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"Atmospheric-Derived Element Tracers on Damaged Stone"

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Atmospheric-derived element tracers on damaged stone

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ABSTRACT

Samples of damage layers on stone monuments and historical buildings collected in eight urban sites of Northern and Central Italy have been analysed. The composition of the matrix and the concentration of elemental tracers constituting the black crusts, which can be considered the areas where the products of stone damage and atmospheric deposition accumulate, are reported. The evaluation of enrichment factors with respect to the stone and to the soil dust showed the main components of the atmospheric deposition to be due to anthropogenic sources embedded within the damage layers.

Key words: stone; damage; aerosol; elemental analysis; enrichment factor

INTRODUCTION

There is general agreement in the scientific literature that atmospheric pollution is the main agent responsible for the damage of monuments and historical buildings in urban areas [1,2]. The weathering of marbles and limestones, natural building stones found widely in the European cultural heritage, leads to the formation of damage layers.

Depending on the geometry of the stone surface, only the areas protected by the leaching of rain wash-out present crusts, black in colour, which are mainly constituted by gypsum (calcium sulphate dihydrate), resulting from the transformation of calcium carbonate [3]. The colour of these layers must be ascribed to the presence of atmospheric particles, mainly soots, which are embedded within the crust during its formation. The black crusts can be considered the areas where both the products of the chemical transformation of the stone and the deposition of atmospheric gas and particles accumulate [4].

The aim of this work is to evidence the component due to atmospheric deposition present on damage stone and to discriminate the natural and anthropogenic fraction which contribute to the formation of the damage layers.

EXPERIMENTAL

Sampling

Samples of black alteration patinas were collected from marble and limestone monuments of different historical epochs. Only samples of black crusts were collected, neglecting other types of deterioration, since these crusts constitute the point of maximum accumulation of both alteration products and environmental deposition.

The samples were taken from eight sites in Northern and Central Italy (Fig. 1): Milan, Venice, Rome, Bologna, Ravenna, Verona, Trento and La Spezia (where sampling was also performed on natural limestone outcrops).

Fig. 1. Location of the eight urban sites where samplings of damage stone on monuments and historical buildings in marble and limestone were performed. The typologies of urban centers studied were: large ■, medium ●, small • maritimes ▲.

The choice of sites was made in order to cover all typologies of urban centres: large (Milan and Rome), medium (Bologna and Venice), small (Verona and Trento), industrialized (Milan and Ravenna) and maritime (Venice, Ravenna and La Spezia).

At each site, black crusts were collected on monuments situated in different areas and conditions, for example, town centres, suburbs and streets with varying levels of traffic, so as to ensure that the samples were representative not of a single monument but of the town taken as a whole.

Analysis

On the various monuments and historical buildings (e.g. the Trajan Column and Constantine Arch in Rome), only very small quantities of material could be collected, for evident reasons of respect for the works of art in question. Thus, the choice of analytical techniques permitting a comprehensive chemical characterization of the samples tended to favour non-destructive methods or techniques requiring only very small quantities of samples.

Once collected, the samples were dried, ground and preserved at a temperature of 20°C in an inert environment (N_2), after which they underwent the following analytical procedures.

X-ray diffractometry (XRD), to identify the main chemical species present, by means of a Philips PW 1730 Diffractometer using Cu $K\alpha$ radiation (Ni filter) and 40 KV/30 mA, 2 dg/min rate, TC = 4, $R = 2 \cdot 10^3$ as operative conditions.

Differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) to determine gypsum and carbonates. DTA and TGA were simultaneously performed with Netzsch Simultane Thermoanalyse STM Mod. 429 apparatus, under air flow at heating rate 10°C/min.

Carbon and sulphur were measured by combustion and IR technique (LECO apparatus carbon-sulphur Determinator Mod. CS-44). With regard to the measurement of carbon, it must be pointed out that the samples analysed contained both carbonates and non-carbonate carbon (C_{nc}), which can be defined by the following relation:

$$C_{nc} = C_t - C_c$$

where C_t is the total carbon and C_c is the carbonate carbon. C_{nc} can be determined by means of two different procedures: (a) the measurement of C_t by combustion of the bulk sample and of C_c using DTA and TGA; (b) the preliminary elimination of carbonates and determination of carbon from the residual part containing only C_{nc} by the LECO apparatus. Previous

TABLE I

Mean concentrations of the main components characterizing the black crusts sampled on marble and limestone at the sites examined

Sites	Components							
	$CaCO_3$ (%)	Ca (ppm)	C_t[a] (%)	C_{nc} (%)	$CaSO_4.2H_2O$ (%)	S (gypsum) (ppm)	S (total) (ppm)	ΔS[b] (%)
Milan	1.4	204576	1.8	1.6	78.4	146012	151579	2.3
Venice	Traces	205458	1.6	1.6	86.9	161843	163796	1.2
Rome	2.9	217586	2.5	2.2	86.7	161471	161522	0.03
Bologna	7.0	212329	2.4	1.6	78.9	145267	191942	24.3
Ravenna	6.5	183082	3.6	2.8	56.4	105039	116628	9.9
Verona	8.2	201732	3.4	2.4	66.9	124594	138944	10.3
Trento	18.2	225180	3.6	1.4	57.3	106715	110263	3.2
La Spezia	19.3	232156	3.4	1.1	64.0	119194	119922	0.6

[a] Calculated as $C(CaCO_3) + C_{nc} = C_t$.

[b] $\Delta S = (S(total) - S(gypsum)) \cdot 10^2 / S(total)$.

analyses on expressly prepared standard samples showed that more accurate results are obtained with the second method. In view of this, the following procedure was developed and adopted for all samples: 100 mg of previously ground sample material was placed for 48 h in an atmosphere saturated with HCl vapours, thus obtaining a slow, gradual and complete elimination of carbonates. The sample was then put in a dryer on KOH until the complete elimination of humidity and residual HCl took place. The subsequent combustion of the previously treated sample provided the C_{nc} value.

For elemental analyses, all samples were examined by the proton induced X-ray emission (PIXE) technique, using a 2.8 MeV proton beam of the 3.5 MV CISE tandem Van de Graaf accelerator.

In addition, Na, Mg, Al, Si and K were analysed by inductively coupled plasma emission spectrometry (ICP Perkin Elmer 5500), through the digestion of samples in Teflon vessels with a HF-HNO_3 mixture at 120°C.

In cases where the quantity of the single samples did not allow a complete series of analyses, several samples from the same site were mixed together.

RESULTS AND DISCUSSION

Table 1 shows the main constituents of the black crust matrix averaged for the single sites. The predominant species is calcium sulphate dihydrate (gypsum), confirming that black crusts are the accumulation area of the products generated by the sulphation of the calcium carbonate constituting the original rock. The percentages of calcium carbonate present in the crusts, mainly due to secondary reprecipitation, vary from trace values in Venice to 19.3% in La Spezia.

Sulphur is present mainly in the form of gypsum (reported in Table 1 as S gypsum); the amount of sulphur found in different forms (ΔS) varies from 0.03 to 24.3% of the total sulphur and can be attributed to the presence of other sulphates, residual SO_2, H_2S and organic compounds of sulphur [5,6].

The amount of non-carbonate carbon (C_{nc}) was taken to be a quantitative index of soots, the carbonaceous particles embedded in the black crusts, giving rise to their characteristic colour. The presence of these particles on damage stones has been indicated by several authors [7–9]; however, apart from optical and electronic microscope observations, no quantitative evaluation has yet been made as to their concentration on the mass of black crusts. Soots emitted by combustion processes have a carbonaceous matrix constituted in part by organic carbon and in part by elemental carbon [10]. These particles play an active role in the damage processes affecting stone surfaces since, with their content of sulphur, heavy metals (Fe, V, Ni) and elemental carbon, they contribute to the catalytic oxidation of atmospheric gaseous SO_2 [11] and to the sulphation of calcium carbonate [12].

The mean C_{nc} value found was 1.8%; thus, C_{nc} results to be the fourth element in terms of quantity after Ca, S and Si. In assessing the relevance of this result, it must be pointed out that the total mass of the carbonaceous fraction in the patina is greater than that of C_{nc}, since carbonaceous particles are only in part constituted by elemental carbon, as mentioned above. Moreover, the characteristics and properties of soots (high specific surface, catalytic action) are such that their effect is considerable even when present in very low concentrations.

Table 2 shows the mean concentrations of the elements measured by means of the PIXE and ICP techniques for the eight sites under study. They reveal the presence of a high number of elements with a wide range of variability, covering five orders of magnitude from a few ppm of certain heavy metals to about 10% in the case of Si.

Among the most abundant elements, Si (in third place after Ca and S), with a concentration varying between 2 and 9%, and Al (0.07–2%) must also be mentioned. This is followed by Fe, which is the most abundant of the heavy metals, with percentages of between 0.4 and 2, and then Na, Mg, K and Cl. Following Fe, the highest values of metals were found for Pb (range 100–900 ppm), Ti, Sr, Zn and Mn.

These data show an homogeneous trend as regards the order of abundance of the elements, essentially indicating that the components giving rise to black crust formation are of common origin in all the sites under examination. Furthermore, some differences between the sites are highlighted. Pb has the lowest values at the two maritime sites of Venice and La Spezia: in the former, automobile traffic is absent, while in the latter case, the samples were taken from a natural outcrop near the sea which is little affected by the traffic inland.

V is found in all samples, as a tracer of oil, which is the main fuel used in Italy for both electric energy production and domestic heating. This element is generally associated with the carbonaceous particles which, as the C_{nc} data show, are present in considerable quantities in all the samples examined.

In La Spezia the concentration of As, a tracer for coal combustion, must be attributed to the presence of a coal-fired power station in the vicinity (one of the few existing in Italy).

Since our purpose was to identify the component due to the deposition of atmospheric gases and aerosol on carbonate surfaces, the enrichment factor of the various elements with respect to the carbonate rock ($EF_{carb.}$) has been calculated using the following equation:

$$EF_{carb.}\,(X) = \frac{(X/Ti)\ \text{Black crust}}{(X/Ti)\ \text{Carb. rock}}$$

TABLE 2

Mean elemental concentrations (ppm) measured in the black crusts at the eight sites examined.

Elem.	Milan	Venice	Rome	Bologna	Ravenna	Verona	Trento	La Spezia
Na	12108	2379	1309	1678	5195	2890	3677	1538
Mg	7945	2054	176	1831	4140	18539	18539	7422
Al	17227	4717	704	8201	10708	8810	9387	8748
Si	89566	17100	23756	46676	55990	31804	36926	32035
Cl		3349		189	6705	289		7451
K	2145	5551	8514	72	84	1130	8630	7058
Ti	695	178	481	360	627	539	305	602
V	72	29	44	58	87	86	23	21
Cr	18	16	43	22	16	25	20	46
Mn	236	58	133	113	239	238	81	150
Fe	18796	3779	8061	14090	11567	9138	4515	9588
Ni	13	38	22	Traces	24	8	8	17
Cu	50	11	245	195	49	49	33	15
Zn	258	59	118	177	189	254	73	96
As			7					14
Se								3
Br	33	23	33	—	21	40	22	33
Rb	—	—	24		21	15	13	22
Sr	146	123	215	142	296	182	94	243
Zr	23	12	35	3	31	19	25	65
Ba	233	96	9	337	298	625	276	40
Pb	883	123	532	427	530	615	214	149


MILAN
a
VENICE
b
ROME
c
BOLOGNA
d
RAVENNA
e
VERONA
f
10^3
10^2
10^1
1
10^{-1}
10^{-2}
Enrichment factor (carb)
Elements
S
Pb
Na
Ba
Cu
Zn
Cl
Al
Si
K
Fe
Ni
Br
Mn
Mg
Sr

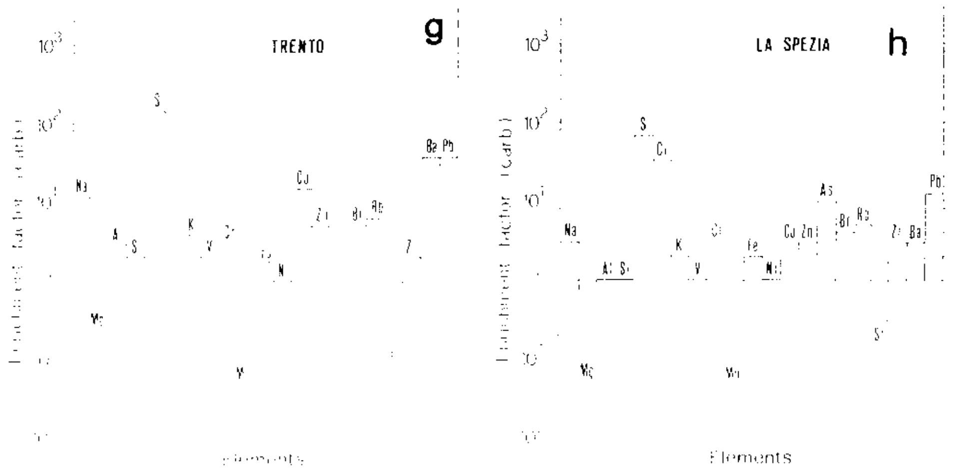
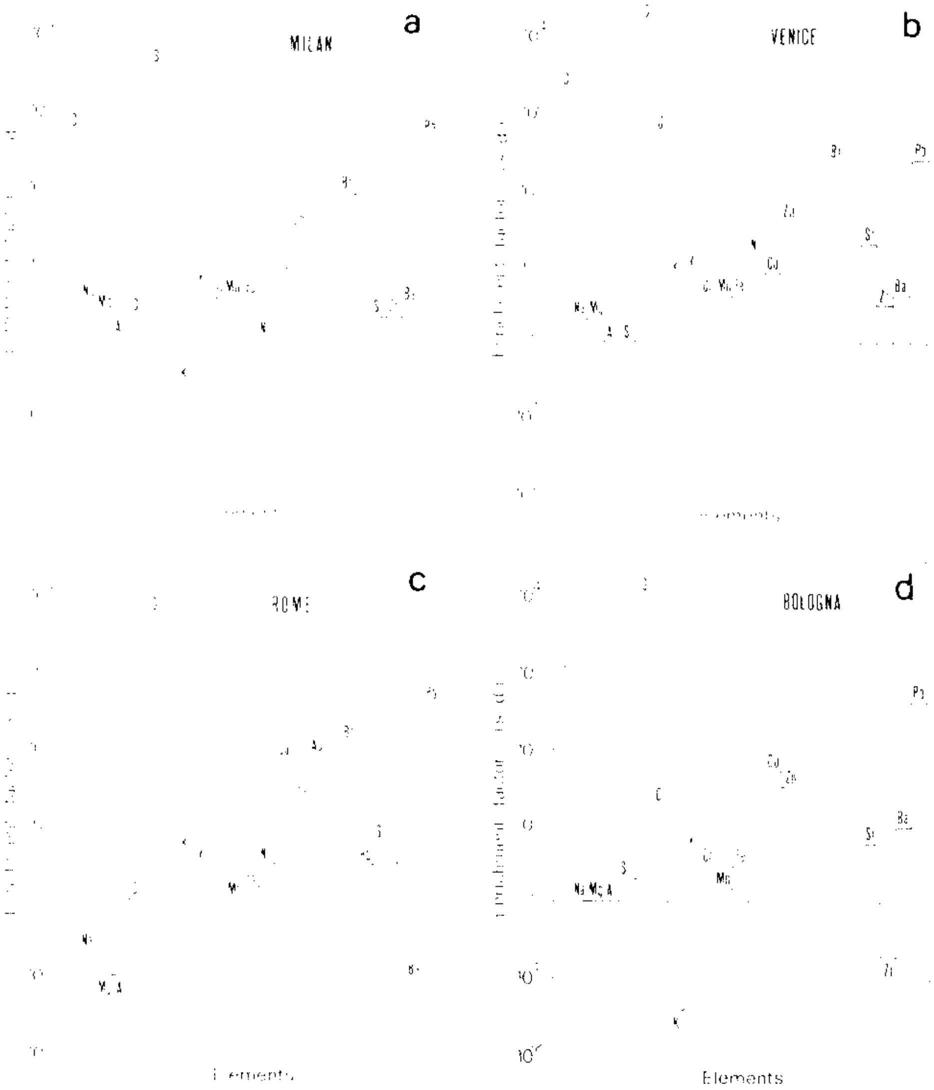


Fig. 2. The enrichment factors of the elements measured within the stone damage layers calculated for the carbonate rock (EF_{carb}). The geometric means of EF_{carb} for the eight sites examined are reported.

where X and Ti are the concentrations of element X and titanium in the black crusts and carbonate rocks, respectively. The elemental composition of carbonate rock reported by Mason [13] was used in these calculations. Enrichment factors close to unity are considered to indicate that an element has an origin that can be ascribed to the underlying carbonate stone, while those greater than 1 indicate that a substantial proportion of an element has a non-carbonate source and must be considered to be due to atmospheric deposition. Ti was taken as a reference element since its concentration, measured by PIXE (for the small quantities of material required), was known for all the samples of the various sites. It was therefore possible to calculate EF_{carb} for all the elements analysed in each sample; the mean EF_{carb} values for the eight sites studied are shown in Fig. 2a–f.

At all sites, S is the element with the greatest enrichment factor. This element, which is deposited on the surfaces as both gaseous SO_2 and sulphate, is undoubtedly the main one attributed to atmospheric deposition. On the other hand, it was observed that elements with high absolute concentrations, that is Na, Al, Si and Mg, reveal small EF_{carb} values (lower than 10 in all cases), compared with other elements. This limited enrichment indicates that their presence in the black crusts can largely be attributed to the carbonate rock. Moreover, in the case of magnesium, which has EF_{carb} values <0.1 at all sites, a non-carbonate contribution is to be excluded. As was expected, Cl has high EF_{carb} values in the three maritime sites: Venice, Ravenna and La Spezia (Fig. 2b, e and h).

With regard to metals, several considerations can be made as to their presence in the black crusts. It can be clearly seen that some elements, such as Fe, present in high concentrations in the black crusts, show limited EF_{carb} ranging between 2 and 4. Therefore, iron is an element whose presence in the black crusts is strongly conditioned by the dissolution of the underlying stone. In view of this, its presence in our system should certainly not only be attributed to atmospheric aerosol deposition. Alongside elements such as Mn (EF_{carb}: 0.1–0.3) and Sr (EF_{carb}: 0.2–1), which show enrichment factors with respect to the carbonate rock of less than 1, are shown to be of clear carbonate origin. At the same time, other elements, some of which



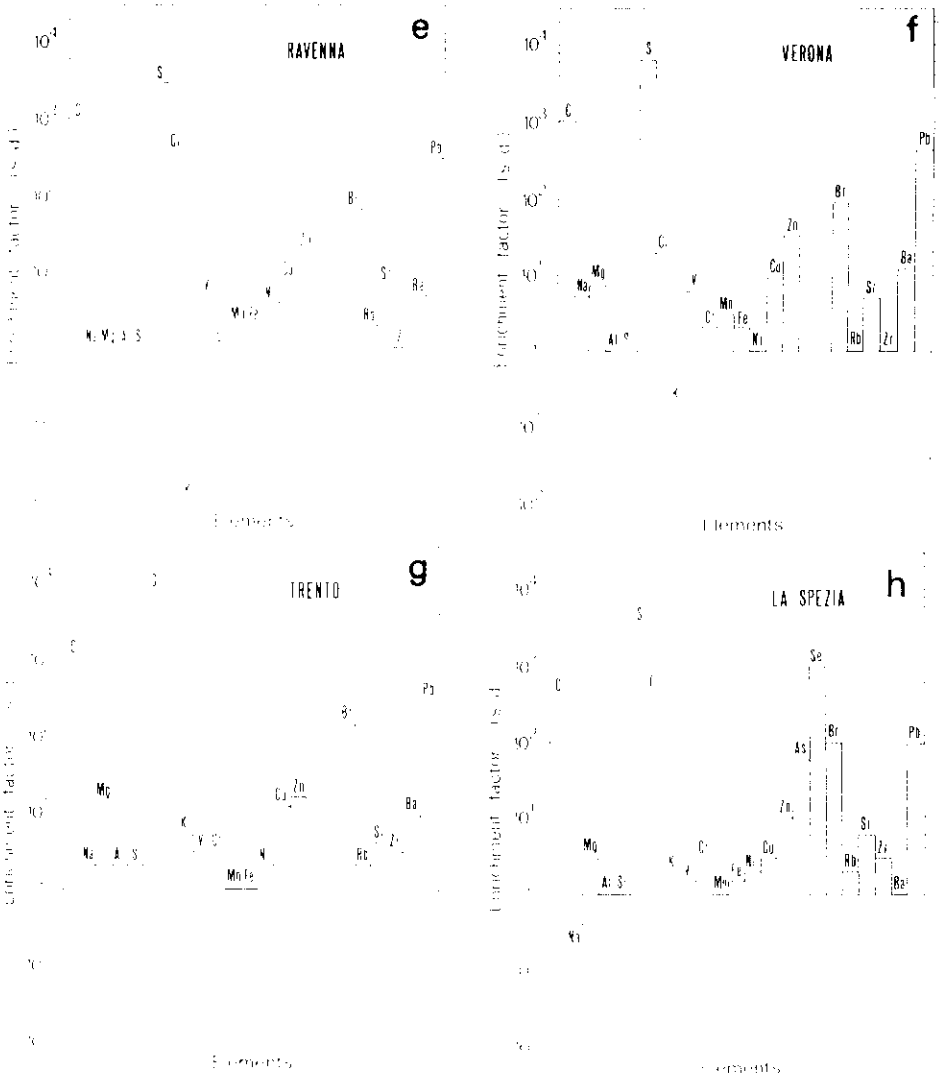


Fig. 3. Geometric means of the damage layer – soil dust enrichment factors ($EF_{s.d.}$) for the elements measured in the damage layer for the eight sites examined.

are present in limited concentrations, reveal considerable enrichment: Pb, Cu, Zn, Br, V, Cr and As. Their origin is clearly linked to atmospheric deposition.

Furthermore, a distinction between the natural and anthropogenic components of the atmospheric deposition embedded in the black crusts has been effected. Natural sources of aerosol containing trace elements include terrestrial dust, sea spray, volcanic emissions, forest fires and biogenic emissions. In a previous work on black crusts in maritime areas the authors identified the presence of a remarkable concentration of atmospheric aerosol of natural origin, such as sea salt and soil dust [14]. In addition, the concentrations of sea-derived elements (Na, Cl, Mg) were found to be markedly higher than those of black crusts in non-maritime sites; the Cl/Na ratio was in good agreement with the ratio of 1.8 for sea salt.

To indicate the elemental tracers typical of anthropogenic sources (power plants, incinerators, vehicle exhaust), the enrichment factor with respect to soil dust ($EF_{s.d.}$), using the average crustal rock of Mason [13] as a reference material, has been calculated as follows:

$$EF_{s.d.}(X) = \frac{(X/Ti)\ \text{Black crust}}{(X/Ti)\ \text{Crustal rock}}$$

where X and Ti are, respectively, the concentration of an element X and titanium, used as normalising element, in the black crust and in the crustal rock [15]. The geometric mean values of the calculated enrichment for each sample is reported in Fig. 3a–f for the eight sites studied.

It can be seen that elements such as Al, Si, Na and Mg present enrichment factors close to unity, indicating that they are present in soil-like ratio in the black crusts. While sulphur and non-carbonate carbon (reported as C in the graphs) show the highest $EF_{s.d.}$ and can be considered the main pollutant elements interacting in our system, giving rise to the formation of the black crusts.

Pb and Br, both show high enrichment factors, close to or higher than 100, and they can be considered to have primarily the same pollution origin, namely automobile exhaust gases. Again, the lowest $EF_{s.d.}$ values for Pb are those relating to Venice and La Spezia (with 234 and 84, respectively) as shown in Fig. 3b and h. Zn turns out to be enriched at all sites with $EF_{s.d.}$ variable between 10 and 40. This element, a tracer for incinerators, clearly indicates that particles emitted by these urban sources are embedded in the black crust.

The $EF_{s.d.}$ of As and Se present the maximum enrichments in La Spezia (Fig. 3h), with values of 58 and 963, respectively, emphasizing the presence of fly ash within the damage layers, as was to be expected given the proximity of a coal-fired power station. Cu, with its wide ranging $EF_{s.d.}$ values (3–70), has a variety of anthropogenic sources.

Finally, elements such as Cr, Mn and Ni, showing $EF_{s.d.}$ values of less than or close to unity at all sites, were assumed to be 'non-enriched' and predominantly derived from the carbonate rock, although these elements are present in the anthropogenic aerosol.

CONCLUSIONS

The measurement of the main components and elements in the black crusts forming on the carbonate surfaces of monuments and historical buildings, indicates that they are the result of both gas and aerosol deposition on the carbonate surface and the damaging interaction between the surface and the components of atmospheric deposition.

Our results show that by calculating EF_{carb} values it is possible to distinguish the origin of the various components (whether atmospheric or from the carbonate rock) which become embedded in black crusts during formation. The processing of the elemental data through the calculation of the enrichment factors relative to soil dust (EF_{sd}) allowed the highlighting of those elements considered in the literature to be typical tracers of the atmospheric aerosol emitted by natural and anthropogenic sources.

The presence of aerosol emitted by various anthropogenic sources, such as coal and oil combustion, automobile traffic and incinerators was identified in the black crusts at the sites examined. These results confirm that damage layers have formed in recent times and therefore embed all those components which are typical of present-day atmospheric pollution. Finally, the importance of evaluating the enrichment factors of elements instead of simply considering their absolute concentrations has been underlined.

Future work will be directed towards determining the quantitative impact of the various components linked to atmospheric deposition. An accurate evaluation of these data requires the measurement of the composition of the carbonate rock on all monuments studied and its correlation with the historic composition of the atmospheric aerosol at the site under examination.

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