Proceedings of the

3rd Balkan Symposium on Archaeometry

29-30 October 2012
Bucharest, Romania

Art restoration and archaeological material study are inseparately related to scientific investigation and scientific data processing of the information. This reality makes the mentioned field of the most attractive one and a very generous one for professional development.

The e-proceeding, published by INTEGRA NATURA ET OMNIA - INOE, brings together a large part of the contribution to The Third Balkan Symposium on Archaeometry organized in Bucharest on 29 and 30 October 2012, and is following the close related volume that was published by The Kultur Intitute University from Istanbul. The biennial event gathers scientists, conservators, restorers, architects, companies, decision-makers, professors and students involved in projects on all aspects of archaeometry, the application of modern experimental methods and techniques used in investigation, identification and dating of ancient artifacts, as well as related fields of archaeology and art history. Appreciated researchers from multidisciplinary groups, not only from Balkans, have been invited to contribute with keynote speeches and to support the dissemination of recent results. The event continues the tradition of previous symposiums, the first being held in Ohrid - Republic of Macedonia in 2008 and the second in Istanbul – Turkey in 2010.

Special support for present e-proceeding publishing have been received from Dr. eng. Roxana Savastru – general manager of INOE, who was sustaining all initiatives of the Center for Restoration by Optoelectronical Techniques and who permanently, and who generously offers her experience and professional skills.

The editors wish to remind to all participants to The Third Balkan Symposium on Archaeometry that the devoted specialist and initiator of the Balkan Network on Archaeometry – permanently close to each edition organization- is Prof. Prof. Biljana Minceva-Sukarova from Institute of Chemistry, Faculty of Natural Sciences and Mathematics "SS. Cyril & Methoidius" University, Republic of Macedonia.

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Study of vulnerability and characterization of stone columns from Seville (Spain)

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Abstract: The aim of this research was the characterization of archeological columns of different periods found in Seville (Spain) by studying their conservation degree and vulnerability situation. This work is part of a project which is being carried out in the Historical City of Seville and consisting on the analysis of the risk and vulnerability in Historical Centers. In the city of Seville, a large number of these columns could be recognized as reused in the cathedral, inside and outside churches, in civil Monuments and as a reinforcement of building corners in the city. Marble, limestone and granite columns have been investigated in order to carry out the mineralogical and petrographical description of the stones and to evaluate their conservation degree and vulnerability to environmental hazards. Several analytical techniques have been employed to determine composition of specimens and their weathering forms.

1 INTRODUCTION

The quality of the stones used in columns made them attractive for subsequent reuse in the same places or in a new location. Only when they are broken or mainly destroyed, they are employed for mortars as lime or aggregates. In the city of Seville, a large number of these columns could be recognized as reused in the cathedral, inside and outside churches, in civil Monuments and as a reinforcement of building corners in the city.

Marble, limestone and granite columns have been investigated in order to carry out the mineralogical and petrographical description of the stones and to evaluate their conservation degree and vulnerability to environmental hazards.

The effects of weathering on stone columns require a multidisciplinary approach to understand the damage mechanisms and the vulnerability conditions.

This work is part of an Andalusian Project titled “Design and validation of a methodology to carry out risk and vulnerability maps in Historical Centers” that has been carried out in the Historical City of Seville and which aim is the analysis of the environmental influence in the weathering of monuments, and the proposal of a new standard methodology to evaluate vulnerability and conservation degree.

With this purpose, more than 150 columns have been studied to evaluate the conservation degree and the mechanism of the main weathering forms.

2 MATERIALS AND METHODOLOGY

The stone columns studied are calcareous and granite stones of different sizes and shapes. Most of them are roman columns reused in different Churches, or monuments. Meanwhile only three of the columns are maintained in their original place (*Fig. 1*).

These natural stones are under exterior conditions, so they are directly exposed to temperature changes, erosion and pollution in the center of the city.

The study of the weathering forms has been carried out on 175 columns by means of visual inspection. These macroscopic pathologies have been described by the terminology of NORMAL regulation 1/88 (1990), Ordaz and Esbert (1988), Martin (1990), Fitzner et al. (1992 & 1995) and the ICOMOS recommendations (2008).

For this work, five samples have been taken from deposits and black crusts on columns following the recommendations of the technical commission CNR-ICR NORMAL 3/80 (1980).

Sampling has been carried out on five columns according to the most common variety found in the city: white and green marble, red and black limestone and grey granite.

Figure 1: *Column of granite from roman period in their original location.*

For the mineralogical and petrographical study, we have used an optical microscope Kyowa with a digital camera and X-ray difractometer brand Bruker (model D8 Advance), using CuKα.

The elemental chemical analysis over the stratigraphies of the crusts and deposits has been studied by means of an electron scanning microscope JEOL JSM-5400, with x-ray energy detector, Inca X-sight. The chemical composition has also been analyzed with an X-rays fluorescence spectrometer Panalytical (model AXIOS) with Rh tube.

LIBS measurements were carried out by a set-up consisting of a conventional arrangement including pulsed Nd:YAG laser, focusing and collecting optics, spectrograph and detector and it was described elsewhere (*Ctvrtnickova et al., 2009*). The laser operated at its second harmonic 532 nm wavelength with a pulse duration of 5 ns and its maximum energy output was 300 mJ/pulse. The laser beam was directed normally to the sample surface and focused by a planoconvex quartz lens. Microplasma created on the sample surface was collected by a quartz optical fiber and transmitted to an Echelle spectrograph coupled to an ICCD camera. The spectrograph spanned the spectral region of 200–850 nm simultaneously with high resolution, thus it allowed multi-elemental analysis under the same experimental conditions for each element. The detector delay time and integration time were set to 1 μs and 10 μs, respectively. The data acquisition was carried out in two modes, either accumulation of 5 pulses on the sample surface in order to determinate the elemental composition of the deposit layer, or firing 100 pulses to the same position in order to acquire the depth profile of the layered sample. All experiments were performed in air under atmospheric pressure.

The interest of LIBS over other techniques is the fact that the analysis does not require preparation of the specimens and the damages induced are minimal which has become a crucial point for cultural heritage artifacts. Hence, a higher number of measurements can be carried out leading to a more complete study of crusts and contamination species responsible of degradation.

3 RESULTS AND DISCUSSION

3.1 *Vulnerability of stone columns*

The most dangerous weathering forms found in the granite columns is detachment of different size, whilst marbles has pitting and limestones present loss of material mainly in veins or zones of different porosity.

Chromatic alteration is very usual in the columns due washing of metal structures of reinforcement or ornamental purpose, but also it is caused by the internal oxidation of iron.

Losses of materials are common in most of the column due to the man action. Fissures were detected in a few columns mainly related to changes of texture and rarely to mechanical effects.

Biocrust are located in granite columns associated to vegetation and humidity, while black crust and deposits were found in any column near traffic (*Fig.2*).

Figure 2: *Granite column affected by crust, deposits and iron spots.*

3.2 *Mineralogical and Petrographical Description*

Thin section microscopy and XRD analysis was carried out on the materials of five columns. The results show that four samples are mainly composed of calcite (marbles and limestones) with micas in green marbles while the granite column is composed of quartz, K-feldspar and biotite.

The main weathering product is gypsum that has been detected by XRD and OM. The epigenetic layer of gypsum is a product of transformation of calcite in surface, what implies a direct relationship with the presence of sulfur oxides in the atmospheric environment of the columns. Deposits on granite samples are mainly composed of terrigenous particles and/or organic compounds that are not detected by XRD.

XRF results show that calcium is the main component in the four calcareous samples; meanwhile silicon is the main component in granite column according to the lithotype descriptions.

Sulfur content is over 2% w/w in limestones and white marble. It corresponds with the gypsum, according to DRX and petrographical characterization that implies a chemical process of weathering.

The profile of crust and deposits allow knowing the origin of the damage and the vulnerability of each material. For this reason, this study has been completed by LIBS and SEM-EDX.

3.3 *Study of crusts and deposits depth by LIBS*

LIBS analyses have been performed on black and clean zones of samples to obtain a representative spectrum of each zone with an accumulation of five pulses in order to get a suitable signal.

LIBS spectra of marbles and calcareous stones are dominated by Ca emission lines, according to their composition that is based on calcite. In contrast, Si, Al, and Li emission lines dominate the LIBS spectra on granites in a range of relationships due to their mineralogical composition (quartz, K-feldspars and biotite).

LIBS measurements show also the presence of Al, Si, Mg, K, Sr, Na and Ba lines both in black crusts and clean zones of marbles, while granite present mainly Si, Al and Li over the stone and Ca, Mg and Na on the deposits.

V and Ti lines appear in the layers of black crust on calcareous stones. The presence of both elements could be explained by pollution and, in case of titanium, it could be caused by dessert sand storms (*Colao et al., 2004*).

Depth profiling has been performed in the samples shooting in the same point to evaluate the evolution between the crusts or deposits (upper part) and the stones (inner part). In such profiles, while the intensity of characteristic element of the upper layer diminishes in depth, the base material element intensity increases. The intersection of corresponding curves represents the deposits/stone interface (*Mateo et al., 2006*).

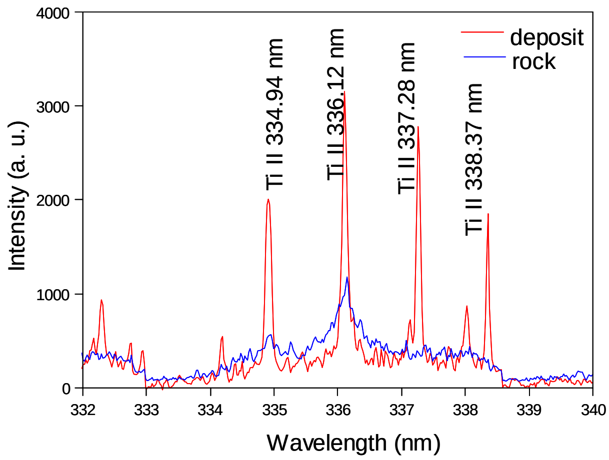

Figure 3: *Titaniun from the deposits and crust over the white marble column.*

The interface is reached after 10-20 pulses in calcareous stones while the interface is reached after 5 pulses in granites, which implies that the encrustation is thinner in calcareous stones, surely due to the presence of gypsum crust though LIBS was not suitable to detect sulfur in the current experimental set-up.

3.4 *Study of crusts and deposits depth by SEM-EDX*

Line scans of main components have been carried out on the perpendicular sections by SEM-EDX, showing different types of surface alteration:

A) Surface alteration composed by sulfur and calcium (Fig. 4).

The green and white marbles, red and black limestones are in this group (green marble and white marble). This weathering form is caused by the reaction of calcite with the sulfur oxides present in the environment. The porosity and texture of these samples define the extension of the weathering surfaces.

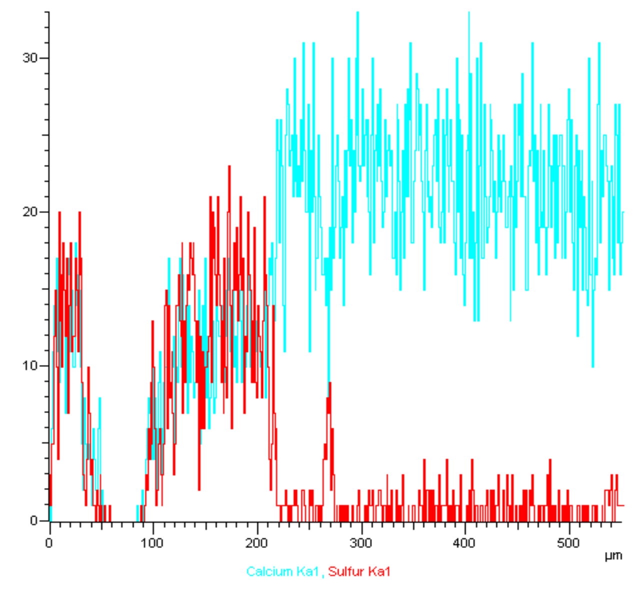

Figure 4: *Ca/S Depth profile of marble encrustation by SEM-EDX.*

B) Surface alteration composed by deposits, where chemical reaction has not occurred. These deposits are mainly composed by dust from terrigenous and anthropogenic particles or organic remains. These deposits have mainly been found in granite.

Similar weathering layers have been described by *Bromblet* and *Verges-Belmin (1996*) in calcareous stone or *Silva et al., (1994)* and *Schiavon et al., (1994)* in granites. The crusts over calcareous stones are mainly caused by the epigenetic formation of gypsum generated by SO_2 from traffic pollution, but the mineralogical composition and texture of granite prevent the gypsum crust and allow deposits or biocrusts.

The Historical Center of Seville has environmental conditions that show a clear influence of the traffic in the presence of black crust on calcareous stones *(Ortiz et al., 2010*). Similar studies of the influence of sulfur oxides in monuments has been largely analysed by *Lefevre et al. (2005), Thi Ngoc Lan et al.(2005), Camuffo et al. (2006)* and *Grossi et al (2006)* in different cities.

Parallel surface section has also been analyzed by SEM-EDX to study the atmospheric particles. The results show aggregates of variable habits of gypsum (Fig. 5) and other particles with calcium, silicon, magnesium, iron, chloride, sodium, potassium and aluminium.

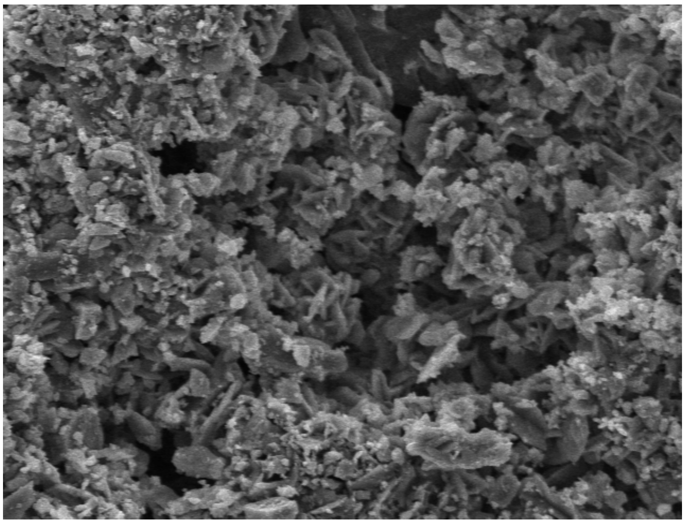

Figure 5: *Gypsum on encrustation over marble column.*

4 CONCLUSIONS

The main weathering forms in granites are detachments, deposits and biocrusts in contrast to marbles and calcareous stones that present pitting and black crusts with gypsum (CaSO4.2H2O). Other damage depend on the location and other anthropogenic factors. In summary, the vulnerability of the column depends on the location, building owners and the mineralogical and petrographical conditions of the stone.

According to LIBS and SEM-EDX results, the surface weathering forms are composed of Al, Si, Ba, K, Na, Ti, V, Mg and Ca, while XRF technique also detects S, Fe, Mn and P. The atmospheric particles on the superficial alteration can have an anthropogenic or terrigenous origin, including the weathering of the building materials and its restoration products, except the gypsum that is due to the traffic pollution.

AKNOWLEDGEMENT

This Project has been carried out thanks to the funds of the Junta de Andalucía Project RIVUPH (HUM 6775).

REFERENCES

Bromblet, P. Verges-Belmin., V. 1996. L`élimination del sulfates sur la statuaire calcaire de plein air: une habitude discutable. Le dessalement des Materiaux Poreux. Jornées d`études de la SFIIC. 55-64.

Camuffo, D. Pagan, E. Del Monte, M. Lerevre R.A. Ausset, P. 2006. Modelling the penetration of SO2 within the pores of calcareous stones and the concentration of gypsum in the near surface layer . Heritage, Weathering and Conservation, London, 435-440.

CNR-ICR. 1980. Materiali lapidei: Campionamento. Normal 3/80, 1-6.

CNR-ICR. 1990. Alterazione macroscopiche dei materiali lapidei: Lessico. Normal 1/88, 1-36.

Colao, F. Fantoni, R. Lazic, V. Morone, A. Santagata, A. Giardini, A. 2004. LIBS used as a diagnostic tool during the laser cleaning of ancient marble from Mediterranean areas. Applied Physics A Materials Science & Processing, Volume 79, Issue 2, 213-219.

Ctvrtnickova, T. Cabalin, L. Laserna, J.J. Kanicky, V. Nicolas. G. 2009. Laser ablation of powdered samples and analysis by means of laser-induced breakdown spectroscopy. Appl. Surf. Sci. 255: 5329-5333.

Fitzner, B. Heinrichs, K. Kownatzki, R. 1992. Classification and mapping of weathering forms. Proceedings of the 7th International Congress on Deterioration and Conservation of Stone, Lisboa, II, 957-968.

Fitzner, B. Heinrichs, K. Kownatzki, R. 1995. Weathering forms - Classification and mapping. Denkmalplege und Naturwissenschaft. Natursteinkoservierung I. Ed. Ernst & Sohn, 41-88.

Grossi, C.M.. Brimblecombe, P. 2006. Sulfate and carbon compounds in black crusts from the Cathedral of Milan and Tower of London . Heritage, Weathering and Conservation, London, 441-446.

ICOMOS-ISCS. 2008. Illustrated glossary on stone deterioration patterns. ICOMOS International Scientific Committee for Stone (ISCS) .

Lefevre, R.A. Jonescu, A. Ausset, P. Chabas, A. Girardet, E. Vince, F. 2005. Modeling the calcareous stone sulphation in polluted atmosphere after exposure in the field. In: R. Priklyl & B. Smith (eds.), Natural Stone Decay. London: Geological Society. Submitted.

Martín, A. 1990. Ensayos y experiencias de alteración en la conservación de obras de piedra de interés Histórico-Artístico. Ed. Fundación Ramón Areces. Madrid, 609.

Mateo, M.P., Nicolas, G. Piñon, V. Yañez, A. 2006. Improvements in depth-profiling of thick samples by laser-induced breakdown spectroscopy using linear correlation. Surf. Interface Anal. 38: 941-948.

Ordaz, J. Esbert. R.M. 1988. Glosario de términos relacionados con el deterioro de las piedras de construcción. Materiales de Construcción, Madrid, 38, 209, 39-45.

Ortiz, P. Vázquez M.A., Ortiz, R. Martin, J.M. Ctvrtnickova, T. Mateo, M.P., Nicolas, G. 2010. Investigation of Environmental Pollution Effects on Stone Monuments in the Case of Santa Maria La Blanca, SEVILLE (SPAIN). Applied Physics A: Materials Science & Processing. Volume 100, Number 3, 965-973.

Schiavon, N. Chiavari, G. Fabbri, D. Shiavon, G. 1994. Microscopical and chemical análisis of black patinas on granite. III Symposium on the conservation of Monuments in The Mediterranean Basin. Venecia, 93-99.

Silva, B. Casal, M. Prieto, B. Rivas, T. Guitián, F. 1994. Forms and factors of weathering in the Cathedral of Santiago de Compostela. III Symposium on the conservation of Monuments in The Mediterranean Basin. Venecia, 743-748.

Thi Ngoc Lan, T. Thi Phuong Thoa, N. Nishimurab, R. Tsujino, Y. Yokoi, M. Maeda, Y. 2004. New model for the sulphation of marble by dry deposition Sheltered marble - the indicator of air pollution by sulfur dioxide. Atmospheric Environment 39: 913-920.