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Diagnosis, Photogrammetry and Conservation Treatment with Nanomaterials of Sacidava Fortress †

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Abstract: The diagnosis, thermography, aerial photogrammetry, and conservation treatment with nanomaterials (CHAp) for some samples from Sacidava Fortress, Romania, are analyzed and the results are discussed accordingly in this paper.

Keywords: nanomaterials; Sacidava fortress; stone; analytical investigations

1. Introduction

Sacidava Citadel is a Geto-Dacian settlement and a Roman castrum, from the Roman era (Trajan era), located on the right bank of the Danube, on the plateau of the Musait hill, between the towns of Rașova and Dunăreni, dating back to the II-VII centuries AD [1].

Currently, the fortress is in an advanced state of deterioration, with only a few walls excavated through partial archaeological works, which led to a significant loss for this monument of cultural heritage. Physico-chemical environmental factors and biological factors participate synergistically or antagonistically in the process of deterioration of the remaining walls of this monument [2–4]. The degree of stone deterioration depends on the physico-chemical environmental factors, the composition and nature of the stone material itself, and biological factors. These latter factors are responsible for biodeterioration, which is defined as "any undesirable change in the properties of a material caused by the vital activities of associated organisms" [5]. The European standard EN15898 defines the main general terms used in the field of conservation of cultural goods (2011) [6].

In this paper, several samples from the Sacidava Fortress are analyzed, in order to identify the origin of the raw materials and the deterioration processes that took place at this monument. Many nanomaterials have been used up to date for chemical consolidation and antimicrobial restoration of different surfaces from everywhere in the world [7–13]. In this paper, a conservation nanomaterial such as carbonate hydroxyapatite (CHAp) will be tested, and the results are discussed accordingly, together with some planned-flight aerial photogrammetry scans for systematic mapping correlated with thermogrammetry.

2. Materials and Methods

2.1. Locations and Collection of Archaeological Evidence

This study was conducted on a number of samples collected from 10 collection points in October 2022 from this archaeological area using non-invasive methods. Four samples were taken from the south-western sector, positioned at distances of approximately 1.5–2 m, being collected from areas with visible structural damage (Figure 1). Sector walls built of large stone blocks, at the base of marble pieces, were 4 m in height.

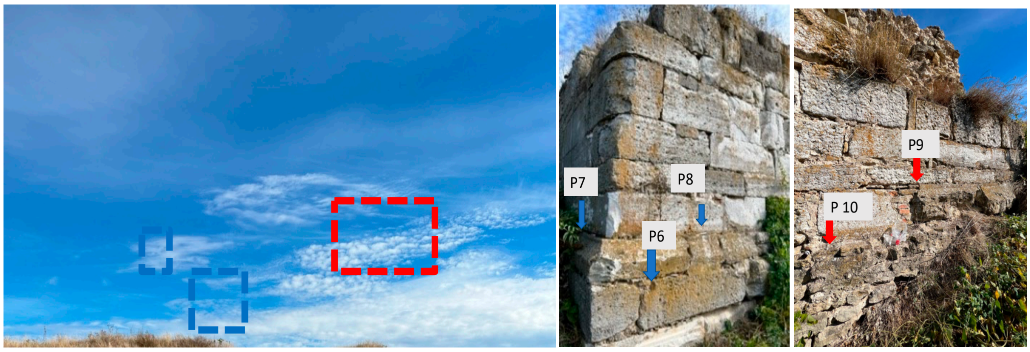

Figure 1. Collection area and their location (blue and red frames indicate the places where the samples have been collected)**.**

2.2. Methods and Equipments

Some advanced analytical techniques such as X-ray diffraction (XRD) (Rigaku Corporation, Tokyo, Japan), X-ray fluorescence wavelength dispersed (WDXRF) (Rigaku ZSX Primus II spectrometer (Rigaku, The Woodlands, TX, USA), Fourier-transformed infrared spectroscopy (FTIR) (Vertex 80 spectrometer (Bruker Optik GMBH, Ettlingen, Germany), with the attenuated total reflectance mode, ATR), Raman spectroscopy (Raman wavelength portable analyzer (Rigaku, USA)), scanning electron microscopy (SEM) (FEI Quanta Inspect FEG Scanning Electron Microscope (FEI, Hillsboro, OR, USA), optical microscopy (OM) (Video Microscope EdmundOptics - magnifications: 2×, 8×, 12×, 14×), equipped with a digital video camera AmScope 3.2MP MT9T001 CMOS C-Mount camera), and stereo-microscopy (SM), (magnification of 20× or 40×) (both microscopes and accessories from EUROMEX Microscopen B.V., Papenkamp 20, BD Arnhem, The Netherlands).

For microbiological analysis, harvesting was carried out from the surfaces of the stones using a sterile swab (4 cm^2). Twelve samples were taken from flat surfaces and with different porosities. The samples were transported to sterile enclosures and inoculated directly into Sabouraud Dextrose Agar culture media (selective medium for fungi) and Nutrient Agar (selective medium for bacteria), solids located in Petri dishes. The plates were placed in the incubator at 350 °C. Colonies were analyzed 24 h and 48 h after inoculation. The morphological characters were examined under stereomicroscope (OPTIKA) and epifluorescence microscope (Optika B350).

For thermography, a Catepillar 61 thermal serial camera with FLIR system was used, and for the **photogrammetry,** a professional drone type Mavic 2 Enterprise was used for the acquisition of aerial images and on a series of application programs designed to analyze and process images captured from archaeological sites.

Carbonated hydroxyapatite (CHAp), used in this paper as a consolidant, has been synthesized as reported in our previous paper [7].

3. Results and Discussion

The microclimate analysis was carried out via thermographic evaluation of the main analyzed pieces [14,15]. This method allows for the identification in situ of temperature and humidity variations, physico-chemical parameters that allow us to understand the specific distribution and variation of biota [16]. The temperature identified on the investigated samples indicates good connection between the type of material and the temperature values recorded (Figure 2).

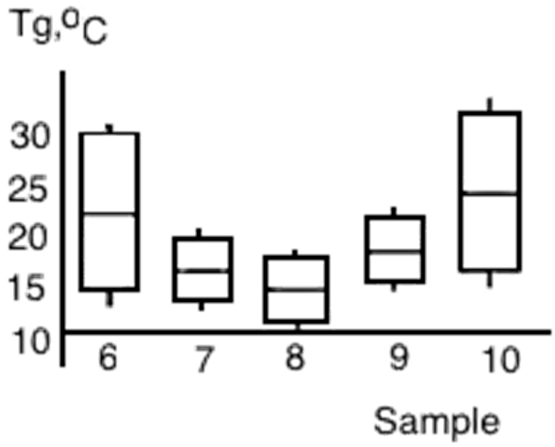

Figure 2. Variations in temperatures recorded at the surface of the analyzed stones (minimum, maximum and average values).

It can be found that, on the same stone component, there can be differences of about 10–15 °C, which give the organisms associated with these surfaces' adequate ecological adaptations and allow them to survive in this type of microhabitat. Meanwhile, the thermography allowed us to highlight the fact that the presence of crusty lichens makes the covered surfaces register much higher temperature values than the support stone, without lichens, at the measured humidity of about 50%. Except the visible surface cracks, thermographic inspection put into evidence further cracking, difficult to be detected through visual testing (Figure 3).

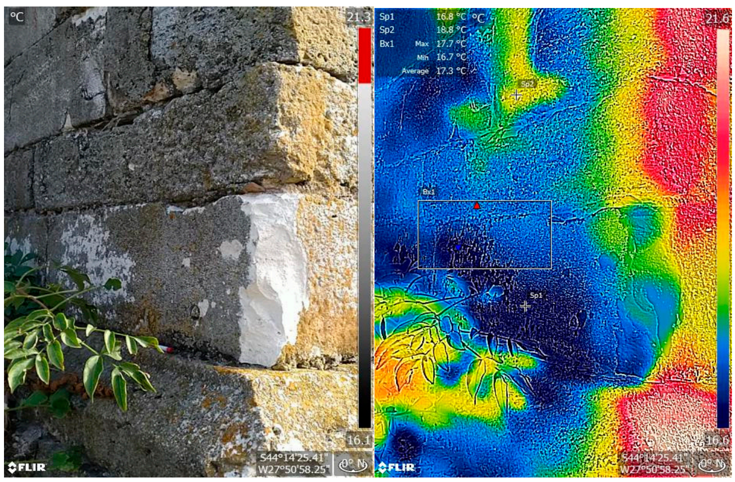

Figure 3. The thermogramms of Sacidava sample.

The physicochemical analysis, absolutely necessary in such experiments [17], was performed in this paper using WDXRF, XRD and FTIR. WDXRF allowed to see the elemental composition of mortar samples taken from the bricks existing in the fortress, revealing the presence of CaO, SiO_2, Al_2O_3, and Fe_2O_3 (Table 1). XRD correlated with WDXRF analysis of mortars evidenced some minerals such as quartz, calcite, small amounts of feldspars, berlinite, brucite, the last one being responsible for the reinforced resistance structure inside the walls of this fortress (Figure 4).

Table 1. The composition of the samples via WDXRF.

Oxide	P6	P7	P8	P9	P10
MgO	2.4011	1.6644	1.0592	1.4296	0.8489
Al_2O_3	11.9456	5.287	3.232	4.1713	5.3351
SiO_2	36.5953	19.6787	16.1793	34.2572	27.5152
P_2O_5	0.1737	0.3992	0.2756	0.1994	0.2019
SO_3	4.2702	4.5216	0.768	1.6915	0.8456
K_2O	1.7329	1.0856	0.6601	0.8146	1.3518
CaO	37.5752	64.415	76.1097	55.5546	61.45
TiO_2	0.4807	0.4936	-	-	-
MnO	0.2462	-	0.0944	0.1327	0.1156
Fe_2O_3	4.5125	2.2019	1.5603	1.6012	2.2787
SrO	0.031	0.1949	0.0614	0.073	0.0571
ZrO_2	0.0246	0.0171	-	-	-
Cl	-	0.041	-	0.074	-

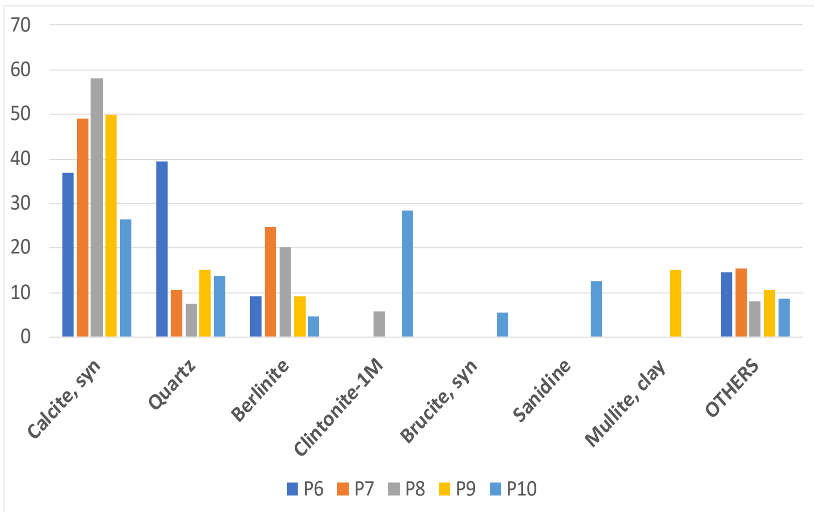

Figure 4. XRD distribution of the main components.

XRD technique (Figure 4) correlated with XRF analysis of mortars identified several crystalline phases: quartz (SiO 2-28 (2q)) and calcite/dolomite (carbonate Ca and Mg-30, 38(2q)), small amounts of feldspaths (cations containing alkali metal aluminosilicate and alkaline earth metals), as well as mica and berlinite [18].

FTIR spectra Figure 5, put into evidence the bands assigned to the carbonate phases (1800 cm^{-1}, 1406–1440 cm^{-1}, 873 cm^{-1} and 711 cm^{-1}), bound water (bands at 3370 and 1630–1640 cm^{-1}), most probably linked to silicate and aluminate hydrates (strong silicate bands (Si–O) at 1011–1022 cm^{-1}) and Al–O bands around 1000 cm^{-1}. Similar results have been reported in the literature [19,20].

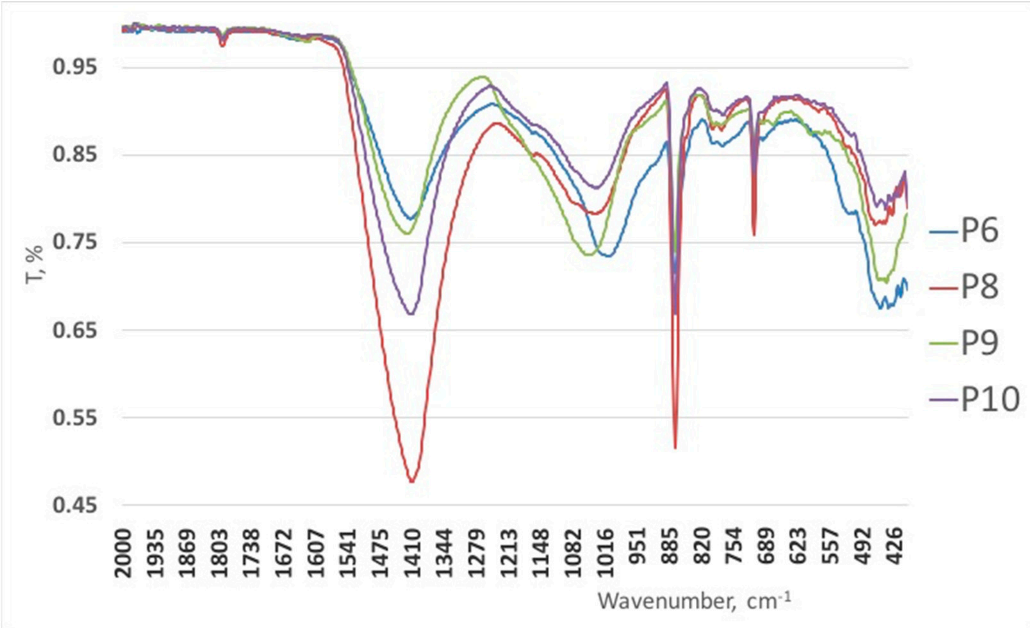

Figure 5. FTIR spectra of the Sacidava samples.

Macroscopically, crusty, folious lichens and mosses are distinguished; Figure 6. Lichens with crusty thallus form compact elements on the surface of the stone substrate [21,22]. All species are tolerant to environmental pollutants. The degree of microcolony coverage is high on intensely uneven calcareous structures. The identificated species were *Physcia tenella* (a,b), *Caloplaca saxicola* (Hoffm.) *Norden* (c), *Rhizoplaca chrysoleuca (Sm.) Zopf sin Lecanora chrysoleuca* (d), *Aspicilia calcarea* (L.) *Mudd (Circinaria calcarea (L.) A. Nordin Savić & Tibell)* (e), *Xanthoria parietina* (f); Figure 6.

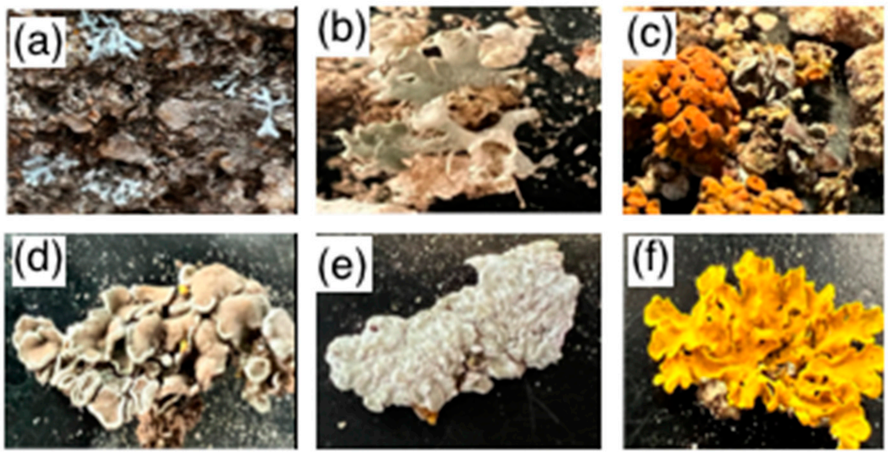

Figure 6. The lichens identified on Sacidava samples *Physcia tenella* (**a**,**b**), *Caloplaca saxicola* (Hoffm.) *Norden* (**c**), *Rhizoplaca chrysoleuca (Sm.) Zopf sin Lecanora chrysoleuca* (**d**), *Aspicilia calcarea* (L.) *Mudd (Circinaria calcarea* (L.) *A. Nordin Savić & Tibell)* (**e**), *Xanthoria parietina* (**f**).

Treated with carbonated hydroxyapatite, the samples collected from Sacidava fortress became homogeneously covered. The acicular formations of the initial samples, most probably due to gypsum, mica or cuartz, became completely covered by carbonated hydroxyapatite through an homogeneous layer, as could be seen in Figure 7, in good agreement with other literature reports [23].

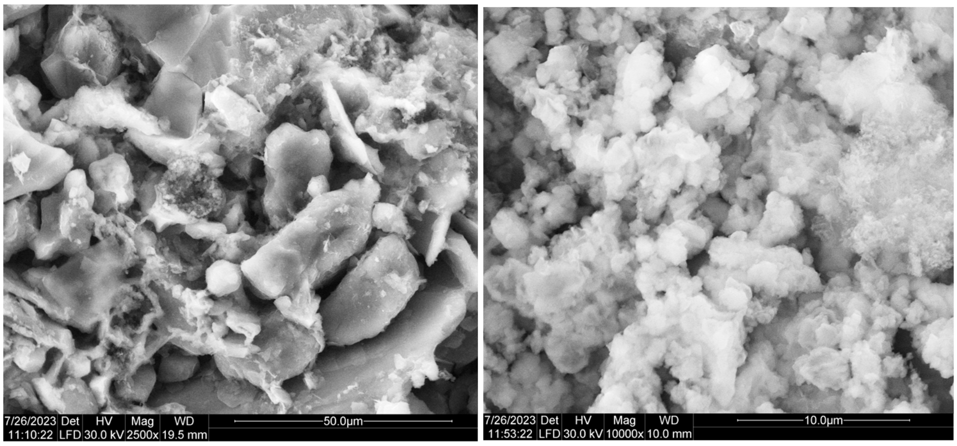

Figure 7. Sacidava samples non-treated (**left**) and treated (**right**) with (CHAp).

As far as 3D technologies are concerned, preliminary studies have shown that the software processing technique and procedures used are feasible [24,25]. Aerial scans were performed, and precise locations were made of the places from which the samples subjected to investigations were taken. Aerial photogrammetry scans will be extended with planned flights for systematic mapping of the area of interest. For this archaeological objective, the drone was tested in manually controlled flight to capture images with size 4000 × 3000 pixels. The local weather conditions were wind speed 3.5 m/s with gusts up to 5 m/s, air temperature 11 °C, air humidity 56%, very good visibility, and sunny. The areas with visible ruins were scanned, and panoramic video sequences of larger areas of the fortress perimeter were captured, including photo and video with the areas of recent archaeological excavations (Figure 8).

Figure 8. The aerial image of Sacidava fortress with drone.

4. Conclusions

The samples from Sacidava Fortress, Romania, are analyzed for the diagnosis, aerial photogrammetry, thermography and conservation treatment with nanomaterials (CHAp), and the results are discussed accordingly in this paper. Non-invasive techniques, such as WDXRF, XRD and FTIR, allowed to see the elemental composition of mortar samples taken from the bricks existing in the fortress. Also, some imagistic techniques such as SEM and thermographic inspection put into evidence further cracking, difficult to be detected through visual testing. Lastly, the identification of different lichens has been put into evidence, and the conservation technique with carbonated hydroxyapatite nanomaterials have been promoted in this paper.

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