EasyChair Preprint

№ 7278

Non-Invasive Techniques for Characterization of Original Roman Mosaic Fragments

Cristiana Radulescu, Rodica Mariana Ion,
Ioana Daniela Dulama, Anca Irina Gheboianu and
Ioan Alin Bucurica

December 30, 2021

Non-invasive techniques for characterization of original Roman mosaic fragments

Cristiana Radulescu[a,b*], Rodica Mariana Ion[c,d], Ioana Daniela Dulama[b], Anca Irina Gheboianu[b], Ioan Alin Bucurica[b]

[a]Valahia University of Targoviste, Faculty of Sciences and Arts, 130004 Targoviste, Romania;

[b]Valahia University of Targoviste, Institute of Multidisciplinary Research for Science and Technology, 130004 Targoviste, Romania;

[c]Valahia University of Targoviste, Materials Engineering Department, Doctoral School of Materials Engineering, 130105 Targoviste, Romania;

[d]National R&D Institute for Chemistry and Petrochemistry–ICECHIM, Research Group "Evaluation and Conservation of Cultural Heritage", 060061 Bucharest, Romania.Type the author addresses here

*E-mail: radulescucristiana@yahoo.com

Abstract. In this study, it was reported the preliminary results on the chemical and structural composition of decorative elements remains from original Roman mosaic fragments collected from the Roman Mosaic Museum, Constanta (Romania). These investigations were carried out by using non-destructive and micro-invasive techniques such as optical microscopy, X-ray diffraction, field emission - scanning electron microscopy - energy dispersive X-ray spectroscopy, vibrational spectroscopy (i.e., FTIR and Raman). The studied fragments, apart from being beneficial to different restoration opportunities of this Roman mosaic, could be also included in its modification through air pollution. The major and minor phase components of the studied mosaic fragments were determined, the crystal structure of the main phases was analyzed, and their three-dimension spatial arrangement was reconstructed. The similar composition of the major phases of all mosaic fragments can indicate a generic recipe for making mosaic elements, but minor phases were presumably added for coloring of mosaic pieces. Some degradation areas inside the volume of the mosaic fragments were found by means of the X-ray diffraction method. The areas are probably related to the formation of iron hydroxides during chemical interactions of mosaic fragments with the sea and urban polluted atmosphere. The results can also offer important information about the original materials that were used in the Roman period.

Keywords: Roman mosaic; X-ray diffraction; field emission - scanning electron microscopy - energy dispersive X-ray spectroscopy; vibrational spectroscopy.

1. Introduction

The Roman mosaic edifice from Constanta (part of the ancient city of Tomis), Romania was discovered during the urban works undertaken in 1959 and declared historical monument. This edifice was built in the Roman-Byzantine period, at the end of the 3rd century and the beginning of the 4th century AD. Towards the end of the 5th century the building was destroyed by an earthquake [1-4].

In ancient times, the mosaic floor had an area of two thousand square meters, of which about 850 m^2 have been preserved. The mosaic was worked in stone and marble cubes fixed in a layer of Roman mortar and mounted in different geometric (e.g., circles, squares, rhombuses) and floral motifs (Figure 1).

Figure 1. The Roman mosaic edifice from Constanța, restored and hosted in the National History and Archeology Museum of Constanța, Romania.

This study focuses on the qualitative investigation of original samples collected from Roman mosaic fragments, hosted in the Museum of National History and Archaeology of Constanța, Romania. Non-invasives methods used to investigate these samples can provide information regarding ancient preparation technologies, geological origins and quality of raw materials.

2. Materials and Methods

2.1. Sampling procedure and sample preparation

The samples were collected on the same day and under same conditions (using disposable gloves, plastic ustensiles and packaged in plastic bags for further analysis) from four points at the surface of the original structure (coded P1–P4), by non-destructive methods. Most of the collected samples had different voids or gaps, cracks and scratches on the surfaces, and internal degradation tracks which required investigations [4,5].

2.2. Optical microscopy and Scanning electron microscopy

The qualitative structural investigations of the original samples were performed with Primo Star microscope (Carl Zeiss, Germany), a flexible equipment, easily adaptable to multiple working conditions. The equipment offers the possibility to examine the samples both in transmitted light and in reflected light, at a magnification factor between 4x and 100x. The Primo Star microscope is equipped with a digital video camera (Axiocam 105) which, through the microscope software, allows real-time image acquisition, with the conversion from 2D to 3D.

The morphological investigations of the original samples were performed by scanning electron microscopy, using the SU-70 scanning electron microscope (Hitachi, Japan), a high-sensitivity field

emission research equipment (FE-HRSEM) and electron source type Schottky. The equipment includes several modules required for surface analysis of materials: energy dispersion spectrometer (EDS) and wavelength spectrometer (WDS). All these modules are attached to the entire equipment. The acceleration voltage can vary from 0.1 kV to 30 kV. The magnification range of the SEM is from 30X-800.000X, and the resolution at the acceleration voltage of 15 KV is 1 nm. The attached EDS spectrometer allows qualitative and quantitative analysis (from Be (Z=4) to Pu (Z=94)) of point, rectangle, circle or area of your choice, line and grid type analysis, X-ray mapping (item distribution maps).

2.3. Vibrational spectroscopy

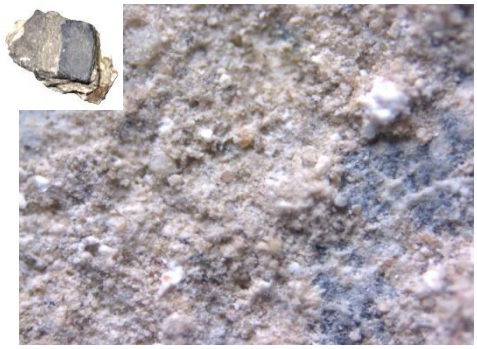
FTIR vibrational spectroscopy was used for qualitative analyzes of the original samples. The Fourier Vertex 80v Infrared Spectrometer (Bruker, Germany) is an advanced research equipment that offers good stability and sensitivity of peaks (spectral range 350-8000 cm^{-1}, spectral resolution 0.2 cm^{-1} and accuracy 0.1% T; 32 scan). The analysis was performed using the ATR (total attenuated reflection) accessory with diamond crystal and platinum tip mounting unit that ensures a very good contact between the sample and the diamond crystal. Total attenuated reflection is a technique used in conjunction with IR spectroscopy, which allows direct examination of solid or liquid samples without further preparation. Raman spectroscopy is complementary to FTIR analyzes, providing complete information on the analyzed samples. The Raman qualitative analysis used the Raman Xantus 2 spectrometer (Rikagu, Germany), with two sources (wavelength 785 nm and 1064 nm), which allows rapid fingerprinting of spectra in the range of 200-2000 cm^{-1}. It also provides a unique combination of high sensitivity and low fluorescence.

2.4. X-ray diffraction

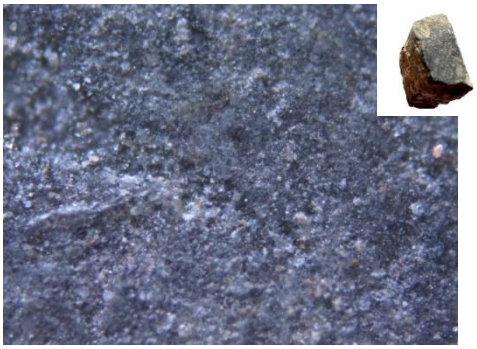
X-ray diffraction is the analytical technique for characterizing solid, organic or inorganic materials, the diffraction intensities being generated by the interactions of X-rays with the electrons of the atoms in the network. For investigations, the Rigaku Ultima IV X-ray diffractometer (Rigaku, Germany) was used, equipped with software for command, control, respectively data acquisition and conversion.

3. Results and Discussion

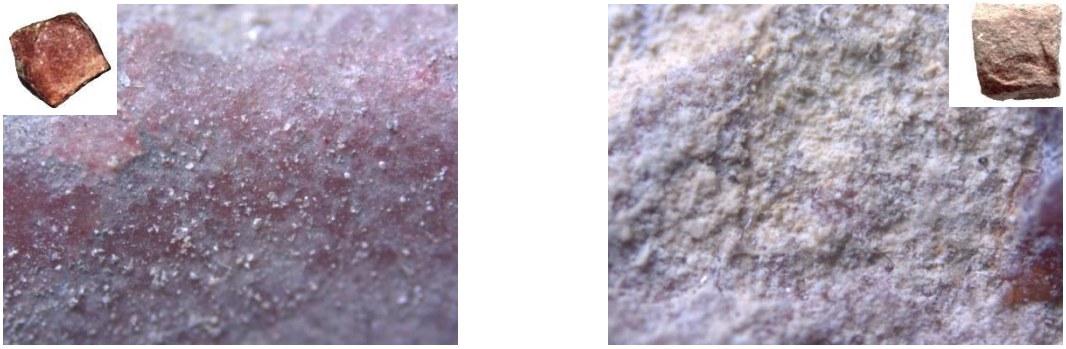
Scanning electron microscopy (SEM) in conjunction with optical microscopy showed a degradation of the structure of the original samples (Figures 1 and 2) under the action of microclimatic factors. Also, the electron microscopy images allowed the observation of the dust particles (SiO_2) attached to the surfaces of the analyzed samples (sample P2, Figure 2). The morphology and grain aspect of samples (Figure 3) was obtained using secondary electrons detection mode and highlights the mixture of the fine-grained base with crystallized grains, specific to calcite structure (all samples), as well as the formation of plated calcite crystals (P4).



P1

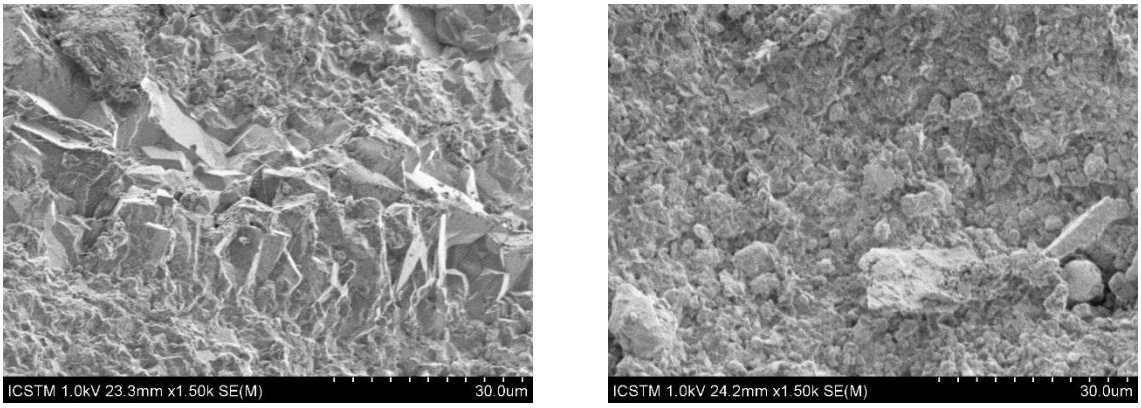


P2

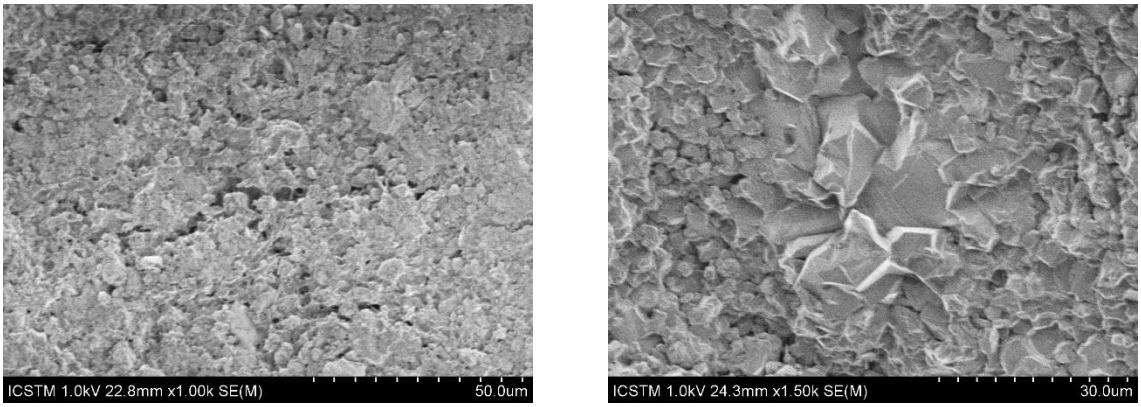


P3 P4

Figure 2. Optical images of samples P1-P4.



P1 P2



P3 P4

Figure 3. FE-SEM images of the mosaic samples (P1-P4) recorded at Vacc = 1 kV, WD = 22.8–24.3 mm, ×1000-1500 magnification.

The mineralogical compositions of the studied mosaic fragments are mainly representative of carbonaceous stones and are determined by X-ray diffraction (XRD) technique. On the other hand, the diffractometric data clearly emphasizing the size of the β-SiO_2 (tridymite) crystallites, as well as the Miller indices corresponding to this form of SiO_2. The main minerals present in the original structure are calcite, β-SiO_2, orthosilicates and other impurities acording to data presentend in Table 1.

Table 1. Mineral composition of the mosaic fragments determined by XRD, expressed in mass% ± S.D.%, normalized to 100%

	P1	P2	P3	P4
Calcite	74.13±0.23	76.67±0.23	75.16±2.51	75.43±2.34
β-SiO_2	3.32±0.05	2.97±0.02	3.24±0.05	3.19±0.02
Orthosilicates	21.47±0.37	19.24±0.44	20.51±0.56	20.24±0.78
Other	1.08±0.03	1.12±002	1.09±0.01	1.14±0.01

FTIR and Raman data (Table 2) for the analyzed samples showed similarities in terms of spectra, in the wavelength range of 4000-400 cm^{-1} and 2000-200 cm^{-1}, respectively, with the main spectral characteristics in the range 1800-400 cm^{-1}; the observed peaks were attributed to different bonds depending on their chemical structures.

Table 2. The vibrational spectra to the different mineral phases of the mosaics fragments.

Sample	**Wavenumbers [cm^{-1}] and relative intensity***	
FTIR		
P1	1786/1376/1087/873/712/462/416/394	w/s/s/m/w/w/m/s
P2	1796/1374/1086/874/712/557/487/395	w/s/s/m/w/m/s
P3	1735/1326/1084/874/712/395	w/w/m/s/w/m
P4	1737/1321/1085/873/711/395	w/w/m/s/w/m
Raman		
P1	1610/1375/1325/1085/873/796/712/637/557/480/463/395/358	w/s/s/s/w/w/m/w/s/w/w/s/w
P2	1615/1374/1321/1084/873/792/712/462/430/397/369/358	m/s/s/w/m/w/s/w/w/m/s/w
P3	1620/1378/1323/1086/873//782/712/602/557/462/395/253	s/w/w/w/w/w/m/m/s/m/w/m
P4	1610/1374/1322/1081/874/780/712/637/552/460/395/304/283	s/w/w/w/w/w/s/w/s/m/w/s/s
**w – weak; m – medium; s - strong*		

The tentative assignments of the FTIR and Raman spectra according to wavenumbers and relative intensity are presented in Table 2. In addition to the phases already described above, the Raman lines associated with hydroxides and oxides of iron and manganese were observed on Raman spectra of red crystallites on the surface of mosaic samples 3 and 4. The FTIR and Raman peaks in the wavenumber region of 873–1087 cm^{-1} are related to the presence of some silicates in the studied samples [4-6]. The combination of these additional phases probably indicates the presence of a mixture of natural pigments; "yellow ochre" and "red ochre" were used as paint for mosaic [4]. The blue layer of sample 2 is characterized by two additional peaks at 1796 and 1615 cm^{-1}. They are associated with a pure carbon phase [6,7]. On the other hand, typical carbonate (calcite) spectra include major absorption bands in the range of 4000-660 cm^{-1}, each of which can be identified by the deformation vibration attributed to the carbonate ion (Table 2). These bands are due to the vibration of asymmetric stretching, respectively of the planar bending of the carbonate radical [6-8]. Peaks of 1376/1374 cm^{-1} (asymmetric stretch of the carbonate radical), intense peak around 873/874 cm^{-1} (off-plane bending of the carbonate radical) and 712/711 cm^{-1} (flat bending of carbonate radical) are attributed to carbonates, suggesting the presence of both polymorphic forms, calcite and aragonite [6,7]. The differences can be partly attributed to changes involving the structure of the lattice (a change in the coordination of the metal ion from six times in calcite to nine times in aragonite) and also to a change in the symmetry of the crystal lattice [6,9-11].

4. Conclusions

In this research several non-invasive methods have been used in order to investigate the decorative mosaic fragments from Constanta, Romania, (representative for the cultural heritage of the ancient Roman and Byzantine Empire). Optical and electronic microscopy along with vibrational spectroscopy studied in detail the structural features of the surfaces, as well as the chemical composition of mosaic fragments. The results are important for further analysis (probably destructive) in the attempt to create

a clear image about the ancient techniques and materials that were used, not only for this edifice but also for others as this, which were built in those ages.

Acknowledgments. *This research was funded by Bilateral Project 04−4−1121−2015/2020, between Valahia University of Targoviste and Joint Institute for Nuclear Research, Dubna, Moscow Region; Protocol 4755−4−2018/2020 "Micro−structural and compositional characterization of supports and coating layers on different substrates applied in biomaterials, photoelectrochemicals catalysis and cultural heritage" and by the project 51PCCDI/2018, financed by Romanian National Authority for Scientific Research (UEFISCDI) "New diagnosis and treatment technologies for the preservation and revitalization of archaeological components of the national cultural heritage".*

References

[1] Ricciardi P, Colomban P, Tournié A, Macchiarola M, and Ayed N 2009A Non-Invasive Study of Roman Age Mosaic Glass Tesserae by Means of Raman Spectroscopy *J. Archaeol. Sci.* **36** 2551

[2] Boschetti C, Corradi A, and Baraldi P 2008 Raman characterization of painted mortar in Republican Roman mosaics *J. Raman Spectrosc.* **39** 1085

[3] Witts P 2005 *Mosaics in Roman Britain: Stories in Stone* (1st ed.) (Stroud: Tempus) pp 35

[4] Ion RM, Bakirov BA, Kichanov SE, Kozlenko DP, Belushkin AV, Radulescu C, Dulama ID, Bucurica IA, Gheboiuanu AI, Teodorescu S, Stirbescu RM, Iancu L, David ME, and Grigorescu RM 2020 Nondestructive and micro-invasive techniques for characterizing the ancient Roman mosaic fragments *Appl. Sci.* **10**(11) 3781

[5] Olteanu RL, Radulescu C, Stihi C, Dulama ID, Nicolescu CM, Stanescu SG, Bucurica IA, Gurgu IV, Stirbescu RM, Gheboianu AI, Let DD, Teodorescu S, Olteanu L, and Stirbescu NM 2020 Indoor Microclimatic Variables Assessment by Vibrational Spectroscopy on Original Structure of Tropaeum Traiani Monument, Adamclisi *J. Sci. Arts* **4**(53) 977

[6] Adler HH and Kerr PF 1963 Infrared adsorption frequency trends for anhydrous normal carbonates Amer. Mineral. **48** 124

[7] Anderson FA and Brecevic L 1991 Infrared Spectra of Amorphous and Crystalline Calcium Carbonate *Acta Chem. Scan.* **45** 1018

[8] Bintintan A, Gligor M, Radulescu C, Dulama ID, Olteanu RL, Teodorescu S, Stirbescu RM, and Bucurica IA 2019 Multielemental and Chemical Characterization of Eneolithic Petresti Painted Pottery from the Alba Iulia-Lumea Noua Archaeological Site, Romania *Anal. Lett.* **52**(15) 2348

[9] Radulescu C, Stihi C, Ion RM, Dulama ID, Stanescu SG, Stirbescu RM, Teodorescu S, Gurgu IV, Let DD, Olteanu L, Stirbescu NM, Bucurica IA, Olteanu RL, and Nicolescu CM 2019 Seasonal Variability in the Composition of Particulate Matter and the Microclimate in Cultural Heritage Areas *Atmosphere* **10**(10) 595

[10] Ion RM, Iancu L, Vasilievici G, Grigore ME, Andrei RE, Radu GI, Grigorescu RM, Teodorescu S, Bucurica IA, Ion ML, Gheboianu AI, Radulescu C, and Dulama ID 2019 Ion-Substituted Carbonated Hydroxyapatite Coatings for Model Stone Samples *Coatings* **9**(4) 231

[11] Ion RM, Tincu S, Ion N, Bucurica IA, Teodorescu S, Dulama ID, Stirbescu RM, Gheboianu AI, Radulescu C, Ion ML, Iancu L, and Grigorescu RM Archaeometric Studies of Mural Paints from Matia Loggia (Corvins' Castle) *Rom. Rep. Phys.* **71**(3), 804