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**"Decay of Sandstone in Urban Areas Correlated with  
Atmospheric Aerosol"**

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# DECAY OF SANDSTONE IN URBAN AREAS CORRELATED WITH ATMOSPHERIC AEROSOL

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**Abstract.** The decay of sandstone in urban areas has been investigated. Patterns and composition of the damage layers sampled on monuments and historical buildings are described. The elemental concentrations of black surface crusts are reported. Enrichment factors in relation to the sandstone and crustal rock composition have been calculated in order to point out the component due to atmospheric deposition. The presence of anthropogenic aerosol and its role in the process of damage is evidenced.

## 1. Introduction

The damage of materials, particularly those commonly found in our cultural heritage, is a problem of focal interest which is correlated with the present composition of the urban atmosphere, rich in gaseous and aerosol pollutants ( $\text{SO}_2$ ,  $\text{NO}_x$  and carbonaceous particles).

Most of the papers in the literature reporting experimental results, both in the laboratory and in field campaigns, refer to carbonate rocks of low porosity, such as marble and limestone (Thomson, 1986; Graedel and Mc Gill, 1986; Lipfert, 1989). Particular attention has been devoted to these natural stones since they have been used in many world-famous monuments and because the relative chemical homogeneity and low porosity of carbonate rocks have permitted the unification of weathering mechanisms within a few simple models.

As yet, far less attention has been accorded to natural stones of high porosity, such as calcareous sandstones and calcarenites (Stambolov and van Apseren de Boer, 1972; Rosvall, 1988). Sandstones are sedimentary rocks composed mostly of mineral and rock fragments within the sand size range (2 to 0.06 mm) and having a minimum of 60% free silica, cemented by various materials including carbonates; while calcarenite is a limestone composed predominantly of clastic sand-size grains of calcite (ASTM, 1989). In the literature, the main weathering mechanisms proposed for these materials are as follows:

(i) the formation of damage layers mainly composed of gypsum on the surface, varying in thickness from a few millimeters to a few centimeters, which are weakly linked to the underlying rock and therefore subject to easy exfoliation (Rossi

Manaresi, 1975; Andersson, 1985; Weiler, 1985; Twilley and Podamy, 1986). This process is due to the sulphation of the carbonate component of sandstone owing to atmospheric acid deposition, with formation of a gypsum patina embedding carbonaceous particles and soil dust (Sramek and Eckart, 1986; Leysen *et al.*, 1989).

(ii) the dissolution and transport of soluble salts by water circulating within the rock (Winkler, 1982; Subbamaran, 1985; Blaeuer, 1985); the subsequent recrystallization of these salts produces mechanical stress which can disaggregate these materials (Lewin, 1982).

(iii) mechanical erosion due to the action of sand and marine salts transported by the wind (Lal, 1978). This kind of damage produces the segregation of grains, the formation of step profiles and leaves a rough, honeycombed surface (Blaeuer, 1985; Agrawal *et al.*, 1986).

(iv) biological weathering due to the action of microorganisms, such as fungi and lichens at the surface (Eckhardt, 1985; Andersson, 1985; Krumbein, 1988; Warscheid *et al.*, 1990). Jones and Wilson (1985), in their review on the chemical activity of lichens on mineral surfaces, mention that calcium oxalate has also been identified on sandstones, while Alaimo *et al.* (1986) report the presence of whewellite and weddellite (mono- and dihydrate calcium oxalates, respectively) on calcarenite without considering their origin.

Finally, some studies have been performed on sandstone in weathering chambers using simulated atmospheres with the aim of investigating the chemical weathering of this type of rock (Gilardi, 1966; Vale and Martin, 1986).

The aim of this paper is to study the damage mechanisms affecting sandstones and calcarenites in the urban environment and to correlate the patterns and composition of the damage patinas with the different components of atmospheric aerosol.

## 2. Experimental Work

### 2.1 DAMAGE PATTERNS

The first experimental approach consisted of verifying the present state of preservation of sandstone monuments in comparison with their condition in the past, as can be deduced from archive photographs. The images of sandstone monuments in urban areas taken at the end of last century and at the beginning of the present one show an appreciable state of preservation: at present the same monuments appear irretrievably damaged (Figure 1).

Furthermore, the damage patterns were studied in relation to the extrinsic factors of the material, such as location of the monument, geometry of the surface, exposure to solar radiation, rain wash-out, etc. The damage patterns observed on porous stones present deep differences when compared to those found on marble and limestone monuments: on materials with low porosity the black and white areas are the indicators of leaching by rain water (Del Monte *et al.*, 1981; Camuffo *et*



Fig. 1. Detail of the Palazzo Re Enzo, an example of a historical building in sandstone situated in the center of Bologna. On the left (a), the wall decoration as appeared in a photograph taken at the beginning of this century (from the Poppi archives, by kind permission of the Cassa di Risparmio di Bologna), on the right (b), the same detail as it appears as of 1988, where evident signs of damage can be seen.

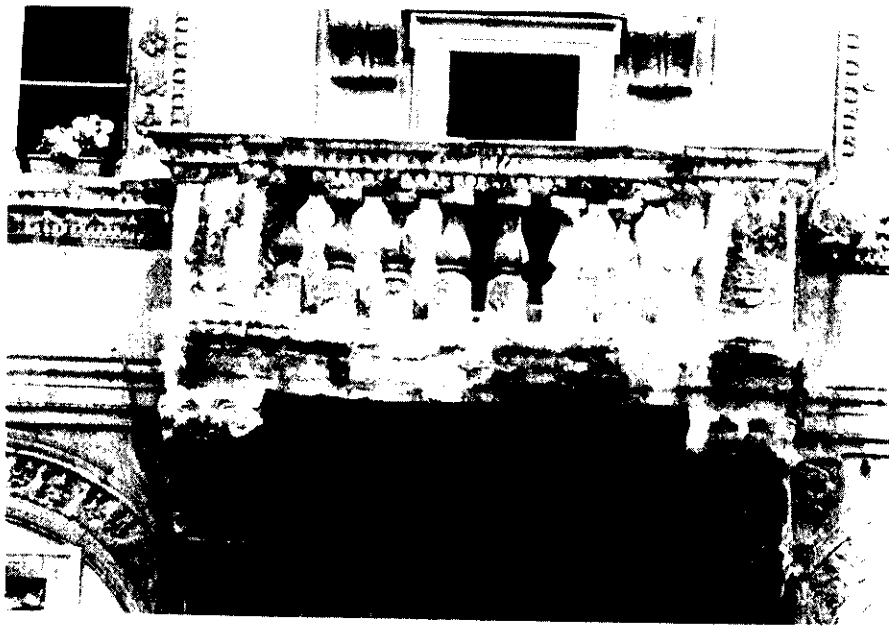


Fig. 2. Black patterns as can be observed on the surface of porous natural stones, such as calcarenites and sandstones.

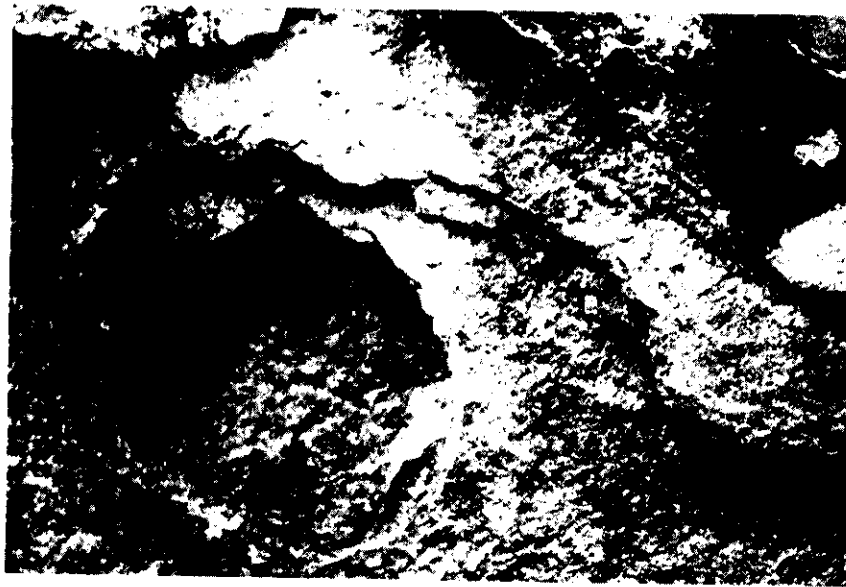
**a****b**

Fig. 3. (a) An example of sandstone damage: the black surface crust (layer *A*) is clearly shown; where exfoliation occurs, the underlying powdered layer (*B*) is lost within a short time, exposing the undamaged rock to a new cycle of chemical weathering. (b) The decayed sandstone surface shows exfoliation revealing concentric cracks which have been produced by dissolution of the calcium carbonate, the soluble portion of the rock.

*al.*, 1983). On considering the color and appearance of the surface of sandstones and calcarenites, the blackening is observed on the whole surface independently of its geometry or exposure to rain water (Figure 2). The damage layer presents an inhomogeneous structure, consisting of a thin black crust at the surface and a thicker underlying layer white-beige in color with a crumbled powdered consistency (Figure 3a). Where the black crust has come away, part or all of the powdered layer is removed, laying bare the underlying rock. In this case a loss of material of the order of one centimeter is observed and the unaltered sandstone is exposed to a new cycle of weathering (Figure 3b). Thus, the blackening can affect the whole surface of a monument; the color of the original rock is shown, only where the black crust has fallen off.

These patterns are characteristic of urban areas, while observations performed on sandstone monuments in rural areas reveal a good state of preservation, apart from the layers of lichens and algae partially covering the surfaces.

## 2.2. SAMPLING

The experimental work was performed by studying a series of monuments in sandstone and calcarenite of different epochs. The historical center of Bologna, a town in Northern Italy known for the extensive use of these materials in the

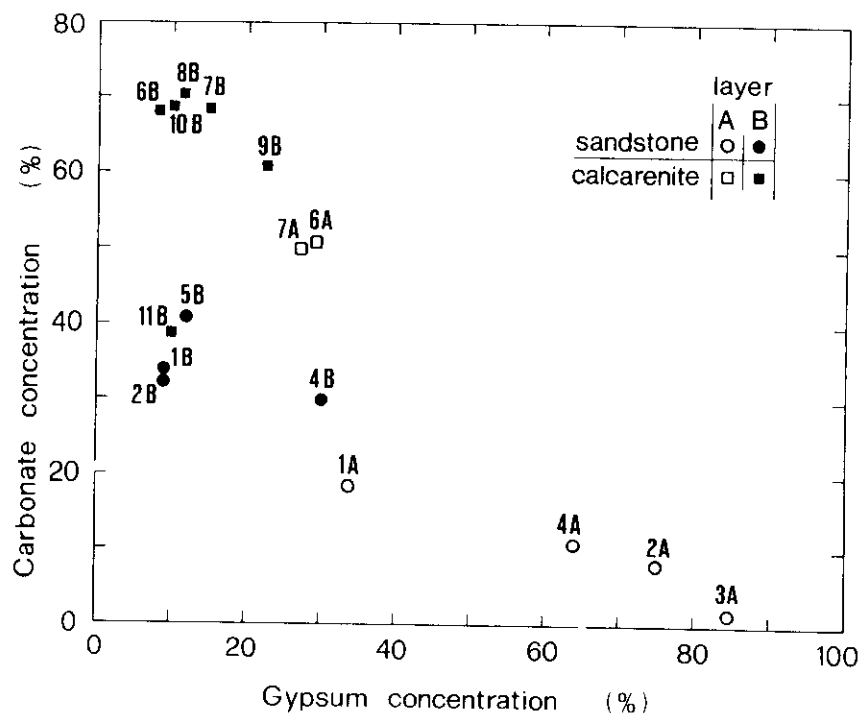


Fig. 4. Gypsum and calcium carbonate concentrations measured in layers A and B of the analyzed sandstones and calcarenites.

TABLE I  
Elemental concentrations measured in layers A (ppm)

Elem.	Sandstones				Calcarenites	
	1A	2A	3A	4A	6A	7A
Li	<5	<5	<5	<5	<5	<5
Be	<1	<<1	<<1	<1	<<1	<<1
Na	5915	2202	2285	3804	2083	4314
Mg	286	106	116	178	637	509
Al	2291	813	834	1367	361	398
Si	152015	56632	52923	95739	14983	8374
S	63185	139719	157517	119250	54285	50726
K	482	273	239	268	420	290
Ca	181481	218717	198640	199019	329029	336086
Ti	52	18	22	30	44	57
V	44	44	38	9	9	29
Cr	16	13	13	15	17	19
Mn	325	117	49	119	59	42
Fe	1028	494	362	729	585	518
Co	<5	<5	<5	<5	<5	<5
Ni	19	5	10	15	14	11
Cu	24	2	7	48	21	17
Zn	87	65	55	93	389	302
As	<10	<10	<10	<10	<10	<10
Se	<10	<10	<10	<10	<10	<10
Sr	79	78	55	493	301	258
Zr	1	3	<1	5	1	6
Mo	<5	<5	<5	<5	<5	<5
Cd	5	3	3	5	3	3
Sn	<10	<10	<10	<10	<10	<10
Ba	37	48	33	28	33	26
Pb	218	315	48	59	32	42

construction of churches and buildings, was selected as the area of investigation.

The sampling was performed by separating the thin black patina at the surface (samples A) from the underlying incoherent layer (samples B). In some cases, it was difficult to strictly divide the two layers, therefore some samples A contain variable quantities of the corresponding layers B. This problem arose particularly in the case of calcarenite.

The two layers A and B vary widely in thickness according to the monuments studied and the different areas of a same monument: however, the black surface crust (layer A) is generally of the order of millimeters and the underlying layer B of the order of centimeters.

### 2.3. ANALYSIS

Once collected, the samples were dried, ground and preserved at a temperature of 20 °C in an inert environment (N<sub>2</sub>), after which the following analyses were performed: (a) x-ray diffraction (XRD) to identify the main chemical species present,

by means of a Philips PW 1730 Diffractometer; (b) differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) to determine gypsum and carbonates. DTA and TGA were simultaneously performed with a Netzsch Simultane Thermoanalyse STM Mod. 429 apparatus, under air flow at heating rate  $10\text{ }^{\circ}\text{C min}^{-1}$ . The concentration of gypsum and carbonates (expressed as percentages of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{CaCO}_3$ , respectively) are reported in Figure 4.

For samples A, the elemental composition was also determined by Plasma Spectroscopy (ICP Perkin Elmer 5500) through the digestion of samples in Teflon vessels with a  $\text{HF-HNO}_3$  mixture at  $120\text{ }^{\circ}\text{C}$ .

The results obtained are listed in Table I.

Analyses of C were finally performed on layers A. To quantify the C the samples were previously treated with HCl in gas phase, eliminating the carbonates: the content of non-carbonate carbon (Cnc) was thus obtained by combustion and IR techniques (LECO apparatus Carbon-Sulphur Determinator - Mod. 762-300), as discussed in a previous work (Zappia *et al.*, 1990). The mean Cnc concentration found was 1.1%.

### 3. Results and Discussion

#### 3.1. BLACKENING PATTERNS

The difference of blackening patterns observed on porous stones in comparison with materials of low porosity must be ascribed to the different mechanisms of deposition and resuspension at the surface of the atmospheric particles, mainly soot, which is responsible for the colour of the damage patina.

Materials such as sandstone and calcarenite, always present high degree of roughness due to both their intrinsic porosity and their mineralogical dishomogeneity, which prevent a surface treatment of smoothing and polishing. The surface roughness enhances the deposition of particles due to turbulence mechanisms, with respect to smooth surfaces. The irregularity of the surface modifies the spectra of local turbulence favoring particle deposition (Clough, 1973).

Furthermore, the wetness of a surface is highly favored by the presence of pores and capillaries; condensation occurs in fact at relative humidity (RH) below 100% and, depending on the geometry of the pore system, adsorption and desorption of water vapor are triggered by critical RH levels within each microcavity, giving rise to a hysteresis loop for the entire system (Camuffo, 1984). The resuspension of particles is influenced by the characteristics of the surface: roughness and wetness favor adhesion of particles at the surface (Nicholson, 1988).

Finally, the action of rain water leaching on the surface appears to produce negligible effects in removing the particles entrapped within the stone pores.

Thus it can be concluded that on porous materials, the mechanisms of particle deposition are more efficient, while those mechanisms tending to remove particles from the surface after their deposition are less efficient. The combination of these



effects is responsible for the blackening observed on historical buildings and monuments built of porous stones.

### 3.2. CHEMICAL WEATHERING

As shown in Figure 4 gypsum is present in all samples with higher values in layers A as compared to layers B, while carbonates show an opposite trend, with more enrichment in layer B than A. These data confirm that the main damage mechanism is the transformation of calcite into gypsum and that this reaction proceeds from the surface to the interior of the material.

As mentioned in the case of the sandstone samples, it was relatively easy to separate layers A from layer B; in fact, samples A consisted of a thin black patina with an average composition ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ : 64.4% and  $\text{CaCO}_3$ : 9.3%) similar to the black crusts found on damaged marbles and limestones (Zappia *et al.*, 1989; Bacci *et al.*, 1990).

In the case of calcarenites, both layers A and B present as expected higher values of carbonate (mean concentration of  $\text{CaCO}_3$  layers A: 50.2% and layers B: 62.5%) compared to the A and B sandstone samples.

The elemental concentrations of layers A reported in Tab. I indicate that, in the case of sandstones, Ca (with an average concentration of 20%), S (varying from 1 to 16%) and Si (5–15%) are the major elements found. These are followed by Na, Al, Fe and K. Calcarenites, although showing considerably lower concentrations of Si and Al, due to the composition of this type of rock, present a similar trend with regard to the order of abundance of these elements. Furthermore, following Fe, in both materials the metals with the highest values were found to be Sr, Mg, Pb, Zn, V, Cr, Ni, and Ti.

In all samples, the concentration of non-carbonate carbon (mean Cnc equal to 1.1%), is a quantitative marker of the amount of carbonaceous particles (essentially soot) deriving from fossil fuel combustion, embedded within the layer A. As carbonaceous particles are only partly composed of elemental and organic carbon (containing also other elements, such as S and heavy metals), their absolute concentration must be considered higher than the Cnc values (Goldberg, 1985). With their elemental C and metal content, these particles, mainly concentrated at the surface of the damage layer, act as catalysts in the oxidation of  $\text{SO}_2$  (Novakov *et al.*, 1974), thus favoring the formation of gypsum (Camuffo *et al.*, 1982). So the characteristics and properties of soot (high specific surface, catalytic action) are such that their effects must be considered even when present in low concentrations.

### 3.3. ELEMENTS CORRELATED WITH ATMOSPHERIC AEROSOL

With the aim of identifying the component due to atmospheric deposition present in layers A, the enrichment factors of the various elements with respect to the sandstone rock ( $EF_{\text{rock}}$ ) were calculated following the equation:

$$EF_{\text{rock}}(X) = \frac{(X / Ti)_{\text{layer A}}}{(X / Ti)_{\text{rock}}}$$

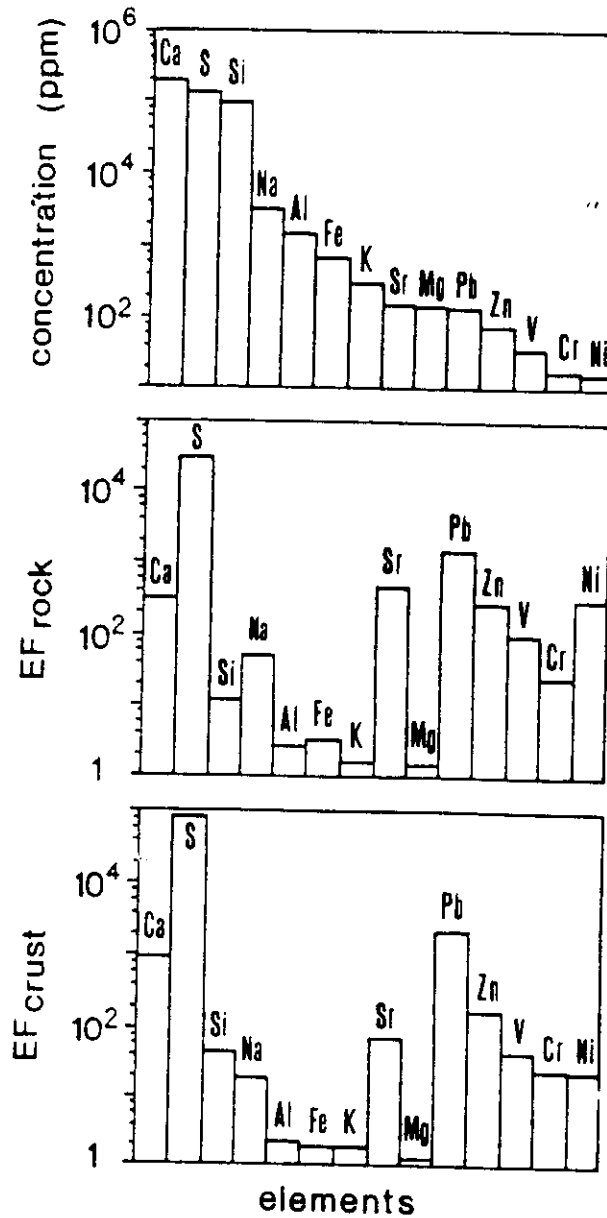


Fig. 5. Mean concentrations, rock enrichment factors ( $EF_{rock}$ ) and crustal enrichment factors ( $EF_{crust}$ ) of some of the elements measured in the sandstone layers A.

where  $X$  and  $Ti$  are the concentrations of the element  $X$  and  $Ti$  in the layer  $A$  and in the sandstone, respectively. The element  $Ti$  was assumed as a normalizing element. The elemental composition of sandstone reported by Mason (1966) was used. Rock enrichment factors close to unity are considered to indicate that an element has an origin that can be ascribed to the underlying sandstone, while  $EF_{rock}$

$>>1$  indicates that a substantial proportion of this element has a non-rock source and must be considered to be due to atmospheric deposition. The mean  $EF_{\text{rock}}$  of sandstone layers *A* is reported in Figure 5.

As can be seen, *S* is the element with the greatest enrichment, indicating that sulphates are the dominant additional component in stone damage to be associated with atmospheric deposition (both gaseous  $\text{SO}_2$  and aerosol). The rock enrichment of *Ca* must be attributed to the chemical reaction between the carbonate matrix of sandstone and the *S* components of atmospheric deposition, giving rise to the formation of gypsum. In addition, elements with high concentration values, that is *Al*, *Fe*, and *Mg*, show  $EF_{\text{rock}}$  lower than 5, indicating that their origin within the layer *A* must be attributed to the underlying sandstone. Otherwise elements presenting limited concentrations in layers *A*, such as *Pb*, *Sr*, *Ni*, *Zn*, and *V*, show  $EF_{\text{rock}}$  greater than 100: their origin is clearly linked to atmospheric deposition.

Although the composition of sandstone is similar to that of soil dust, a tentative attempt was made to discriminate between the natural and anthropogenic components of atmospheric deposition embedded within layer *A* during its formation. In order to investigate thoroughly the resemblance of the elements measured with the behavior of soil dust, the crustal enrichment factors ( $EF_{\text{crust}}$ ), calculated relative to average crustal rock and using *Ti* as reference element, were evaluated as follows:

$$EF_{\text{crust}}(X) = \frac{(X / Ti) \text{ layer } A}{(X / Ti) \text{ crustal rock}},$$

where *X* is respectively the concentration of an element *X* in layer *A* and in the crustal rock (Mason, 1966). The geometric mean values of the calculated enrichments are given in Figure 5.

Elements such as *S*, *Pb*, *Zn*, *Sr*, *V*, *Cr*, and *Ni* have  $EF_{\text{crust}} > 20$ ; these enrichments above crustal values appear to be typical of aerosol emitted by anthropogenic sources. Again, *S* shows the highest  $EF_{\text{crust}}$  and can be considered the main element linked to anthropogenic emissions (mainly combustions) interacting with our system. *Pb*, presenting crustal enrichment  $> 2000$ , is a tracer of gasoline combustion; thus, the particles emitted by vehicle traffic are found to be an important component embedded within the damage layers *A*.  $EF_{\text{crust}}$  of *Zn*, which is a tracer of refuse incinerators (Olmez *et al.*, 1988), indicates that particles emitted by this source are also present in the black crust. *V* is enriched in all samples ( $EF_{\text{crust}} = 44$ ) being a tracer of oil, which is the main fuel used in Italy for both electric energy production and domestic heating. This element is always associated with the carbonaceous particles.

#### 4. Concluding remarks

The main damage mechanisms affecting porous stones, such as sandstone and calcarenite, give rise to the information of two different layers *A* and *B*: (*A*) a surface black crust of the order of one millimeter, mainly composed of gypsum and

embedding carbonaceous particles, which are responsible for the color of the patinas; these crusts are due to the sulphation of the calcium carbonate constituting the matrix of these rocks; (B) a powdered inner layer of the order of one centimeter, where the dissolution and partly the sulphation of the carbonate matrix occur, producing the disaggregation of grains, silicatic in the case of sandstones, and calcitic for calcarenites.

Where the detachment of layer *A* occurs, due to the incoherence of the underlying layer *B*, the loss of the powdered material proceeds reaching the undamaged stone within a very short time. Therefore, a new cycle of weathering, that is sulphation – decohesion – detachment, starts causing irreparable damage to these natural stones.

The black crusts, that is the gypsum layers embedding black carbonaceous particles, present patterns completely different from those reported for low porous materials, due to the different resuspension mechanisms, affecting atmospheric aerosol after deposition.

The evaluation of enrichment factors regarding the sandstone rock ( $EF_{\text{rock}}$ ) and the crustal rock ( $EF_{\text{crust}}$ ) indicates the presence of different components of atmospheric deposition embedded within layer *A* during its formation, with particular evidence of aerosol emitted by anthropogenic sources.

These results reveal that the damage was produced in recent times and therefore embed all those components which are typical of present-day atmospheric pollution. Furthermore, the importance of evaluating the rock and crustal enrichment factors, instead of simply considering the absolute elemental concentrations, has been shown.

This work represents a first step in the study of the decay of porous natural stones. Future work will consider the comparison of different urban areas and the correlation of the rock composition of monuments with the historic composition of atmospheric aerosol at all sites.

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