



Application of Different Methods of Surface Analysis for the Early Diagnosis of Art-Stone (Calcarenite) Deterioration

Laura Scrano¹, Laura Fraddosio-Boccone¹, Fausto Langerame², Rocco Laviano³, Zbigniew Adamski⁴, Sabino A. Bufo^{1*}

¹Department of Agriculture, Forestry and Environment, and ²Department of Chemistry
University of Basilicata, Via dell'Ateneo Lucano 10, 85100, Potenza, Italy

³Geomineralogical Department, University of Bari, Via Orabona, Italy 70125, Bari

⁴Department of Animal Physiology and Development, Adam Mickiewicz University, Poznan, Poland

Abstract

The deterioration process of historical buildings is progressive and irreversible, and the timing and mode of impact are different depending on the characteristics of building materials used, local microclimate, air pollution, presence of specific flora and fauna. The surface structural characterisation of building materials is mandatory in preventing and eventually recovering degradation effects. Ideally, the analysis of structural stones should be complete, efficient, rapid, and non destructive when dealing with a precious or unique construction.

For this purpose a building sample (*ca.* 1m³) was constructed by using calcarenite stones (33x15cm), collected from a local quarry, and placed between the archaeological site of Lavello, a little town located in the Basilicata Region (Italy), and the industrial area surrounding this town.

In this case study in progress on the degradation of stone materials, we set as an objective the characterization of the state of conservation of stone surfaces.

The intact calcarenite stone was characterised by using different methods of surface analysis (XRD, XPS, SEM), and exposed to outdoor conditions. The analyses of the stone material were repeated after three and six months to early evaluate the progression of alterations and the forward modifications of calcarenite structure. Results obtained by using all the applied surface analysis methods were compared. Climatic parameters (temperature, light irradiation, wind intensity, humidity), and air pollutants (SO₂, CO, NO₂, NO, O₃, and heavy metals) were determined. Biological attacks on the surface of calcarenite stones were also investigated.

After only three months of the stone sample exposures, the adopted analytical methods were able to provide a series of data, which as in the arrangement of a simple jigsaw puzzle, allowed the assessment of the incipient modification of the stone surfaces confirmed by observations performed on six months replicates, given that climatic conditions and air pollution undermined the structure and the compactness of stones favouring the biological colonization especially in the South-East direction of prevailing winds.

Keywords: calcarenite, surface analysis, XRD, XPS, SEM, surface modification, climatic parameters, air pollution.

1. Introduction

For thousand of years, when magnificence and beauty were the goals of architecture, stones were the most widely used durable materials. Unfortunately, the deterioration of art-stones causes irreparable damages to our cultural heritage, not only as loss of architecture and ancient art, but

especially as loss of symbols of human cultural identity and continuity.

The degradation of historical buildings begins immediately after their implementation, and the speed of corrupting phenomena depends on both natural and anthropogenic factors. The process of deterioration is progressive and irreversible, and the timing and mode of impact are different depending

*Corresponding author: sabino.bufo@unibas.it

on the characteristics of the monument (location, orientation, mineralogical and structural properties), microclimate (temperature, humidity, solar radiation, wind regime, precipitations), air pollution (particulate, concentrations of SO₂, NO₂, NO, CO₂), presence of specific flora and fauna that are settling the building [1-4]. The artistic heritage of Southern Italy offers a remarkable example of classic architecture typical of the Mediterranean basin. Calcarenite is the lithotype widely used in the past as building material in the Mediterranean area (Warscheid and Braams 2000). Because of its chemical and physical nature, this material easily undergoes deterioration due to the high percentage of calcium carbonate contained. Moreover, its porosity make building stones particularly sensitive to chemical, physical and biological agents.

The critical factor in the deterioration of calcarenite is the solubility of calcium carbonate, which is low in pure water but increases as the percentage of water dissolved carbon dioxide increases. In unpolluted areas, rainfall can gradually give rise to the dissolution of calcium carbonate. Under this phenomenon, building materials can crumble and become even more porous, consequently accelerating further decay (Shaffer 1932). The 'natural' deterioration of calcarenite stones may be further promoted and accelerated by acid pollutants in the atmosphere (especially sulphur dioxide and nitrogen oxides) produced by industries and other human activities (Welton et al. 2003).

Early damage diagnosis of natural stone is the first stage of planning needed for proper remedial action and restoration. The surface characterisation of building materials is compulsory in preventing and eventually recovering degradation effects. Ideally, the analysis of structural stones should be complete, efficient, rapid, and non destructive when dealing with a precious or unique construction. Thus, measurement should be carried out in-situ or by removing very small amounts of material. X-ray diffraction (XRD), X-ray induced photoelectron spectroscopy (XPS), Ground Penetrative Radar (GPR), Micro-Geo-Electrical Measurements (MGE), and Fourier Transform Infrared spectroscopy (FT-IR) are some techniques widely applied to study materials used in historical or artistic artefacts.

Usually, one or two methods of surface analysis are adopted at time to evaluate the current phase of deterioration of a historical building (Papida et al. 2000, Warscheid and Braams 2000, Duran et al. 2008).

The main objective of this work was to evaluate different methods for the early diagnosis of incoming deterioration and decay progression of intact calcarenite stones after three and six months of outdoor exposure. For the purpose, a new building sample was prepared and placed close to an industrial area. XRD, XPS and Scanning Electron Microscopy (SEM) were employed to explore the evolution of surface alteration of stones. Meteorological parameters as temperature, solar radiation, wind intensity, humidity, and air pollutants (SO₂, CO, NO₂, NO, O₃) were determined together with PM10 air diffused. Deposition of heavy metals was evaluated by bioaccumulation analysis. Biological attacks on the surface of calcarenite stones were also ascertained.

2. Materials and Method

2.1 Experimental Design

On July 16th, 2009, a new building sample of about 1 m³ obtained using Gravina's calcarenite stones (33 x 15 cm each) was placed in a site of geographical coordinates: 41° 03' 36.28"N and 15° 48' 26.69"E (Basilicata Region, Southern Italy), between the archaeological park of Lavello and the incineration plant named "La Fenice" located in the industrial area of S. Nicola di Melfi (Figure 1). The intact calcarenite stones, previously characterised by using different methods of surface analysis, were exposed to outdoor conditions. The analyses of the stone material were repeated after three and six months from exposure, scratching off a little amount of calcarenite powder from the four lateral sides of the cubic sample, to evaluate the earlier progression of alterations and the forward modifications of calcarenite surfaces. Microclimate parameters and air quality were monitored by the Agency for the Environmental Protection of Basilicata Region (ARPAB).

The bioaccumulation of airborne metals was monitored using thalli of the lichen *Pseudovernia furfuracea* (L.) Zopf gathered in cotton bags, which

were exposed on trees positioned at the four cardinal points around the building sample.

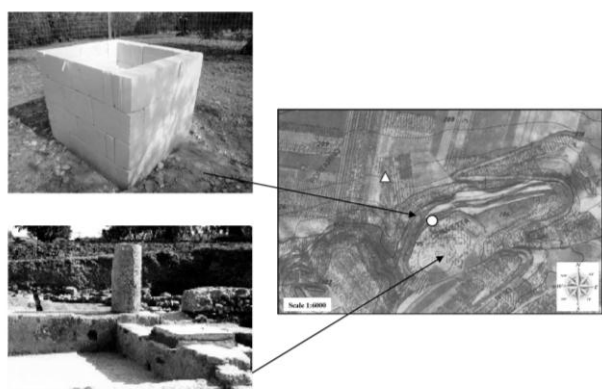


Figure 1. Stone building sample (○), and its location between the archaeological site (▼) and the industrial site (▲).

2.2 Surface Analysis Instrumentation

The scraped powder and some little fragments were examined with different complementary techniques, namely: X-ray diffraction (XRD), X-ray induced photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) equipped with energy dispersive spectrometry (EDS) as detector.

XRD analysis was carried out by using Philips X'pert Pro MPD (The Netherlands), with the following working conditions: Cu-K α_1 filtered radiation, Cu

anode 40 kV, 40 mA, divergence slit 1°, anti-scatter slit 0.5°, receiving slit 0.2°, speed 0.5 2 θ per minute.

XPS analysis was performed by using a Leybold LH X1 spectrometer (Cologne, Germany) equipped with a Mg/Al double anode. The evaluation of chemical shifts (chemical speciation) was obtained by using as external reference the C1s position energy (289.7 eV) of calcium carbonate. According to Castel and Salvi (2001), for XPS quantitative analyses the Newgoogly programme and NIST as database (<http://srdata.nist.gov/xps/>) were used.

SEM investigations were carried out on polished thin sections, after graphite sputter-coating of the samples. Two SEM instruments, a S360 (Cambridge Instruments) and an EVO-50XVP (LEO50XVP Karl Zeiss Group, Germany) were used. Microanalyses were conducted using an Oxford-Link EDS instrument equipped with a Ge detector and a 0.4-mm-thick Super Atmosphere Thin Window (SATW).

2.3 Microclimate Parameters and Air Quality

Meteorological and air quality data were provided by ARPAB. Table 1 reports the equipments used in the monitoring system. The meteorological and air quality stations were placed close to the new building sample and 11 Km far from the industrial area of S. Nicola di Melfi.

Table 1. Equipments used for monitoring the climatic parameters and air quality (ARPAB, S. Nicola di Melfi Station).

Parameter	Used equipment	Sensibility	Precision	Range
Temperature	Lastem DMA 531	0.1 °C	0.1 °C	(-)50°C - (+)705°C
Humidity	Lastem DMA 531	0.50 %	1.50 %	0 - 100 %
Wind speed	Lastem WM	0.25 m s ⁻¹	1.5 %	0 - 60 m s ⁻¹
Wind direction	Lastem WM	0.3°	1.5 %	0° - 360°
Pressure	Lastem LI-COR PY	0.1 mbar	0.5 %	850 - 1050 mbar
Solar radiation	Lastem DPA554	5 W m ⁻²	0.5 %	0 - 1500 W m ⁻²
Precipitation	Lastem DQA 031	0.2 mm	1 %	unlimited
SO ₂	PHILIPS K50033 API 100E	0.5 µg m ⁻³	0.5 %	1 - 500 µg m ⁻³
CO	PHILIPS K50093 API 300A	0.05 mg m ⁻³	0.5 %	1 - 1000 mg m ⁻³
NO ₂ , NO	PHILIPS K50034 API 200A	0.2 µg m ⁻³	0.5 %	1 - 500 µg m ⁻³
PM10	PHILIPS MP 101M	3 mg m ⁻³	6 mg m ⁻³	0 - 1000 mg m ⁻³
O ₃	PHILIPS K50094 API 400	0.5 µg m ⁻³	0.5 %	1 - 1000 µg m ⁻³

2.4 Bioaccumulation Analysis

The lichen materials were frozen using liquid nitrogen and pulverized using an agate mortar to get the same terms as the certified reference material (CRM), then they were placed in a muffle furnace at 600°C for 12 hours. Subsequently, the mineralized materials were digested with 10 mL of nitric acid in a microwave oven. After digestion, samples were analyzed by ICP-MS Agilent 75CX by using the following working parameters: RF power 1550 W; RF matching 1.72 V; carrier gas 1.05 L min⁻¹; make up gas 0.15 L min⁻¹; octopole bias -17.8 V; quadrupole bias -3 V. The limits of quantification (LoQ, based on the 10 σ criterion) and the blank concentrations calculated on replicated measurements of blank digests were determined. The LoQ values were 10.5, 0.01, 0.08, 0.20, 0.10, 0.05, and 0.75 $\mu\text{g L}^{-1}$ for Al, Cd, Cr, Cu, Ni, Pb, and Zn, respectively. The procedural blank values were in any case lower than the LoQs excepting the blank level of Pb, which was 0.1 $\mu\text{g L}^{-1}$. The analytical method was standardized by using the lichen-CRM BRC-482, which gave quantitative recoveries (98-102%) based on six replicate extractions and analytical determination of all the metals considered. Precision expressed as the relative standard deviation (RSD) on six replicates of each CRM digested ranged from 6.8% for Cu to 3.3% for Zn.

3. Results

3.1 Climatic and Air Quality Data

Figures 2 and 3 show the direction of prevailing winds (Wind Rose Plot) and the mean meteorological parameters registered in the observation period, respectively. Figure 4 illustrates the mean monthly concentrations of atmospheric pollutants during the whole period of stones exposure. The prevailing winds (winds that blow predominantly from a single general direction over the sample point) were blowing from the South to East quarter and the dominant winds (the trend in direction of wind with the highest speed over the observation point) were registered in South-East direction (from the archaeological park to the building sample site). Air moisture was rapidly increasing in the second three-months period, but the rainfall intensity became important only in

December, when the mean solar irradiation collapsed to 50 Wm⁻² (starting in July from more than 300 Wm⁻²), and the mean temperature decreased from 26.7 to 8.8°C.

Among the contaminants determined, O₃ was often above the safety level imposed by the EU directive No. 72/1992; the concentrations of other contaminants in the atmosphere were differently ranging during the observation period, but were always under the Italian limit of acceptance (Ministerial Decrees April 15th, 1994, and November 25th, 1998). The high value of ozone concentrations reported for the period July to September may be due to the elevated levels of solar irradiance registered in the same period (Pearson coefficient O₃/irradiance = 0.978). In the main, O₃ is formed in the atmosphere through the photolytic dissociation of NO₂ in the presence of O₂ (Kirkitsos and Sikiotis, 1996). The relevant concentrations of both nitrogen oxides and carbon oxide can be largely due to the presence of the industrial plants in the experimental area and partially to some local agricultural practices (manuring, combustion of stubbles). To coincide with lower values of air humidity levels of sulphur dioxide and PM10 were higher in the summer time than in autumn. Noteworthy, in the summer period the incinerator sited in the industrial area of S. Nicola di Melfi, in the North-West side with respect to the building sample (Figure 1), was treating a large amount of industrial wastes (composition unknown).

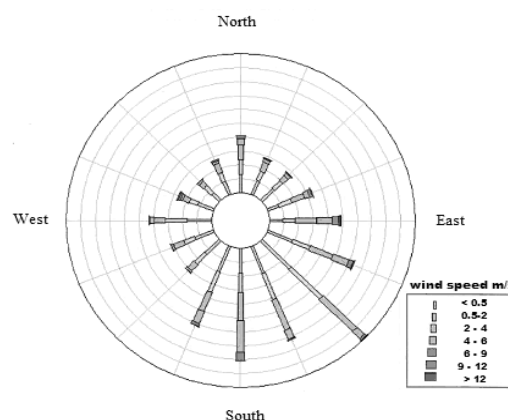


Figure 2. Wind Rose Plot for the period ranging from July 1st to December 31st, 2009

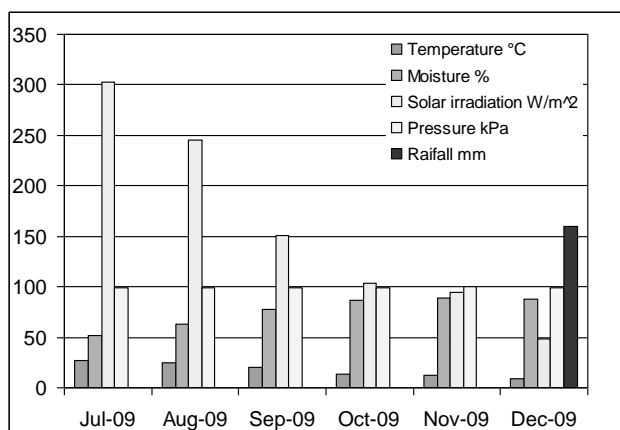


Figure 3. Meteorological parameters logged out for the period ranging from July 1st to December 31st, 2009.

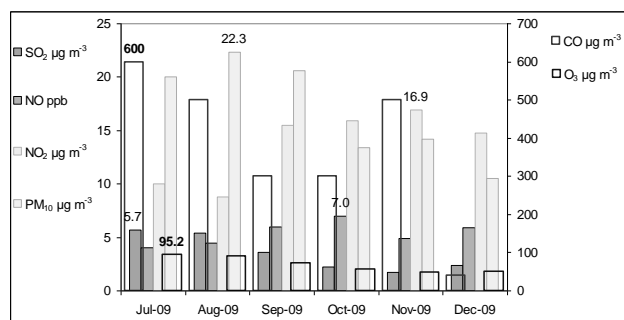


Figure 4. Mean monthly concentrations of atmospheric pollutants for the period ranging from July 1st to December 31st, 2009

3.2 XRD Analysis

X-Ray Diffraction Analysis investigates crystalline material structure, including atomic arrangement, crystallite size, and imperfections. It may also be used to characterize heterogeneous solid mixtures to determine relative abundance of crystalline compounds (Azároff et al. 1974).

Strengths of XRD Analysis are:

- Powerful and rapid (< 20 min) technique for identification of an unknown mineral
- In most cases, it provides an unambiguous mineral determination
- Minimal sample preparation is required
- XRD units are widely available
- Data interpretation is relatively straight forward

Limitations of XRD Analysis are:

- Homogeneous and single phase material is best for identification of an unknown
- Must have access to a standard reference file of inorganic compounds (d-spacings, hkl's)
- Requires tenths of a gram of material which must be ground into a powder
- For mixed materials, detection limit is ~ 2% of sample
- For unit cell determinations, indexing of patterns for non-isometric crystal systems is complicated
- Peak overlay may occur and worsens for high angle 'reflections'

X-ray diffraction analysis on the intact calcarenite mainly shows the presence of calcium carbonate (calcite), a little amount of dolomite and quartz, and traces of feldspars, hematite, goethite, pyrite and clay minerals (Figure 5).

After three months of exposure a slight sulphation was detectable on the surface exposed to South-East direction; this phenomenon remained stable up to the end of December (data not shown). Generally, the calcarenite mineralogical composition was not varying during the observation period for the other sides of the building sample.

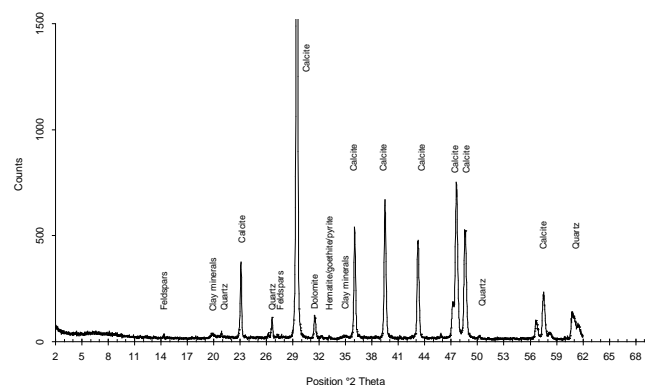


Figure 5. XRD of intact calcarenite sample (reference).

3.3 XPS Analysis

Figure 6 shows XPS spectra of the intact calcarenite and samples scraped off from the East surface of the building trial after 3 and 6 months of exposure, respectively. Table 2 reports the chemical composition of calcarenite samples.

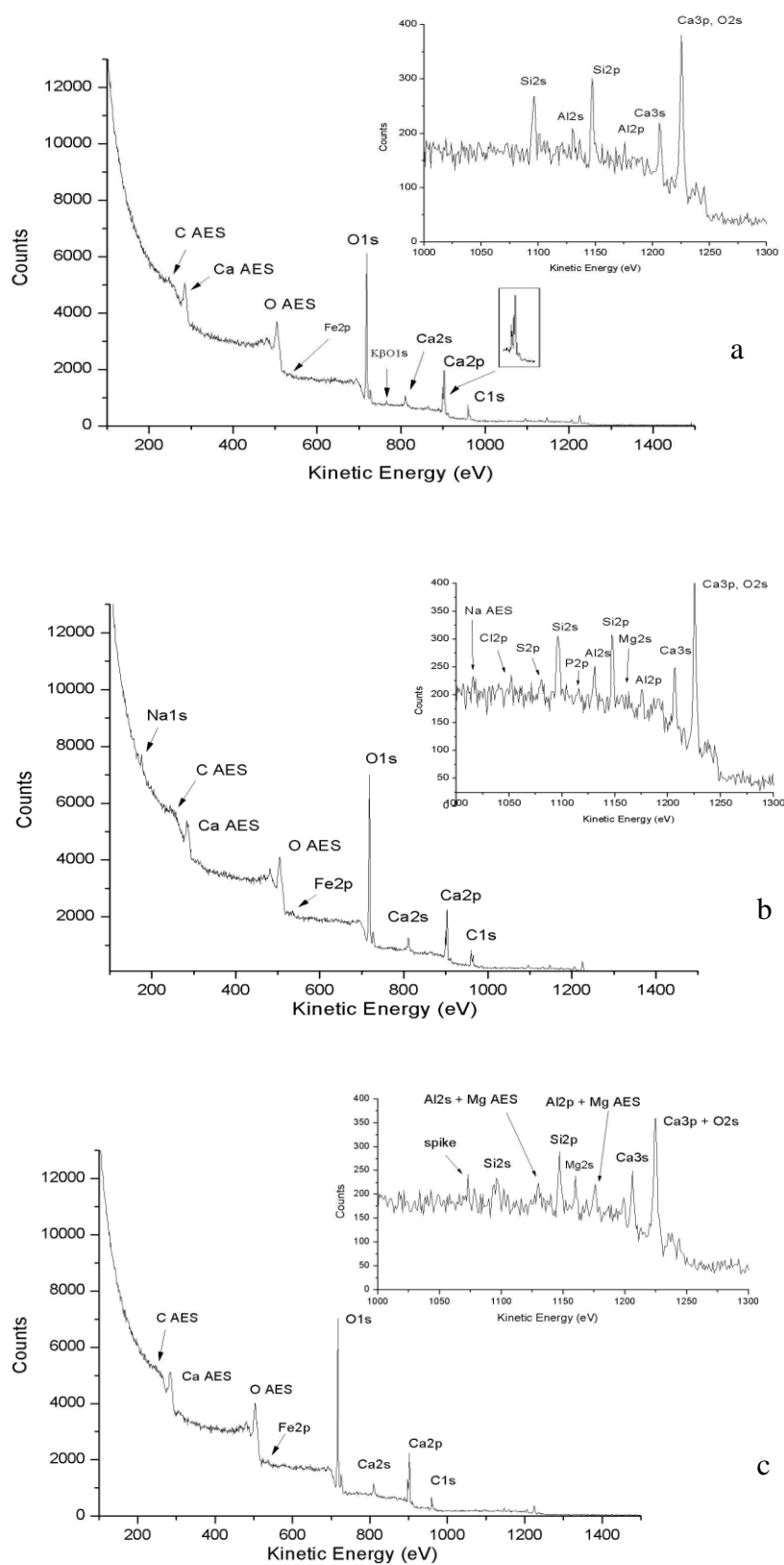


Figure 6. XPS spectra of: (a) intact calcarenite sample (reference); samples collected from the East surface after (b) 3 months and (c) 6 months of exposition to atmospheric agents, respectively; in the insets a wider view of the kinetic energy range 1000-1300 eV.

Table 2. XPS chemical composition (mean atomic percentages and standard deviations on six replicate samples) of calcarenite detected after 3 and 6 months of exposure to atmosphere action using as reference the intact calcarenite (R).

Exposure			East/month		South/month		West/month		North/month	
Chemical species	BEs	R	3 rd	6 th	3 rd	6 th	3 rd	6 th	3 rd	6 th
Carbide	283.3±0.6	0.7±0.1	0.5±0.1	0.7±0.1	1.2±0.2	0.8±0.1	0.5±0.1	0.5±0.1	1.3±0.2	1.1±0.2
C-C	284.6±0.1 285.0±0.3	3.9±0.3	7.0±0.4	4.7±0.3	6.1±0.4	6.0±0.4	2.8±0.2	2.4±0.2	6.9±0.4	4.2±0.3
CO _x	286.1±0.7 287.5±0.2	3.5±0.3	2.8±0.2	2.7±0.2	3.0±0.2	3.0±0.2	3.9±0.2	3.7±0.2	2.6±0.2	2.0±0.2
C (CO ₃ ²⁻)	289.7±0.1	11.5±0.6	11.3±0.6	12.0±0.7	9.6±0.5	13.9±0.7	13.7±0.7	12.7±0.7	13.5±0.7	11.3±0.6
O	529.7±0.4 531.9±0.4 534.0±0.6	62.6±2.2	57.8±2.7	61.2±2.5	60.8±2.5	62.1±2.4	61.3±2.4	63.6±2.1	59.3±2.4	60.9±2.3
Ca 2p _{3/2} (CaCO ₃)	347.2±0.4	11.2±0.5	10.4±0.4	10.7±0.4	9.3±0.3	7.4±0.2	11.8±0.5	10.6±0.4	12.1±0.5	10.0±0.3
Ca 2p _{3/2} (mineral)	344.9±0.5	0.9±0.1	0.7±0.1	1.0±0.1	0.8±0.1	0.5±0.1	1.3±0.2	1.0±0.1	1.2±0.1	1.0±0.1
Si 2p _{3/2}	102.4±0.6	3.6±0.1	3.3±0.1	3.0±0.1	4.7±0.2	2.8±0.1	1.5±0.1	2.7±0.1	1.6±0.1	7.1±0.3
Al 2s	119.0±0.7	1.5±0.1	1.4±0.1	1.0±0.1	2.1±0.2	0.9±0.1	1.1±0.1	1.1±0.1	0.6±0.1	1.5±0.2
Fe 2p _{3/2}	711.5±0.6	0.6±0.1	0.6±0.1	0.8±0.1	0.1±0.05	0.4±0.1	0.9±0.1	uld	0.9±0.1	uld
Mg 2s	89.0±0.3	uld	0.4±0.1	1.6±0.2	0.3±0.1	1.6±0.2	1.1±0.1	1.7±0.2	uld	0.9±0.1
S 2p	168.6±0.2	uld	0.5±0.1	0.5±0.1	0.5±0.1	0.5±0.1	uld	uld	uld	uld
K 2p	293.2±0.4	uld	0.3±0.05	0.1±0.05	0.1±0.05	0.1±0.05	uld	uld	uld	uld
Na	1073±1	uld	2.5±0.2	uld	1.4±0.2	uld	uld	uld	uld	uld
Cl 2s	269.0±0.3	uld	0.3±0.05	uld	uld	uld	uld	uld	uld	uld
P 2p	133.1±0.2	uld	0.2±0.05	uld	uld	uld	0.1	uld	uld	uld

BE = Electron Binding Energy (referred to 1s orbital where not differently indicated).

uld = under the limit of detection (0.01%).

XPS, also known as ESCA (Electron Spectroscopy for Chemical Analysis), is the most widely used surface analysis technique because of its relative simplicity in use and data interpretation. The sample is irradiated with mono-energetic x-rays causing photoelectrons to be emitted from the sample surface. An electron energy analyzer determines the binding energy of the photoelectrons. From the binding energy and intensity of a photoelectron peak, the elemental identity, chemical state and electronic state, and quantity of an element are determined (Grant and Briggs, 2003).

Strengths of XPS Analysis are:

- Chemical state identification on surfaces
- Identification of all elements except for H and He
- Quantitative analysis, including chemical state differences between samples
- Determination of empirical formula
- Applicability for a wide variety of materials, including insulating samples (paper, plastics, and glass)
- Depth profiling with matrix-level concentrations
- Oxide thickness measurements

Limitations of XPS Analysis are:

- Detection limits typically 0.01 - 1 at % sub-monolayer
- Depth resolution 20 - 200 Angstroms (Profiling Mode); 10 - 100 Angstroms (Surface analysis)
- Lateral Resolution/Probe Size 10 μm - 2 mm
- Sample compatibility with ultra high vacuum.

The intact calcarenite (reference sample) contains 94.3% of carbon, oxygen and calcium (sum of standard deviations on six replicate samples = 4.1%): the speciation analysis of C1s region shows the presence of carbide, aliphatic/aromatic carbon (C-C), oxidized components (C-O-C, C=O, O-C-O), and carbonate. The Ca2p region is characterized by a prevalent signal attributable to calcium carbonate, and another weak peak due to structural calcium included in silica minerals according to the presence of silicon, aluminium and iron (6% as a whole), which being strongly hydrated justify the excess of oxygen determined by the mass balance.

The XPS analyses of materials sampled from East, South, West and North sides of the calcarenite

building subjected to the atmosphere action show a variability of the surfaces composition in function of the orientation and time of exposure. In fact, the total percentages of most important elements as C, O, Ca were 90.5, 90.8, 95.3, and 96.9%, respectively, after three months of exposures (sum of standard deviations on six replicate samples ranged from 4.2 to 4.5%), and 93.0, 93.7, 94.5, 90.5%, after six months (sum of standard deviations on six replicate samples ranged from 3.8 to 4.3%), suggesting a continuous transformation of stone surfaces with respect to the original material.

In the XPS spectrum of intact calcarenite (Figure 6a) only signals attributable to native elements as C, O, Si and Al are clearly evidenced. After 3 months of exposure the transformation of stone surfaces is more evident on the South-East sides (direction of prevailing winds) of the experimental building, where a decrease of C, O and Ca percentages and an increase of the Mg, S, K, Na, Cl, P amounts (as atomic percentages) were detected (Figure 6b).

The presence of sulphur and its persistence in the whole period of observation, probably due to the atmospheric pollution, confirmed XRD results. The analysis of C1s region shows in the East and West samples a dominance of the aromatic/graphitic component (284.6 eV) on the aliphatic component (285.0 eV), which on the contrary was prevalent in the original calcarenite sample.

Due to the abrasion effect of December driving rainfall, which could had removed a thin layer of the stone surface, some elements found at the end of the third month were not detectable after six months of exposure with the exception of Mg, which atomic percentages were always high (Figure 6c).

3.4 SEM Analysis

The scanning electron microscope uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. In most applications, data are collected over a selected area of the surface of the sample, and a 2-dimensional image is generated that displays spatial variations in these properties. Areas ranging from approximately 1 cm to 5 microns in width can be

imaged in a scanning mode using conventional SEM techniques (magnification ranging from 20X to approximately 30,000X, spatial resolution of 50 to 100 nm). The SEM is also capable of performing analyses of selected point locations on the sample; this approach is especially useful in qualitatively or semi-quantitatively determining chemical compositions (using EDS) (Goldstein, 2003).

Strengths of SEM Analysis are:

- There is arguably no other instrument with the breadth of applications in the study of solid materials that compares with the SEM
- The SEM is critical in all fields that require characterization of solid materials
- While this contribution is most concerned with geological applications, it is important to note that these applications are a very small subset of the scientific and industrial applications that exist for this instrumentation.
- Most SEMs are comparatively easy to operate, with user-friendly 'intuitive' interfaces; many

applications require minimal sample preparation and data acquisition is rapid (less than 5 minutes/image, including EDS analyses)

Limitations of SEM Analysis are:

- Samples must be solid and they must fit into the microscope chamber
- Maximum size in horizontal dimensions is usually on the order of 10 cm, vertical dimensions are generally much more limited and rarely exceed 40 mm
- For most instruments samples must be stable in a vacuum on the order of 10^{-5} - 10^{-6} torr.
- EDS detectors cannot detect very light elements (H, He, and Li), and many instruments cannot detect elements with atomic numbers less than 11 (Na)
- An electrically conductive coating must be applied to electrically insulating samples for study in conventional SEMs.

Calcarene stone is characterized by a high porosity and a chemical composition dominated by calcium

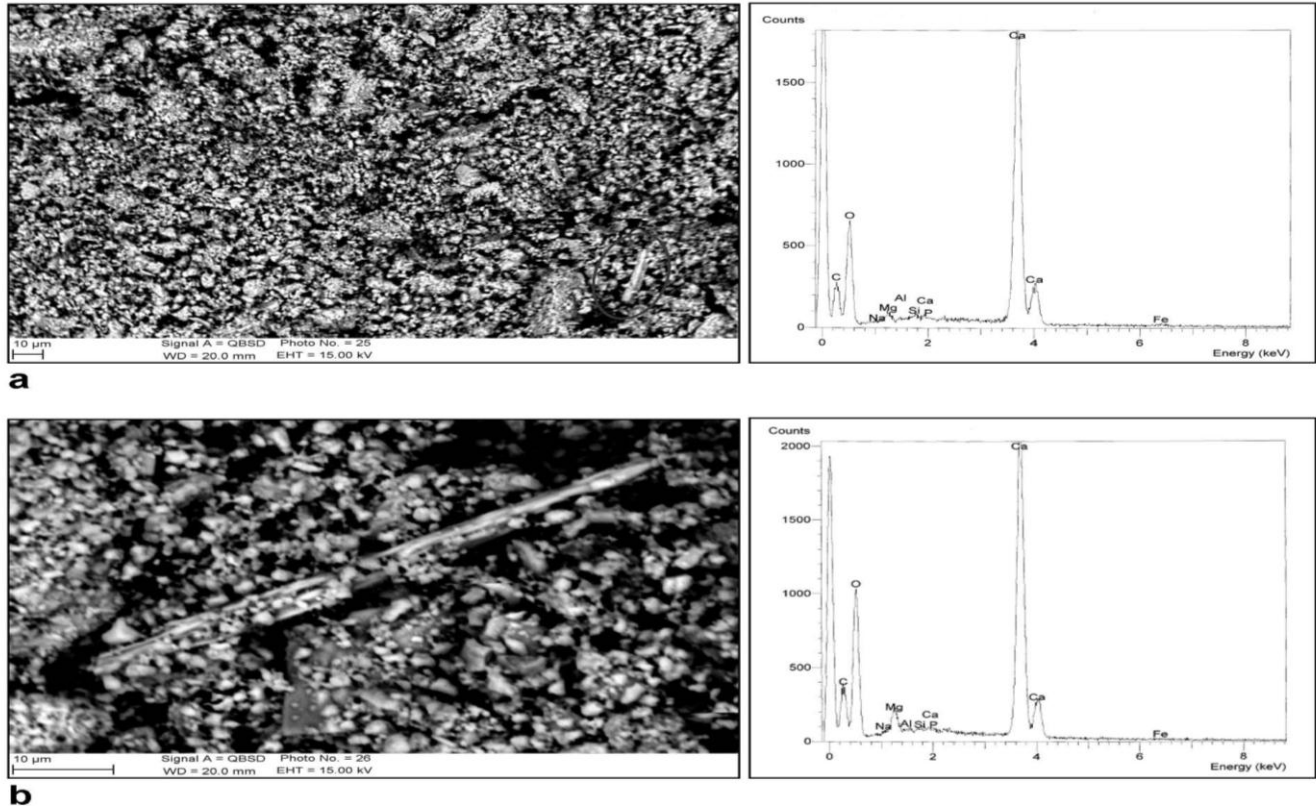


Figure 7. SEM images of the sample collected from the East surface after three months of exposure to atmosphere action; (a) total view and EDS analysis of the core sample, (b) enlarged view and EDS analysis of the evidenced mineral fragment containing a higher quantity of Mg.

carbonates, which rendered the stone highly susceptible to acidic attack by gaseous atmospheric pollutants. Results obtained by SEM were in agreement with XPS analyses, and the chemical composition evaluated through X-Ray microanalysis (EDS) allowed the classification of particles with similar shape, dimension and composition into four groups:

1. C-rich particles that includes organic and inorganic compound
2. Silicates
3. Fe-rich particles mainly composed of oxygen and iron or iron and silicate compounds
4. Sulphates mainly composed of Ca-sulphates

contained in gypsum and black patina particles.

The stone material showed a granular texture with pores and cavities more evident after the outdoor exposure. The SEM image after three months of exposure shows a deteriorated structure, and EDS analysis confirms the increase of Mg, Na, Al, Fe, and P especially on the East side of the building (Figure 7). Figure 8a put in evidence the presence of oxidized Fe in the SEM image and relative EDS spectrum of East calcarenite sample performed after six months of outdoor exposure, while figure 8b shows the SEM image and the EDS analysis of a West calcarenite sample containing high levels of Cu and Zn. The presence of these metals is probably due to the local industry activity.

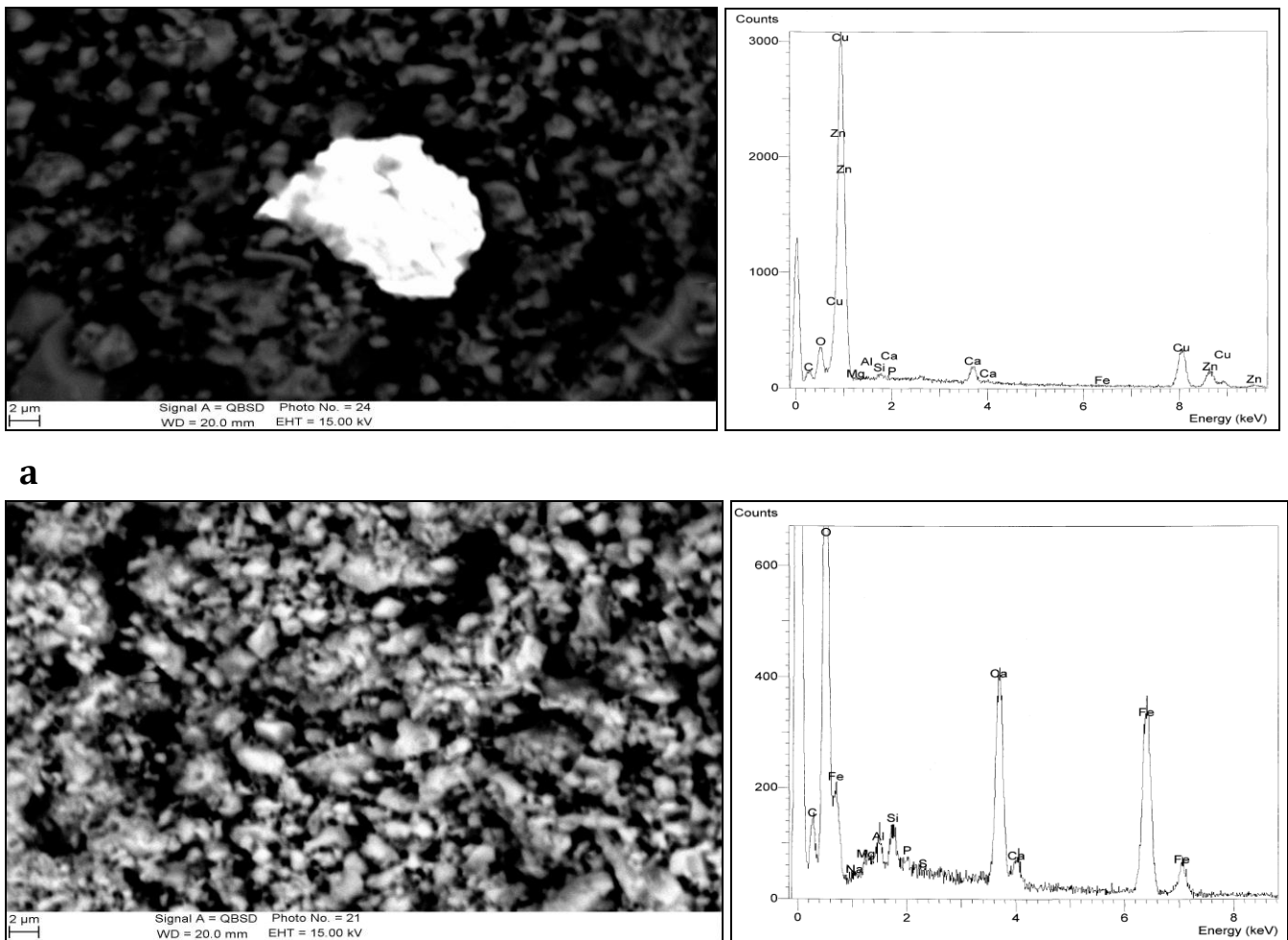


Figure 8. SEM images and relative EDS spectra of (a) oxidized Fe in the East calcarenite sample after six months of outdoor exposure; (b) West calcarenite sample containing high levels of Cu and Zn.

Figure 8. SEM images and relative EDS spectra of (a) oxidized Fe in the East calcarenite sample after six months of outdoor exposure; (b) West calcarenite sample containing high levels of Cu and Zn.

3.5 Bioaccumulation Analysis

Pseudevernia furfuracea, commonly known as tree moss, is a lichenized species of fungus that grows on the bark of firs and pines. The lichen is rather sensitive to air pollution, its presence usually indicating good air conditions in the growing place. Because specimens of *P. furfuracea* tend to bioaccumulate heavy metals like Cr, Zn, Cd, Pb, Ni, Fe, Mn and Cu proportionally to their concentration in airborne particulates, they may be used as a biomonitor of air quality (Bari et al. 2001, Jozic et al. 2008, Sorbo et al. 2008), although it has been noted that both trace metal accumulation (Adamo et al. 2003) and major element accumulation (Vingiani et al. 2004) is partly dependent on the hydration level of the specimen.

Bioaccumulation analysis (Figure 9 and Table 3) shows that the average amounts of Al, Cd, Cr and Cu found in the lichen bags (*P. furfuracea*) are higher in the samples exposed to Eastern winds.

3.6 Biological Attacks

After three months of outdoor exposure colonies of the lichen *Caloplaca flavescens* (Huds.), J.R. Laundon, were widely identified on the calcarenite surfaces (Figure 10). This microorganism is considered a biodeteriogenic agent in archaeological and monumental areas, it was widely found on surfaces of art works where this lichen causes the onset of vacuoles and the crumbling of stone structure. The stone degradation and the presence of biotic agents is more visible in South-East sides of sample building (direction of prevailing winds) confirming the double role of Lichens that can be informative tools not only on the health status of environment, but also for monitoring the deterioration of monuments (Piervittori and Laccisaglia 1993, Piervittori et al. 1996).

Table 3. Mean values and standard deviations of metal contents in six replicate Lichen bags distributed in each exposure side around the building sample and in the reference site (Rifreddo).

Lichen bag position	Water content %	Dry weight g	Al mg Kg ⁻¹	Cd mg Kg ⁻¹	Cr mg Kg ⁻¹	Cu mg Kg ⁻¹	Ni mg Kg ⁻¹	Pb mg Kg ⁻¹	Zn mg Kg ⁻¹
East	9.8±1.2	0.50±0.01	1416±213	0.68±0.12	2.62±0.37	16.93±1.89	2.22±0.33	24.48±6.10	66.59±22.02
North	12.2±1.6	0.36±0.01	1162±135	0.40±0.08	2.36±0.29	8.40±0.85	1.94±0.30	20.06±5.08	65.95±20.21
West	12.1±1.4	0.35±0.01	1389±143	0.40±0.09	2.53±0.32	14.21±1.01	2.14±0.30	14.31±4.65	62.60±23.23
South	10.7±1.4	0.41±0.01	1041±109	0.30±0.06	1.99±0.22	12.40±0.98	1.71±0.24	9.75±3.33	62.61±19.28
Rifreddo*	9.7±1.2	0.50±0.01	781±234	0.22±0.18	1.66±0.42	8.22±6.16	1.70±0.59	20.89±10.45	77.25±27.04

*reference placed in a locality named Rifreddo 100 Km far from the experimental area.

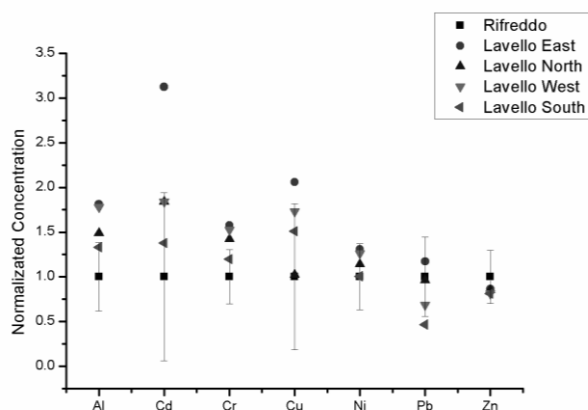


Figure 9. Average values of heavy metals in the lichen samples (*P. furfuracea*) normalized respect to lichen reference (Rifreddo).



Figure 10. *Caloplaca flavescens* (Huds.), on calcarenite stone examined after 3 months of exposure to the atmosphere action.

4. Discussion and Conclusion

The result of the interactions between calcarenite and atmospheric pollutants is the formation of new mineral species on the stone surfaces, often accompanied by structural degradation.

Air pollution is essentially caused by sulphur and nitrogen oxides as well as hydrocarbons which are emitted into the atmosphere by sources related to industrial activities, transportation, heating, and some agricultural practices. Several studies have been carried out on different calcareous stones used extensively in historic buildings: in particular Kirkitsos and Sikiotis (1996) reported that the effects of nitrogen dioxide on three calcareous stones (Pentelic marble, Portland limestone and Baumberger sandstone) under different conditions of relative humidity, mass of stone and grain size of stone. It was found that all three stones are not good sinks for NO₂. Pentelic marble and Portland limestone exhibited relatively low vulnerability to NO₂ and this result does not vary significantly with relative humidity.

On different sites in the world, many authors (Harter 1986, Lipfert 1987, Lipfert 1989, Ukberg 1990, NAPAP 1990) carried out studies on the same issue having in mind that weathering and human action could be responsible of deterioration of monumental, archaeological sites and cultural heritage. About the outdoor degradation these researchers concluded that acidic deposition damage of siliceous stones is negligible, and therefore attention should be confined to calcareous stones, i.e. limestone, marble and calcareous sandstones materials extensively used as building materials in Europe.

In our case, the duration of monitoring activities was too short to observe extremely important modifications, but our investigation underlines that surface analysis methods adopted are able to appreciate the incipient degradation of calcarenite since the first months of observations.

X-ray diffraction analysis gave information on the mineralogical composition of the intact calcarenite, but was not able to detect structural modifications after three or six months of observation with the exception of a slight sulphation on the South-East surfaces after three months of exposure.

The XPS analyses of materials sampled from the four sides of the calcarenite building showed a variability of the surfaces composition in function of the orientation and time of exposure. Moreover this

technique evidenced the presence of sulphur and its persistence in the whole period of observation.

The SEM images after three months of exposure showed a deteriorated structure, and EDS analysis confirmed the increase of Mg, Na, Al, Fe, and P especially on the East side of the building.

The bioaccumulation analysis performed by means of lichen bags confirmed the accumulation of metals transported by atmospheric movements and furnished a simple explanation about the enrichment of metals on the building surfaces.

The visual analysis of biological attacks highlighted the stone degradation and the presence of biotic agents on the South-East sides of sample building, the direction of prevailing winds.

A considerable number of other investigations elucidated also the essential role played by biological agents in the deterioration of stone (Paine et al. 1933, Strzelczyk 1981, Caneva and Salvadori 1989, Griffin et al. 1991, May et al. 1993, Bock and Sand 1993). Physical, chemical, and biological agents act in co-association, ranging from synergistic to antagonistic, to deteriorate stones (bio receptivity) (Koestler et al. 1994, Shirakawa et al. 2003).

The combination of surface analyses SEM-EDS, XRD, XPS was used not only for chemical and structural modification but also to detect photoautotrophic colonisation at an early stage of development when they are still not visually observable (e.g. Lidar measurements based on the LIF technique as in Cecchia et al. 2000).

Microscopy techniques also described in different papers (Brown et al. 1998 and citations) were suitable for characterizing stone samples collected from monuments where only small quantities of material may be removed. Each of these techniques provides different information on a single sample, but through integration of whole data obtained insight is gained into the structure composition, and physical properties of the sample. This combined approach reveals the living community as a complex interacting system affecting the mineral species inside fissures. Possible chemical losses and/or gains are, in some way, determined by the nature of the colonizing microbial populations (Des los Ríos et al. 2002). Thus, it is vital to understand the mineral transformations that occur and obtain relevant cytological information on such microorganisms. More recently, molecular biology techniques have been successfully applied to bio-weathering studies (Sterflinger and Prillinger 2001), and chemical composition and texture of the stone material have

been ascertained to determine the resistance of a building to colonization by forms of life and to atmospheric agents (Lisci et al. 2003).

Finally, our preliminary results showed that climatic agents and pollutants undermine the structure and the compactness of calcarenite stones favouring the biological colonization especially in direction of prevailing winds.

All techniques used confirmed the results and each of them gave important information: surface analyses were essential to study the evolution of the building sample.

5. References

- Adamo, P., Giordano S., Vingiani S., Castaldo Cobiانchi R., Violante P. 2003.** Trace element accumulation by moss and lichen exposed in bags in the city of Naples (Italy). *Environ. Pollut.*, 122: 91-103.
- Azároff, LV., Kaplow R., Kato N., Weiss RJ., Wilson AJC., Young RA. 1974.** X-ray diffraction. McGraw-Hill.
- Bari, A., Rosso A., Minciardi MR., Troiani F., Piervittori R. 2001.** Analysis of heavy metals in atmospheric particulates in relation to their bioaccumulation in explanted *Pseudevernia furfuracea* thalli. *Environ. Monit. Assess.*, 69: 205-220.
- Bock, E., Sand, W., 1993.** The microbiology of masonry biodeterioration. *J. Appl. Bacteriol.*, 74: 503-514.
- Brown, DA., Beveridge TJ., Keevil, CW., Sheriff, BL., 1998.** Evaluation of microscopic techniques to observe iron precipitation in natural microbial biofilm. *FEMS Microb. Ecol.*, 26: 297-310.
- Caneva, G., Salvadori, O. 1989.** Biodeterioration of stone. In: Larraini, L., Pieper, R. (Eds.), *The Deterioration and Conservation of Stone*. UNESCO, Paris, 182-234.
- Castle, JE., Salvi, AM. 2001.** Chemical state information from the near-peak region of the X-ray photoelectron background. *J. Electron Spectrosc.*, 114-116, 1103-1113, and citations.
- Cecchia, G., Pantania, L., Raimondi, V., Tomaselli, L., Lamenti, G., Tiano, P., Chiari, R. 2000.** Fluorescence lidar technique for the remote sensing of stone monuments. *J. Cultur. Herit.*, 1: 29-36.
- De los Ríos, A., Wierzchos, J., Ascaso, C. 2002.** Microhabitats and chemical microenvironments under saxicolous lichens growing on granite. *Microb. Ecol.*, 43:181-188.
- Duran, A., Herrera LK., Jimenez de Haro, MC., Justo, A., Perez-Rodriguez, JL. 2008.** Non-destructive analysis of cultural heritage artefacts from Andalusia, Spain, by X-ray diffraction with Gobel mirrors. *Talanta*, 76. 183-188.
- Goldstein, J. 2003.** Scanning electron microscopy and x-ray microanalysis. Kluwer Academic/Plenum Publishers, 689 p.
- Grant, JT., Briggs, D. (eds). 2003.** Surface Analysis by Auger and X-ray Photoelectron Spectroscopy, IM Publications, Chichester, UK.
- Griffin, PS., Indicator, N., Koestler, RJ. 1991.** The biodeterioration of stone: a review of deterioration mechanisms, conservation case, histories and treatment. *Intern. Biodet.*, 28: 187-208.
- Harter, P. 1986.** Acidic Deposition - Materials and Health Effects. IEA Coal Research TR36.
- Jozic, M., Peer, T., Türk, R. 2008.** The impact of the tunnel exhausts in terms of heavy metals to the surrounding ecosystem. *Environ. Monit. Assess.*, 150: 261-271.
- Kirkitsos, P., Sikiotis, D. 1996.** Deterioration of Pentelic marble, Portland limestone and Baumberger sandstone in laboratory exposures to NO₂: a comparison with exposures to gaseous HNO₃. *Atmos. Environ.*, 30: 941-950.
- Koestler, RJ., Brimblecomb, P., Camuo D., Ginell W., Graedel, T., Leavengood, P., Petushkova, J., Steiger, M., Urzi, C., Verges-Belmin, V., Warscheid, Th. 1994.** Group report: How do external environmental factors accelerate change? In: Krumbein W.K., Brimblecombe P., Cosgrove D.E., Staniforth S. (Eds.), *Durability and Change*. Wiley, Chichester, 149-163.
- Lipfert, FW. 1987.** Effects of Acidic deposition on the atmospheric deterioration of materials. *Materials Performance*, 12, National Association of Corrosion Engineers.
- Lipfert, FW. 1989.** Atmospheric damage to calcareous stones: comparison and reconciliation of recent findings. *Atmos. Envir.*, 23: 415-419.

- Lisci, M., Monte, M., Pacini, E. 2003.** Lichens and higher plants on stone: a review. *Int. Biodet. Biodeg.*, 51, 1-17
- May, E., Lewis, FJ., Pereira, S., Tayler, S., Seaward, MRD., Allsopp, D. 1993.** Microbial deterioration of building stone: a review. *Biodet. Abstracts*, 7: 109-123.
- NAPAP, 1990.** National acid precipitation assessment programme. 1990 Integrated Assessment Report. NAPA, Washington D.C.
- Paine, SG., Linggood, FV., Schimmer, F., Thrupp, TC. 1933.** The Relationship of micro-organisms to the decay of stone. Philosophical Transactions of the Royal Society, London, Vol. CCXXII-B486, B: 97-127.
- Papida, S., Murphy, W., May, E. 2000.** Enhancement of physical weathering of building stones by microbial populations. *Intern. Biodet. & Biodeg.*, 46: 305-317.
- Piervittori, R., Laccisaglia, A. 1993.** Lichens as biodeterioration agents and biomonitors. *Aerobiologia*, 9: 181-186.
- Piervittori, R., Salvadori, O., Laccisaglia, A. 1996.** Literature on Lichens and biodeterioration of stonework. *The Lichenologist*, 28: 471-483.
- Schaffer, RJ. 1932.** The weathering of natural building stones, in Building Research Special Report, n.18, London.
- Shirakawa, MA., Beech IB., Tapper R., Cincotto MA., Gambale, W. 2003.** The development of a method to evaluate bioreceptivity of indoor mortar plastering to fungal growth. *Intern. Biodet. & Biodeg.*, 51: 83-92.
- Sorbo, S., Aprile G., Strumia S., Castaldo, Cobianchi, R., Leone, A., Basile, A. 2008.** Trace element accumulation in *Pseudevernia furfuracea* (L.) Zopf exposed in Italy's so called Triangle of Death. *Sci. Total Environ.*, 407: 647-654.
- Sterflinger, K., Prillinger, H. 2001.** Molecular taxonomy and biodiversity of rock fungal communities in an urban environment (Vienna, Austria). *Ant. Leeuw*, 80: 275-286.
- Strzelczyk, AB. 1981.** Microbial biodeterioration: stone. In: Rose, A.H. (Ed.), *Economic Microbiology*, Vol. 6. Academic Press, London, 62-80.
- Ukberg, K. 1990.** The Effects of acid deposition on buildings and building materials. UK Building Effects Review Group. HMSO, London.
- Vingiani, S., Adamo, P., Giordano, S. 2004.** Sulphur, nitrogen and carbon content of *Sphagnum capillifolium* and *Pseudevernia furfuracea* exposed in bags in the Naples urban area. *Environ. Pollut.*, 129: 145-158.
- Warscheid, T., Braams, J. 2000.** Biodeterioration of stone: a review. *Intern. Biodet. & Biodeg.*, 46: 343-368.
- Welton, RG., Cuthbert, SJ., Mclean, R., Hursthouse, A., Hughes, J. 2003.** Preliminary Study of the phycological degradation of natural stone masonry. *Geochem. Hlth.*, 25: 139-145.