

## EFFLORESCENT COMPOUNDS – CHARACTERIZATION AND INTERACTIONS WITH LITHIC MATERIAL. INSIGHTS FROM THE EXTERIOR WALL OF THE EPISCOPAL CATHEDRAL – CURTEA DE ARGES

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*Abstract.* The study on efflorescence in salts collected from Curtea de Arges cathedral's exterior wall during restorations aimed to characterize compounds and lithic material using SEM-EDX, XRD, Raman, FTIR. Radiocarbon measurements using AMS method and FTIR results demonstrate decarbonation/recarbonation at the compound-lithic interface but further research is required.

*Key words:* XRD (X-Ray Diffraction), Raman and FTIR (Fourier Transform Infrared) spectroscopy, AMS radiocarbon analysis.

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### 1. INTRODUCTION

This case study considers the Curtea de Arges episcopal cathedral which is part of the ensemble with the same name, founded by Neagoe Basarab between 1515 and 1517. The historical ensemble was transformed and developed by Carol I into the necropolis for the royal family of Romania. After two arsons that took place in 1866 and 1867, the complex was restored starting in 1875 by the French architect Pierre Lecomte du Noüy [1]. Since then, several partial restorations have taken place.

This paper aims to make a physico-chemical characterization of the deposits of salts and to qualitatively evaluate their interaction with the lithic material, if any. Some discussions and suggestions regarding the causes that generated the apparition of white deposits of salts are also taken into account.

The interdisciplinary study on the Corbii de Piatră cave ensemble (the oldest cave church on the territory of Romania, with the beginnings placed in the XIII–XIV

centuries AD), located approx. 17 km N-E from Curtea de Arges Monastery, was a very useful guide in approaching the present study. The chapter “Causes and specific forms of degradation” offered a strategy for approaching both the analyzes necessary for the physico-chemical characterization of the sample of salts deposited on the exterior walls of the episcopal cathedral, but also for its correct placement in the group of efflorescent compounds [2].

## 2. MATERIALS AND METHODS

On the sample of deposits of salts, taken from Curtea de Arges episcopal cathedral outer wall, the following analyzes were applied:

SEM / EDX (Scanning Electron Microscopy coupled with Energy Dispersive X-ray), through which an electron microscope image and atomic percentages were obtained for the detected elements under the measurement conditions / limits of the applied method;

XRD (X-Ray Diffraction), by which, the polycrystalline compounds, combinations of the previously determined elements, are inferred, by comparison of the experimental XRD patterns with an inorganic diffraction data library from crystals;

Raman and FTIR (Fourier Transform Infrared) spectroscopy analyses, through which information was obtained on the structure of these chemical compounds / mineral classes noted, by comparison with the data libraries.

Later, for comparison and interpretation, the measurements were repeated on a sample of lithic material that constituted the covering stone of the external walls.

To qualitatively estimate the interaction between the wall, the white salts deposits and the environment, AMS method was used. The level of carbon-14 was determined in a raw homogenized sample from the deposits of salts, and in a raw homogenized sample from the surface of the lithic material, after it had previously been scraped to remove traces of contaminants.

As additional information emerged from the analyzes mentioned above and from cleaning methods usually applied by art restorers, two control samples bearing carbon were taken into account to be measured by the AMS technique: commercial sodium bicarbonate (dietary sodium bicarbonate) and ethylenediaminetetraacetic acid disodium salt dihydrate (EDTA sodium salt), alongside freshly cut quarry limestone (IAEA reference material).

Compositional and morphological characterization were carried out using a Zeiss EVO 50 XVP scanning electron microscope (SEM) coupled with a Bruker Quantax 200 detector energy dispersive spectrometer (EDX).

The XRD measurements were performed with a Rigaku SmartLab diffractometer (Cu K $\alpha$  radiation,  $\lambda = 1.54187 \text{ \AA}$ ), equipped with HyPix-3000 2D Hybrid Pixel Array Detector (Rigaku, Tokyo, Japan) in 1D mode.

Raman spectra were acquired employing a LabRAM HR Evolution Raman spectrometer from HORIBA Jobin–Yvon, equipped with a confocal microscope,

a He–Ne laser and a He–Cd laser, using red and UV excitation wavelengths of 632 nm and 325 nm.

FTIR spectra were recorded with a Spectrum BX II (PerkinElmer) spectrometer in the 4000–350  $\text{cm}^{-1}$  spectral range, with 64 scans and 2  $\text{cm}^{-1}$  resolution. The pigments of the samples were embedded / diluted in KBr pellets in a 1:100 ratio.

Regarding the AMS method, the experiments were carried out at the RoAMS Laboratory at IFIN-HH.

All samples, after a very fine homogenization, were directly graphitized, without pre-treatments, on the AGE 3 system [3]. After total combustion (carbon dioxide being generated thermally) in the Elementar apparatus at 950 degrees Celsius, subsequent separation, purification and drying of the carbon dioxide take place. It was finally reduced to carbon using activated hydrogen, on an iron catalyst, in the AGE 3 unit.

This carbon deposited on the iron catalyst was later enclosed in an aluminum cathode. It was measured at the 1 MV HVEE Cockcroft Walton Tandetron accelerator, together with reference materials and standards: Blank IAEA-C1 and NBS oxalic acid [4]. The AMS data were processed using the Bats program adapted for this accelerator [5], and the conventional radiocarbon ages (CRA values) were transformed into calibrated radiocarbon dates using OxCal Online Program [6].

### 3. RESULTS AND DISCUSSION

#### 3.1. SEM-EDX RESULTS

SEM images of the deposits of salts powder (Fig. 1a) and lithic material (Fig. 1b) are presented. SEM images suggest similar morphology between these two samples, with two distinct areas being observed in the case of deposits of salts. This is easily noticeable due to the white and yellow color shades of the powder.

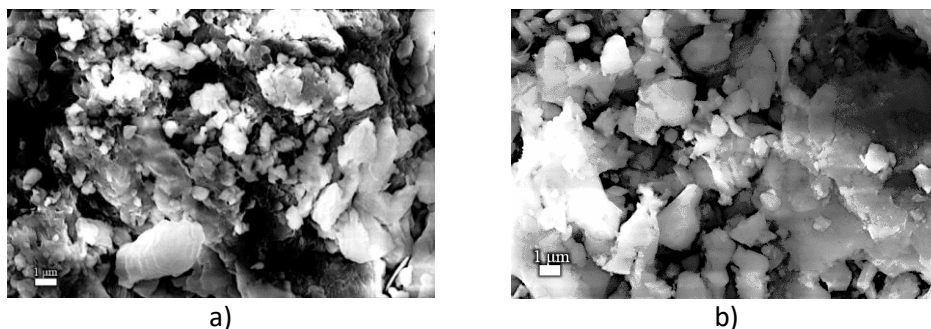


Fig. 1 –Typical SEM images of: a) deposits of salts powder; b) lithic material.

EDX results highlight the atomic elemental composition and are summarized in Table 1. The measurements were made on the two areas of different color from

the salt deposits, and in the fresh slit on the lithic material. The values in Table 1 represent an average of 3 measurements at different points.

Table 1

Elemental quantification by EDX of deposits of salts powder in white and yellow powder, and of lithic material. Here, ND stands for not detected

	C	O	Na	Mg	Al	Si	S	K	Ca	P	Fe
Deposits of salts in white powder	4.65	64.07	29.55	ND	ND	ND	0.99	ND	0.74	ND	ND
Deposits of salts in yellow powder	6.95	66.82	3.39	0.39	0.73	2.10	0.31	0.28	18.77	ND	0.26
Lithic material	4.99	54.83	0.05	0.44	3.07	5.16	ND	1.04	28.78	0.51	1.13

### 3.2. XRD RESULTS

Crystalline phase analysis has been performed on both samples, deposits of salts powder and lithic material, by employing the XRD technique.

In the case of deposits of salts powder, (Fig. 2a), phase analysis revealed two dominating phases of sodium carbonate  $\text{Na}_2(\text{CO}_3)\cdot\text{H}_2\text{O}$ , quantified at 49.2% and calcium carbonate  $\text{CaCO}_3$ , quantified at 43.1%, but also some minor phases of most likely graphite C, polyhalite  $\text{K}_2\text{Ca}_2\text{Mg}(\text{SO}_4)_4\cdot 2\text{H}_2\text{O}$ , most likely fairchildite  $\text{K}_2\text{Ca}(\text{CO}_3)_2$  and 2.8% unassigned phases.

The lithic material (Fig. 2b), consisting mainly of calcium carbonate  $\text{CaCO}_3$  as calcite (over 90%), certifies the calcareous nature of the raw material used in construction, on the surface of which the deposits of salts were formed. It is practically identical to the area of calcium carbonate from deposits of salts and shows similarities with the area where sodium carbonate is predominant. This is in good correlation with the data obtained so far. As minor constituents, a possible natural mineral from Lagalyite group  $\text{Ca}_2\text{Mn}_{14}\text{O}_{27}\cdot\text{H}_2\text{O}$  and up to 5% unassigned phases were found.

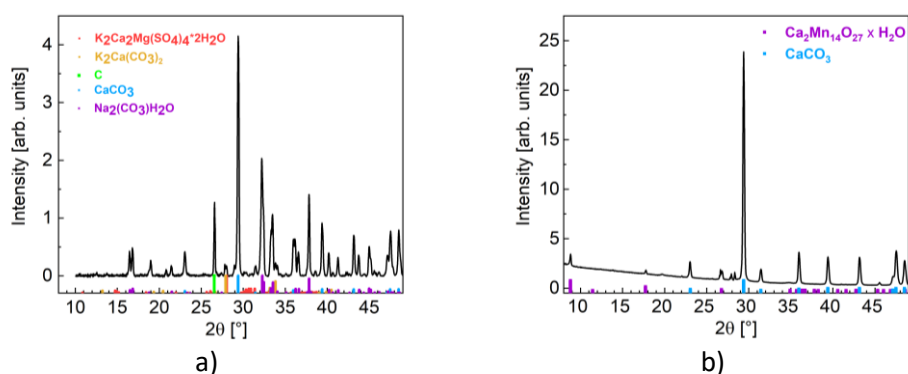


Fig. 2 – XRD Diffractograms obtained on: a) deposits of salts powder; b) lithic material.

### 3.3. RAMAN RESULTS

Raman spectroscopy was employed to further investigate the samples.

In the case of white and yellow powders (Fig. 3a and 3b), characteristic signals were assigned to calcium carbonate  $\text{CaCO}_3$  ( $280\text{ cm}^{-1}$ ,  $712\text{ cm}^{-1}$ ,  $1084\text{ cm}^{-1}$ ) [7]. The  $1068\text{ cm}^{-1}$  band signal is assigned to the carbonate ion in  $\text{Na}_2(\text{CO}_3) \cdot \text{H}_2\text{O}$  [8]. There can also be observed a peak at  $991\text{ cm}^{-1}$  which is associated with polyhalite  $\text{K}_2\text{Ca}_2\text{Mg}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$  [9–11].

Concerning lithic material (Fig. 3c), the identified bands are associated with the calcium carbonate  $\text{CaCO}_3$  phase. The signal from  $150 - 155\text{ cm}^{-1}$  seems to be another band associated with calcite. The one from approx.  $350\text{ cm}^{-1}$  may be of Lagalyite group of minerals  $\text{Ca}_2\text{xMn}_{1-x}\text{O}_2 \cdot 1.5-2\text{H}_2\text{O}$  ( $x = 0.05-0.08$ ). Otherwise, due to over 90% calcite, the other signals are much diminished and difficult to attribute. If the peak from approx.  $350\text{ cm}^{-1}$  or other peaks in the spectrum could be associated with this mineral (Lagalyite), then the XRD and Raman analyzes would support each other.

Other compounds determined by XRD were not observed because they are impurities or either because some compounds did not show characteristic signals by Raman spectroscopy. FTIR spectroscopy will bring complementary information.

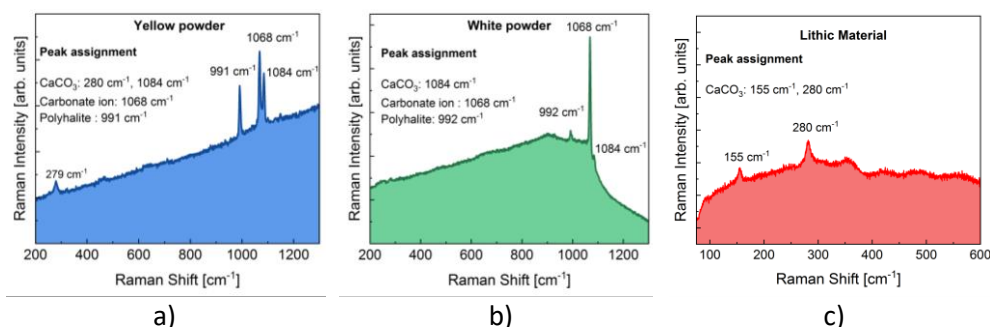


Fig. 3 – Raman spectra acquired on deposits of salts powder on: a) yellow area, b) white area, c) lithic material.

### 3.4. FTIR RESULTS

FTIR spectroscopy, complementary to Raman, highlighted the presence of hydroxides / carbonates, which indicates decarbonation/recarbonation phenomena. The characteristic band from  $930-1100\text{ cm}^{-1}$  highlights the bonds of silicon through oxygen in natural compounds identified by SEM/EDX in Area 2, the 2.8% maximum unassigned from XRD [12, 13].

Practically, the three spectra (Fig. 4a and 4b) are similar and they are a proof of the chemical reactions that take place in the two materials and a possible

exchange of carbon dioxide, through the bicarbonate ion in the presence of water, at the interface [14–15]. Highlighting, qualitative estimation of this exchange, and to what extent contact with the environment takes place in both materials can be explored using stable isotopes (isotopic signature) [16]. In this article, the determination in these samples of carbon-14 levels, based on the principle of the technique with radiotracers, is proposed for the first time for completing the information obtained by FTIR spectroscopy. This is possible due to the particularities of these salt deposits, namely that they contain carbonates as predominant compounds.

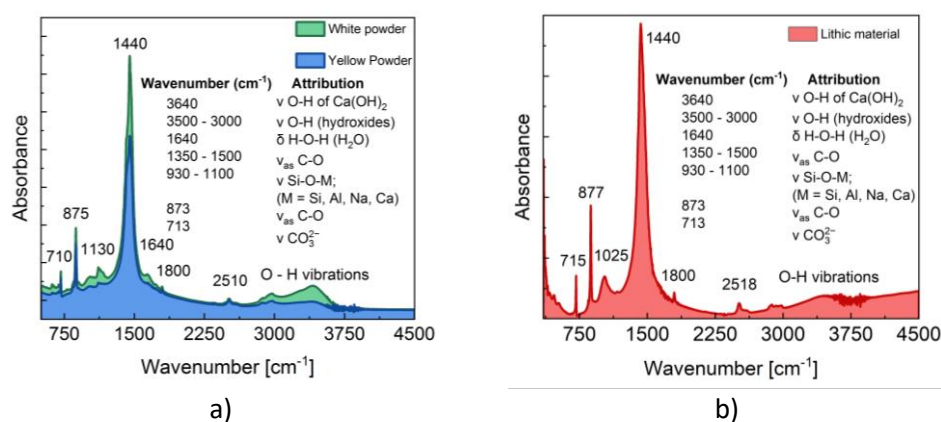


Fig. 4 – FTIR Fourier Transform Infrared spectroscopy analysis of:  
a) deposits of salts powders; b) lithic material.

### 3.5. AMS RESULTS

Usually, the radiocarbon method is used for dating. This time, it is used as a radiotracer to determine the carbon-14 levels in the deposits of salts, in the lithic material and later in other control samples suggested by the information on the cleaning methods for art restorations [17]. Knowing and interpreting these levels will bring additional arguments for or against the chemical interaction between deposits of salts and the lithic material of the outer wall. In the case of efflorescent compounds containing nitrates, the process of appearance and interaction is followed using stable isotope analysis, and  $\delta^{15}\text{N}$  value [16]. The particular character of the composition for the deposits of salts sample from Curtea de Arges, which involves carbon in the dominant anionic species, led to the exploration of the possibility of obtaining similar information not through nitrogen-15, but through carbon-14 measurements.

In the analyzed samples, a pertinent estimate of the real age is given by the calibration of CRA values (Fig. 5).

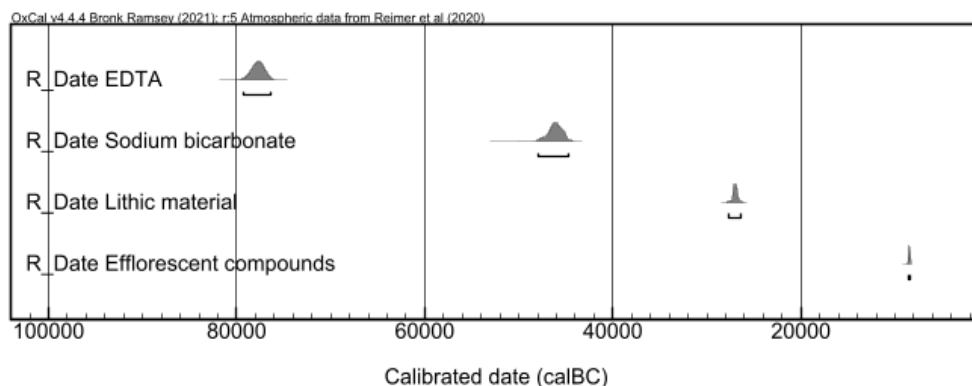


Fig. 5 – Multiplot representation of calibrated radiocarbon results of deposits of salts / efflorescent compounds (RoAMS 2199.34), freshly cut lithic material (RoAMS 2200.34), dietary sodium bicarbonate, and EDTA disodium salt powders.

If the calibrated radiocarbon date is real, it should record the time of formation of the deposits of salts on the walls, and of the lithic material in the geological deposits. For the deposits of salts, the age should have been placed near the moment of measurement, no older than 140 years according to the records about the interventions on the historical monument. But it is approximately 10,500 years old. Concerning the lithic material, being of geological origin, its age should have been in the AMS Blank area (65–55 kyrs); instead, it is approximately 29,000 years old. These ages are not real, but apparent. The deposit of salts is strongly “aged”, while the lithic material undergoes a strong “rejuvenation”. Thus, the permanent chemical contact between the two materials through the bicarbonate ion and moisture was highlighted. This is the main chemical compound involved in the hydration/decarbonation/recarbonation noticed by FTIR spectroscopy.

In order to qualitatively estimate the interaction degree, and if carbon dioxide from the environment is also involved, materials whose age can be tested by the AMS method were analyzed. The deposits of salts, by all the results presented in the previous paragraphs, cannot be included either in the category of crusts that form naturally on the lithic material, nor of the efflorescent compounds that can appear on the walls of historical monuments.

That's why our searches focused on materials used in the restoration. Cements rich in lime can cause the formation of efflorescent compounds. In this case, the portlandite that forms during cement hydration, migrates over time to the surface, reacting with the carbon dioxide in the air, and turning into calcium carbonate which is the cause of the white patina. It does not contain sodium unless the recipe involved sodium-based material. If they do not interact with the lithic material, the white deposit will not be older than 140 years. Ammonium bicarbonate, which could also have been used in restorations, decomposes, after the evaporation of the solution, into ammonia and carbon dioxide. Only if it had available a source of

sodium, like the one mentioned before, it could have formed sodium bicarbonate and finally sodium carbonate. Lye water can provide sodium hydroxide, which is highly reactive with carbon dioxide in the air. If it did not interact with the lithic material from the wall, it would not contain the calcium carbonate evidenced by the other analyses, but only sodium carbonate of modern age. The two candidates (ammonium bicarbonate and lye water) can be essentially represented by sodium bicarbonate, the key compound in the formation of carbonate. On the other side is EDTA. This compound has a special ability to retain cations, through chelation. The solution and the organic compound can disappear from the walls over time, but the chelates are stable compounds. They can wash away from the wall being soluble, but they can deposit cations on solid surfaces, upon contact with acidic traces in the air. Sodium can come either from the use of disodium salt or from cements.

The multiplot representation (Fig. 5) shows the impact of materials with the modern carbon dioxide, having a carbon-14 level 3 – 5 orders of magnitude higher.

### 3.6. DISCUSSION

The SEM/EDX results highlights the similar morphology between the two types of materials and the existence in the deposits of salts of two distinct phases.

The XRD analysis establishes that in the deposits of salts the dominant phase is  $\text{Na}_2(\text{CO}_3) \cdot \text{H}_2\text{O}$ , and the minority phase is  $\text{CaCO}_3$ . Lithic material at the interface is practically composed of calcite, without traces of sodium carbonate, having a structure identical to that of the calcium carbonate zones, distributed in the mass of deposits of salts. The SEM images highlights the interpenetration of the two types of carbonates, through their formation.

Raman spectroscopy confirms the presence of the two types of carbonates in the deposits of salts, the areas of different colors (white and yellowish) having different varieties of impurities. It also demonstrates the purity of the lithic material.

FTIR spectroscopy, complementary to Raman, highlighted the presence of hydroxides/carbonates, which indicates decarbonation / recarbonation phenomena. These are chemical processes that occur in both materials and ensure the exchange of carbon dioxide with different carbon-14 signature between environment, deposits of salts and lithic material. This conclusion is supported by the radiocarbon results which qualitatively express the transformation of real ages into apparent ones, much younger or older.

### 4. CONCLUSIONS

The deposits of salts on the outer walls of the episcopal cathedral in Curtea de Arges and the lithic material from which they are built, were analyzed by SEM/EDX, XRD, Raman and FTIR spectroscopy, as well as AMS technique. The experimental

results are complementary and convergent. They support the inclusion of these deposits of salts in the efflorescent compounds group.

The physico-chemical properties of the efflorescent compounds are not those usually encountered in constructions. They might be the result of the restoration interventions over time.

The presence of carbonates in these efflorescent compounds and in the lithic material allowed the determination of different levels of carbon-14 by the AMS method which highlighted the interaction between atmospheric carbon dioxide, carbonates from the efflorescent compounds and from the surface of the limestone. In the next stage of researches, we proposed to systematically study how carbon-14 is transmitted from the atmospheric air to the surface of the lithic material through the formation of efflorescence compounds.

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