$ and sometimes at 1437 and 1754 $cm^{-1}$ could be attributed to dolomite 1098 $cm^{-1}$; α quartz was identified on the basis of its main Raman bands at 468 $cm^{-1}$ and also, at 696, 807 $cm^{-1}$.

The Raman spectra of HAp presented characteristic lines of apatitic phosphate groups in accordance with the FTIR studies: 960 cm-1, 430–450 cm-1, 1040– 1074 cm-1, and 580–608 cm-1 modes of $PO_4^{3-}$ [10]. Also, Raman spectra, add a real value to these data, putting into evidence the present materials, pointing out that due to the geomorphological and structural compositions of this area, a phosphate compound is formed here as a strong consolidant material, similar with hydroxyapatite.

For argue these statements, XRD should clarify all these aspects, Figure 5.

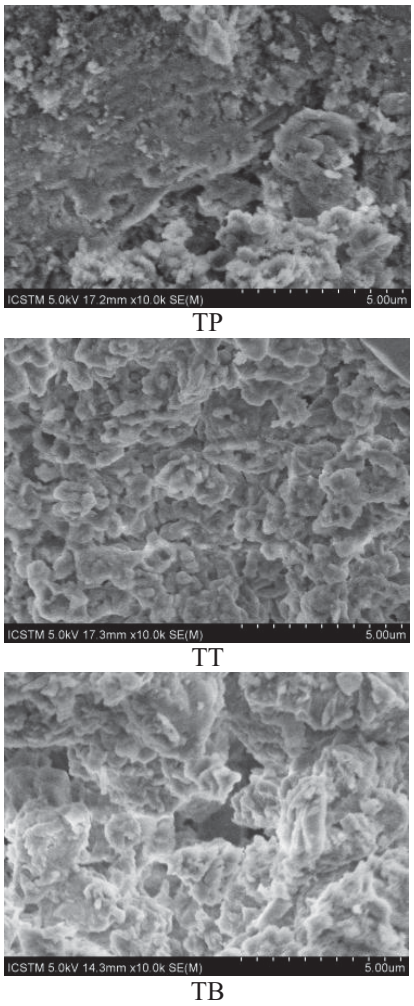


***Fig. 4.*** *The SEM images for the investigated samples.*

The diffraction peaks (2Θ = 25.879° for (002), 31.775° for (211), 31.196° for (112), 32.902 for (300), 33.684 for (202), 35.597 for (301) and 39.853 for (130) respectively), are sharp and well resolved, indicating the obtained phase pure, well crystallized hydroxyapatites [3]. The stone samples are in open areas and they are vulnerable to physical, chemical, mechanical and biological weathering that contributes to the alteration of their structural properties. The atmospheric conditions and air pollutants led to a complex stone ageing process. The various weathering effects of stone, as black crusts, efflorescence and staining could be identified by the presence of salts as sodium sulphate, which is recognized one of the most destructive agents in porous stones. The qualitatively and quantitatively identification of different anions from the soil has been achieved by ion-chromatography, Figure 6 and Table 1. The white stains found in some samples indicated apparently an alterability caused by NaCl, also identified by ion-chromatography technique.

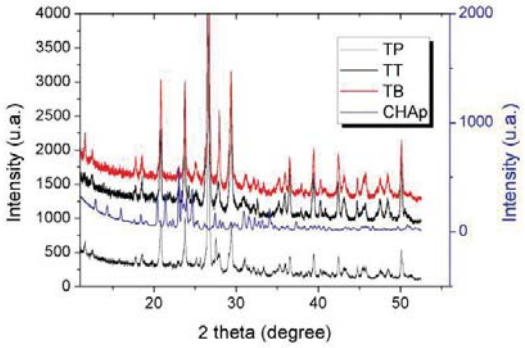


***Fig. 5.*** *XRD diagrams for Corvins'castle towers.*

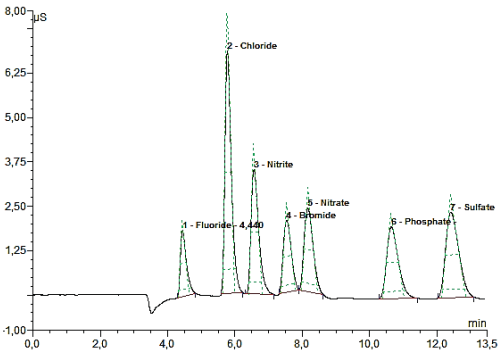


***Fig. 6.*** *Ion-chromatograph of investigated soils around the investigated towers.*

***Table 1.*** *The anions concentration of the investigated soil.*

| $F^-$ | $Cl^-$ | $NO^-$ | $NO_3^{2-}$ | $PO_4^{3-}$ | $SO_4^{2-}$ |
|---|---|---|---|---|---|
| **0.061** | **1.286** | **0.019** | **1.579** | **0.72** | **3.118** |

## IV. CONCLUSIONS

The structural, compositional and morphological aspects have been investigated through physico-chemical properties of the towers' materials, by using FT-IR, Raman spectroscopy, XRD and EDXRF, ICP-MS, ion-chromatography, microscopic investigations (SEM-EDS, Optical microscopy)) have been investigated for Deserted Tower, Drummers Tower and Mace Tower. All these techniques evidenced apatite compounds (carbonated hydroxyapatite, brucide and ardealite), that could justify the time resistence of these monument's towers and application of hydroxyapatite derivatives for their consolidation and conservation.

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