



# An XPS study of stones degradation using a reference Gravina tuff placed outdoor under specified, environmental conditions

M.E.E. Carbone<sup>a</sup>, F. Langerame<sup>a</sup>, L. Scrano<sup>b</sup>, R. Ciriello<sup>a</sup>, A.M. Salvi<sup>a</sup>

<sup>a</sup> University of Basilicata, Science Department Viale dell'Ateneo Lucano, 10, 85100 Potenza

<sup>b</sup> University of Basilicata, DiCEM Department Rione S Rocco, 75100 Matera

Email: [anna.salvi@unibas.it](mailto:anna.salvi@unibas.it)

## INTRODUCTION

The progressive degradation of historical buildings, over the years, is essentially due to the synergic action of atmospheric pollution, climate change, fueling and biological contamination associated to the chemical physical characteristics of the building materials [1].

The prior aid for the restoration, conservation and protection of Cultural Heritages is the collection of all the necessary information for an accurate diagnosis of the alteration forms and of the process of stones degradation, in order to set intervention priorities. Since deterioration of any kind begins from surface reactions induced by either indoor and outdoor conditions, XPS, as a highly surface-specific technique (sampling depth of the order of dozen nanometers, depending on X-ray sources), can be suitably employed for the ex-situ compositional characterization for the early diagnosis of stones damage.

Southern Italy offers a remarkable example of artistic heritage based on porous 'calcarenite lithotype' [2], mainly composed of calcium carbonate, particularly sensitive to the action of atmospheric agents, whose degradation may be further promoted by acid pollutants in the atmosphere, produced by industries and other human activities [3].

In this case study, the XPS diagnostics is reported, over 4 year time (2009-2013), of a reference building sample made of Gravina calcarenite stones, placed in a site where both archeological and industrial activities are located.

## MATERIALS AND METHODS

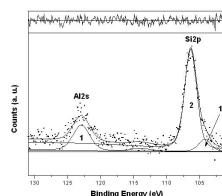
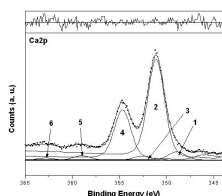
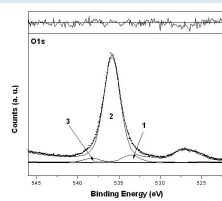
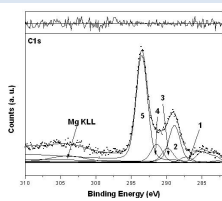
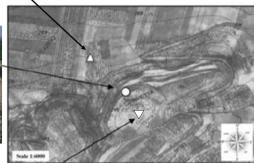
The building sample of about 1 m<sup>3</sup> was constructed using Gravina's calcarenite stones (33x15 cm each) collected from a local quarry. It was placed, on 16th July 2009, between the archeological park of Lavello, a little town in Basilicata Region (Italy), and the surrounding industrial area of S. Nicola di Melfi, where the incinerator plant "La Fenice" is located. The calcarenite stones were analyzed before and after 3, 6, 9, 12, 21 and 52 months of exposition to outdoor conditions.

### XPS analysis

The chemical composition of the stone material was evaluated by X-ray Photoelectron Spectroscopy, scratching off a little amount of calcarenite powder from the four lateral sides (North, South, East and West) of the cubic sample and analyzing that by using a Leybold LH-X1 spectrometer (Cologne, Germany). Wide and detailed spectra were collected at 0° take off angle, using fixed analyzer transmission (FAT) mode with channel widths of 1.0 and 0.1 eV, respectively.

The spectra were analyzed using a curve-fitting program NewGoogly which gives to each individual peak its own intrinsic Shirley-like background [4] and extrinsic tail. Binding energies (BEs) were corrected for surface charging by referring to C1s aliphatic carbon position, used as an internal standard, at 285.0 eV.

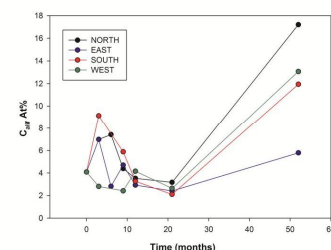
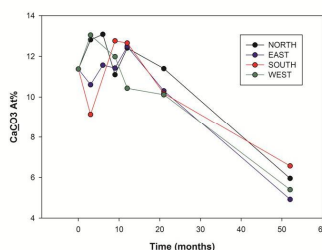
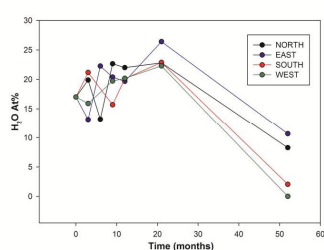
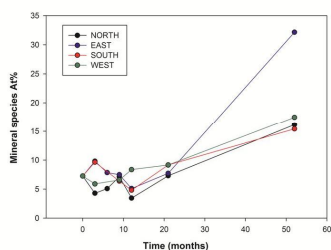
## Detailed XPS analysis of the reference calcarenite sample (2009)



Region	Peak	BE (eV)	Area	Assignment
C1s	1	283.3	86.01	SiC
	2	285.0	509.48	C-C
	3	286.1	197.04	C-O
	4	287.6	251.68	C=O
	5	289.6	1416.67	CO <sub>3</sub> <sup>2-</sup>
O1s	1	529.6	601.11	C-O-Al <sub>2</sub> O <sub>3</sub> +Fe <sub>2</sub> O <sub>3</sub>
	2	531.9	7012.61	CaCO <sub>3</sub> +H <sub>2</sub> O+C=O
	3	533.4	812.53	SiO <sub>2</sub>
Ca2p	1	344.9	79.80	Ca <sub>203/2</sub>
	2	347.2	915.60	CaCO <sub>3203/2</sub>
	3	348.4	38.90	Ca <sub>203/2</sub>
	4	350.8	457.80	CaCO <sub>3201/2</sub>
	5	355.2	45.71	s.u.
	6	358.9	33.53	s.u.
Si2p	1	100.6	78.90	SiC
	2	102.5	446.84	SiO <sub>2</sub>
Al2s	1	119.0	184.95	Al <sub>2</sub> O <sub>3</sub>

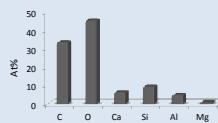
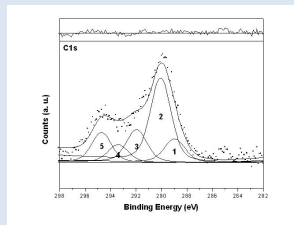
Fe and Mg species were present at trace levels.

## Trend over time of the main calcarenite components

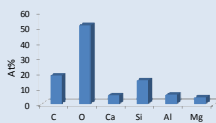
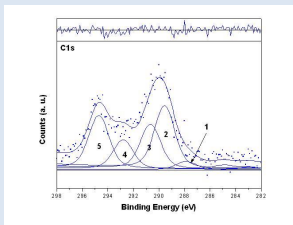


## Detailed XPS analysis after 52 months exposition (2013)

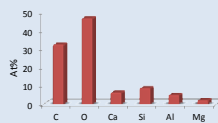
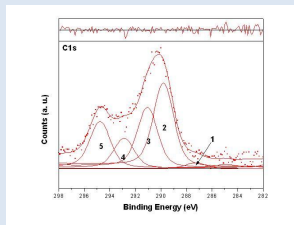
### NORTH



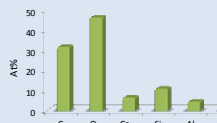
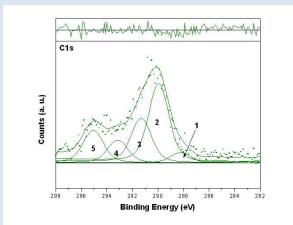
### EAST



### SOUTH



### WEST



## DISCUSSION AND PERSPECTIVES

Waiting for a complete set of climatic and air quality data, to be provided by ARPAB, taking into account the intrinsic accuracy ( $\pm 10\%$ ) in estimating XPS peak areas by curve-fitting, the first outcome from the behavior of the main calcarenite components, over time, is the composition preservation of the reference building in the first two years of exposure followed by a significant degradation in the last stage of the analysis (2013).

The last XPS dataset show a strong relative decrease of the carbonate and water/hydroxyl components opposed by the relative surface increment of carbon-containing contaminants (already present in the 'as prepared' sample) and fluxing ions (visible at very low percentage, sometimes below detection, on the different faces).

However, the underlying, structural components of the calcarenite stones CaCO<sub>3</sub>/(Al/Mg)Si<sub>4</sub>O<sub>10</sub>(OH)<sub>n</sub>\*H<sub>2</sub>O seems to be preserved as shown by details XPS analysis of 2013, thus, as visually supported by the photographs, the main degradation is associated to diminished resistance of the vertical layers to the physical aggression of wind blowing strong in the zone selected for our study. Moreover, the evident porosity of the last photographs confirm the predicted carbonate deterioration due to acid pollutants in the atmosphere, which, given the verticality of the analyzed surfaces, most likely detaches and falls on the ground, together with the associated degraded products.

Work is in progress for the whole set of data to be statistically elaborated in dependence of the exposition side, seasonal time and Wind Rose plot for the entire period of analysis.

[1] Scrano L., Fraddosio-Boccone L., Langerame F., Laviano R., Adamski Z., Bufo S.A., Karaelmas Science and Engineering Journal 1 (2), 1-14, 2011

[2] Warscheid, T., Braams, J. Intern. Biodet. & Biodeg, 46: 343-368, 2000

[3] Welton, R.G., Cuthbert, S.J., Mclean, R., Hursthouse, A., Hughes, J. Geochem. Hlth., 25: 139-145, 2003

[4] Castle J. E., Salvi A.M., Journal Electron Spectroscopy and Related Phenomena, 114-116, 2001