CHARACTERIZATION OF ROMAN MARBLE BUST USING LIBS AND μ-RAMAN SPECTROSCOPY. A CASE STUDY

O. GRUPČE[1*], M. SIMILEANU[2], A. RAŠKOVSKA[1], Lj.DZIDROVA[3], B. Minčeva-ŠUKAROVA[1], R. RADVAN[2], M. ŠURBANOVSKA[3], J. STRIBER[2]

Keywords: *LIBS, micro Raman spectroscopy, marble, gilding, Stobi, pigments, laser cleaning*

Abstract: *Roman marble bust of a woman, dated 1st century A.D., was excavated in Stobi, prominent archaeological site in Republic of Macedonia. The bust is made of white, small grained marble with red painted waist band and gilded with gold. Analysis was performed, using LIBS and micro Raman spectroscopy. Using LIBS, elemental composition of the gilded metal and pigment were established while using micro Raman spectroscopy, the nature of the pigment and mineralogical composition of the marble was determined. Laser cleaning procedure was applied in order to clean the surface of the archaeological find.*

Introduction

Stobi [1,2], situated in the central region of Republic of Macedonia is a significant archaeological site from the Roman period, excavated since 19th century. The remains of several structures are testimonials of the urban and cultural growth of Stobi: the theatre, the Forum, Casa Romana and the Synagoge. The importance of the site from the Late Antiquity is already well documented, but significantly less information is available about the life during the early Kingdom, that is 1st and 2nd century b.c. The campaign funded by the HABO CIS from Palermo in 2007 was focus on unearthing exactly that period. Among the numerous unmovable and movable archaeological objects unearthed during that campaign, are the group of fragments of marble statues which most probably stood in the niches of prominent buildings. It consists of different fragments of

[1] Institute of Chemistry, Faculty of Natural Sciences and Mathematics, "Ss. Cyril and Methodius" University, Skopje, POB 162, Republic of Macedonia; [2] National Institute of Research and Development for Optoelectronics, Bucharest, Romania; [3] Museum of Macedonia, Ćurčiska b.b., 1000 Skopje, Republic of Macedonia; *e-mail: orhideja@pmf.ukim.mk.

heads, torsos and busts.

Here we present the study results of one of the busts, made of white, small grained marble with waistband painted in red and gilded. Archaeologists classified this artifact as 1st -2nd century A.D. female bust, of Ionic provenance.

The analysis of the marble bust comprises: (1) characterization of the gilding foil; (2) analysis of the red pigment, used as under layer for the gilded section; (3) characterization of the marble (including the rare earth elements); (4) laser cleaning procedure, applied in order to clean the remains of dirt and soot on the surface of the fragment, since the fragment has been subjected to fire.

Laser-induced breakdown spectroscopy (LIBS) and micro Raman spectroscopy were used for the characterization of the marble bust. The choice of the techniques was not accidental: Raman spectroscopy [3], which provides the molecular 'fingerprint' of the compounds, is nowadays widely used by the archaeometry community, especially for pigment analysis. Besides the pigment analysis, in assessing the mineralogical composition of the marble, point to point Raman spectroscopy was applied [4]. Laser-induced breakdown spectroscopy (LIBS) [5,6,7] has emerged in the past ten years as a promising technique for analysis and characterization of the composition of a broad variety of cultural heritage objects, including painted artworks, icons, polychromes, pottery, sculpture, and metal, glass, and stone artifacts. Its main advantage is rapid, *in-situ* elemental analysis of the object under investigation. It doesn't require sample preparation, it is almost nondestructive (micro sampling) and information about major and trace elements are obtained simultaneously. It also could provide stratigraphy analysis of the object.

Using LIBS, elemental composition of the gilded metal was established. Elemental distribution in the foil was obtained by in depth profiling which in turn suggested technology of production of the gold foil. LIBS was used for trace elements characterization of the marble, as well, in order to suggest chemical pattern for a possible marble provenance.

Point to point Raman spectroscopy was applied in assessing the mineralogical composition of the marble. The nature of the red pigment applied on the waistband was established by Raman spectroscopy as well.

Laser cleaning [8] was chosen as principle cleaning method for the charred bust, as one of the most effective and controllable method for cleaning.

Experimental

Laser Induced Breakdown Spectroscopy

Two lasers were used for LIBS analysis: Tempest 300 (New Research) at 355nm and Giant G 70 10 (Quanta System) at 1064 nm; 20 mJ and 350 mJ respective energy. Tempest was used for irradiation of surface and Giant, for plasma heating. Respective to Tempest, the delay of Giant pulse was 4 ◎s. Detection system was composed of Spectrograph Mechelle (Andor) and ICCD-DHK734 Gen III (Andor). Detection LIBS signals was with delay 2 ◎s and detection time (gate) 12 ◎s. Impulse generator model 9518 (Quantum composers) synchronized two lasers and ICCD work.

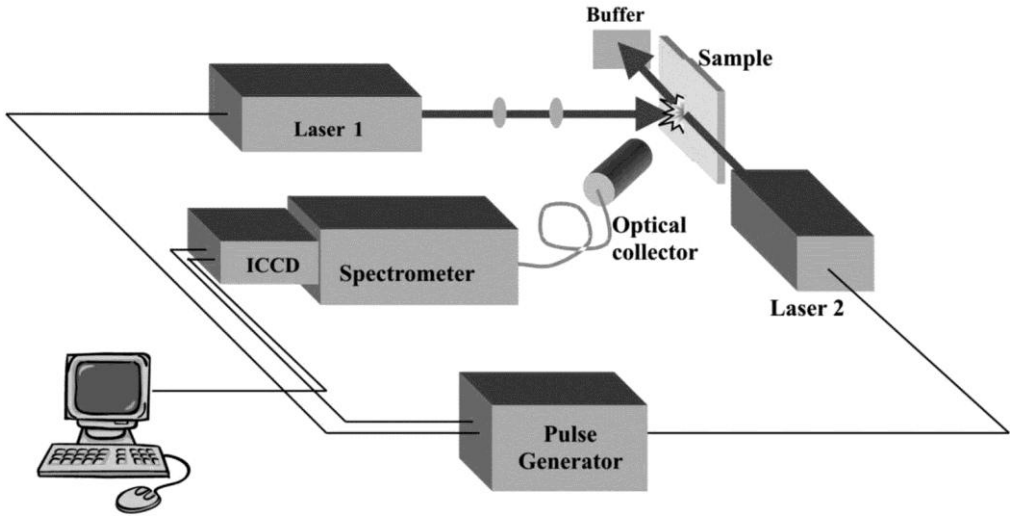


Fig. 1 - Double pulse LIBS system.

Micro Raman analysis

The pigment analyses were performed on a LabRam 300 (Horiba Jobin-Yvon) Raman spectrometer, in the 100–2300 cm^{-1} region, at the Institute of Chemistry in Skopje. The instrument is equipped with two lasers: He-Ne laser operating at 17 mW and 633 nm, used for pigment analysis. An Olympus MPlanN microscope with x50 and x100 magnification was used to focus the laser on the samples. The backscattered light was dispersed using the 1800 lines/mm grating and is detected on a multi-channel air cooled CCD detector, spectral resolution of 3–4 cm^{-1}. The LabSpec software [9] was used for data acquisition and GRAMS software [10] was used for data manipulation.

Point-to-point micro-Raman spectra were recorded on Horiba Jobin-Yvon LabRam 300 spectrometer using frequency doubled Nd:YAG laser operating at 50 mW and 532 nm, used for maping of the marble pallet. The Raman spectra of the marble were obtained, recording pellets prepared from 250 mg powdered marble, placed under the microscope (*f*x50) on a mapping stage (8 x 8, 64 points) and an area of 30 x 30 μm^2 (Fig. 1.b). Raman spectra were acquired, with the resolution of 3–4 cm^{-1}, step of 7 μm, acuisition 15, scans 10.

Laser Cleaning Procedure

The laser cleaning was carried out using a Q-switched YAG:Nd laser at fundamental wavelength – 1064 nm, pulse duration 6ns, at a frequency of 20 Hz, using different fluencies, accordingly to the degree of impurities found on specific areas.

Discussion

The marble bust study covers: (1) analysis of the gold used for gilding; (2)

analysis of the red pigment, used as underlayer for the gilded section; (3) analysis of the marble, including mineralogical composition and trace analysis and laser cleaning of the bust.

Analysis of the metal used for gilding.

LIBS was used in order to obtain information on the composition of the metal used for gilding. Beside surface analysis, in depth analysis was applied as well, resulting in three series of data. As can be seen from the plot 1, the top layer consists of Au, Cu, Hg and Fe. The first thought, based on the presence of Hg in the spectrum implied red Hg based pigment (vermilion, HgS, often used in antiquity as red pigment), the in depth LIBS results of the red pigment, second series of the analysis, plot 2 (Fig. 2) contrary to the expectations, showed decrease in the Hg content. The question arises, if the mercury doesn't come from red pigment, where does it come from?

One of the logical explanations is that the gold ore was purified using amalgamation method, and the mercury persisted heating. The gold leafs used for gilding, in that case, contains mercury. As shown in literature, it is known that gold retains mercury [11]. Having in mind that amalgamation was common procedure for purification of gold and up to 15 % of mercury could be retained in the gold, the presence of mercury leads to conclusion that amalgamation was the procedure used for purification of gold.

In the second series, of the in-depth analysis of the gilding layer, there is slight variation in the elemental composition. In the third series, however, there is profound change in the content of the elements: the presence of mercury dramatically decreases, while the presence of iron dramatically increases, suggesting that the coloured underlayer have been reached by the laser.

It could be concluded, that the gilding layer consisted of gold and copper, with mercury as a residue due to the amalgamation procedure. The presence of iron was more difficult to explain [12], except as accidental residue. The increase of the Fe presence in the third series suggested that Fe may be in the pigment applied underneath the gilding.

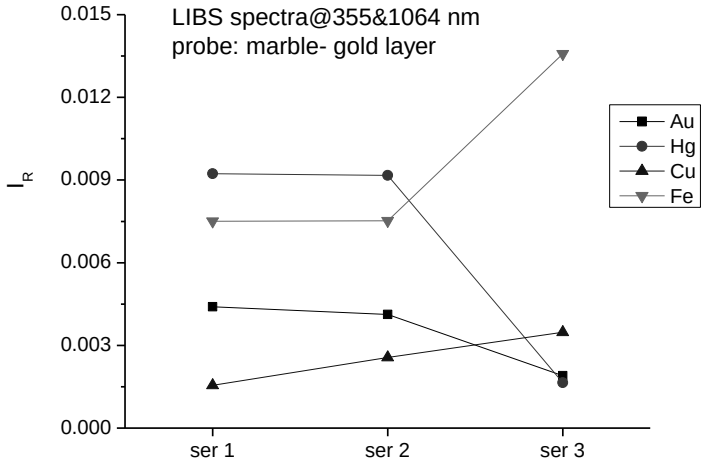


Fig. 2 - LIBS stratigraphy results on the gilding metal on the marble bust.

Analysis of the red pigment

In the first series of the LIBS stratigraphy results on the red pigment of the marble bust, presence of the gold, copper, mercury and iron was identified, that decreased in the next series. The presence of gold, copper and mercury could be explained with the remains of the gilding on the surface of the red pigment, giving rise to signal of gold, copper and mercury. The presence of iron could be connected to Fe based red pigment. In the third series, pronounced decrease of all element was noticed, suggesting that the laser has reached the marble.

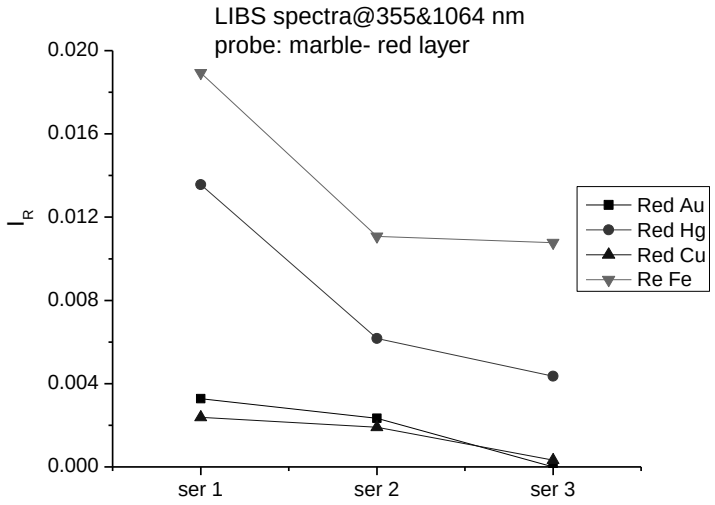


Fig. 3 - LIBS stratigraphy results on the red pigment of the marble bust.

In order to pinpoint the red pigment used for the belt coloration of the marble statue, Raman spectroscopy was used. Raman spectrum of the red pigment revealed that the used pigment was hematite, pigment often used in antiquity as red pigment [13,14]. Fig.4. Band originating from the marble mineral, dolomite is observed in the spectrum as well.

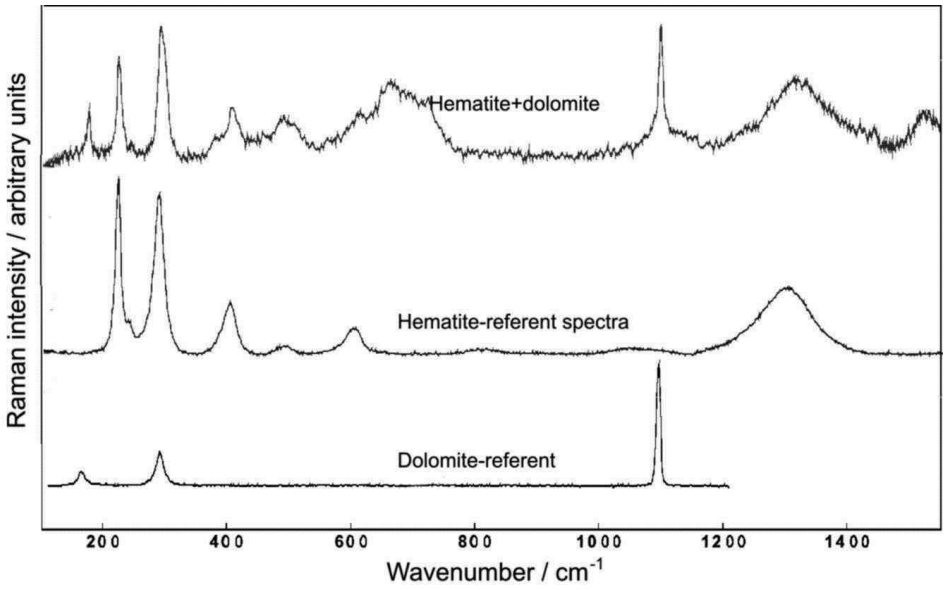


Fig. 4 - Raman spectrum of the red pigment.

Analysis of the marble

LIBS and Raman spectroscopy was combined in order to obtain more information about the composition of the marble. Point to point Raman spectroscopy was used for estimation of the mineralogical composition of the marble. Around 70 spectra were obtained, all showing very similar features (Representative spectra are shown on Fig. 5). As can be seen on Fig. 5 marble is almost pure dolomite, with minor constituents as anatase and carbon (most probably due to the charring of the bust).

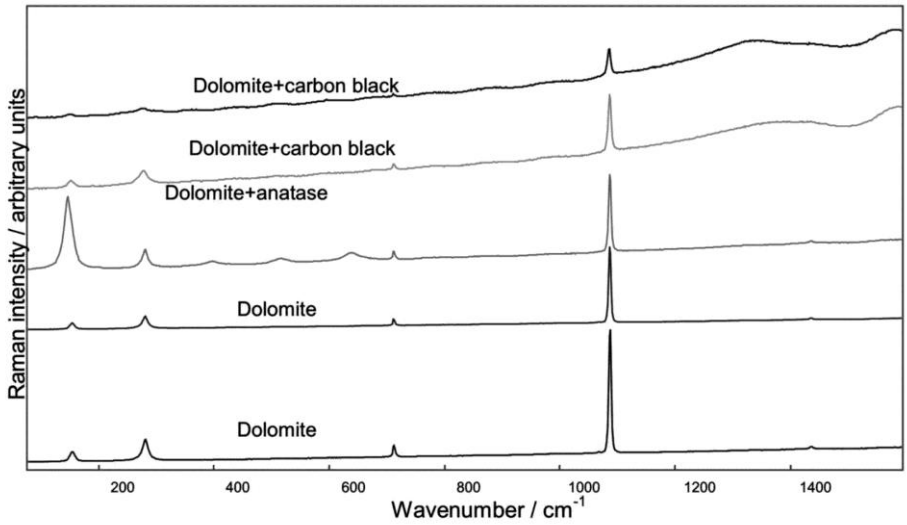


Fig. 5 – Estimation of the mineralogical composition of the marble using point to point Raman spectroscopy.

Although using LIBS, trace elements like Hf, Br, Th. Lu and Sc were determined, the assumption by the archaeologists that the bust is of Ionic provenance could not be confirmed [15,16].

Laser Cleaning Procedure

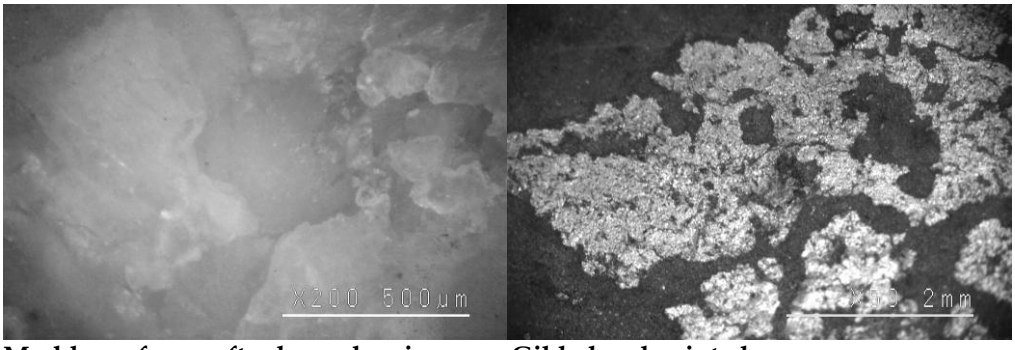
Laser cleaning is a novel technique that applies to inorganic materials substrates as well as organic ones. It has the potential to provide contactless, chemical-free cleaning of historically important documents, overall providing a high accuracy successful cleaning.

The laser cleaning was accomplished using the fundamental wavelength (1064 nm) at energy of 220mJ.

before **after laser cleaning**

before **after laser cleaning**

The laser cleaning procedure was a success, the adherent deposits were removed following closely the marble surface. As it can be noticed in the microscopy images presented below, the cleaning did not affect or deteriorate in any way the gilded or painted substrates.



Marble surface – after laser cleaning **Gilded and painted area on the marble bust – after LC**

Conclusion

1. Gilding foil was found to be gold alloy, containing copper and mercury beside gold. The presence of mercury could be explained by the amalgamation procedure used for purification of gold, often applied at those times. Iron was identified as well, most probably residue of the red pigment applied underneath the gilding.
2. The red pigment used for coloring was found to be hematite.
3. The marble was found to be almost pure dolomite. Trace elements as Hf, Br, Th, Lu and Sc were found in the marble.

Laser cleaning procedure was applied in safety conditions to clean the archaeological artifact. The technique was successful in removing soot, dirt and charred remains and pollution deposits, improving the esthetic appearance of the bust without affecting the sensible degraded substrates.

BIBLIOGRAPHY

BOSHKOV 2007 - G. Boshkov (ed.), *Forum romanum Stobis 2006*, *Archaeological and Tourist Valuation of the Roman Town Stobi*, Skopje.

Studies in the Antiquities of Stobi, (Editors Dj. Mano-Zissi and J. Wiseman) Beograd, 1973.

VANDENABEELE, EDWARDS, MOENS 2007 - P. Vandenabeele, H. G. M. Edwards, L. Moens, *Chem Rew*., 107 (2007), 3, p. 675-686.

TANEVSKA, COLOMBAN, MINČEVA-ŠUKAROVA, O. GRUPČE 2009 - V. Tanevska, Ph. Colomban, B. Minčeva-Šukarova, O. Grupče, *J. Raman. Spectrosc.* 40/9 (2009) 1240-1248.

FOTAKIS *et alli* 2006 - C. Fotakis *et alli*, Lasers in the *Preservation of Cultural Heritage*. /Taylor and Francis Books, USA.

RĂDVAN, ENE, MĂRĂCINEANU, SIMILEANU, DECIU, ANGHELUŢĂ, STRIBER, DRAGOMIR 2008 - R.Rădvan, D.Ene, W.Mărăcineanu, M.Simileanu, C.Deciu, L.Angheluţă, J.Striber, V.Dragomir, *Monitoring and Prediction of Cultural Heritage Artifacts Conservation Status*, The e-Journal of Nondestructive Testing - Proceedings of The 9th Int. Conference on NDT of Art 2008 Jerusalem, Israel, May 2008.

OUJJA, CASTILLEJO, MĂRĂCINEANU, SIMILEANU, RĂDVAN, ZAFIROPULOS, FERRO 2008 - M.Oujja, M.Castillejo, W.Mărăcineanu, M.Simileanu, R.Rădvan, V.Zafiropulos, D.Ferro, *LIBS analysis of metal artifacts from Sucevița Monastery, Romania,* Lasers in the Conservation of Artworks, Ed. Taylor&Francis Group, p.133-139, 2008, ISBN 978-0-415-47596-9.

SIMILEANU, MĂRĂCINEANU, STRIBER, DECIU, ENE, ANGHELUŢĂ, RĂDVAN, SAVASTRU - M.Simileanu, W.Mărăcineanu, J.Striber, C.Deciu, D.Ene, L.Angheluţă, R.Rădvan, R.Savastru, *Advanced Research Technology for Art and Archaeology - ART4ART,* J. Optoelectron. Adv.Mater., Vol.10, No.2, p.470-473, 2008.

GRAMS/32 Spectral Notebase, Version 4.10, Galactic Industries Corporation, 1996.

LabSpec version 5.25.15.

BREPOHL - E. Brepohl, *The Theory and Practise of Goldsmithing*, Brynmorgen Press, 2001.

BŁACHOWSKI, RUEBENBAUER, RAKOWSKA, KAC - A. Błachowski, K. Ruebenbauer, A. Rakowska, S. Kac, *Fractal - like behaviour of the BCC/FCC phase separation in the iron-gold alloys*, Journal of microscopy 237(3):395-8, 2010.

Thermo Galactic, Spectral ID (3.02).

Françoise Froment, Aurélie Tournié, Philippe Colomban, J.Ram.Spec.(2008) 39/5, 560-

568.

GRIMANIS, VASSILAKI-GRIMANI 1988- A.P. Grimanis, M. Vassilaki-Grimani, *Applied Science*, 153, 275-282 (1988).

MELLO, MONNA, ODDOME 1988 - E.Mello, D. Monna, M. Oddome, *Archaeometry*, 30, 102-108 (1988).