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"Non-Carbonate Carbon Content on Black and White Areas of Damaged Stone Monuments"

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Abstract—The carbon present in the black and white areas of stone monuments in nine sites of northern and central Italy has been studied. The samples collected were analysed for their non-carbonate carbon (C_{nc}) and the percentages of gypsum and carbonates were determined. Elemental analyses of black patinas were also performed. C_{nc} was found to be mainly of atmospheric origin and is proposed as a quantitative index of the carbonaceous particles embedded within damaged layers. C_{nc} shows a direct correlation with the concentration of gypsum (the main deterioration product) and an inverse correlation with the carbonate content, originating from the stone. Finally, the elemental analyses revealed the presence of heavy metals, effective catalysts of deterioration reactions.

Key word index: Carbonaceous particles, weathering, historical building, aerosol effect, carbon analysis.

1. INTRODUCTION

In previous works dealing with the formation of alteration patinas on stone monuments in marble, limestone and sandstone, deterioration products were found in association with the various components of aerosol deposition (Zappia *et al*., 1990; Sabbioni and Zappia, 1992a, b). Moreover, carbonaceous particles emitted by fossil fuel, oil and coal combustion were found in the black damaged layers on stone surfaces, together with the two basic components of the patinas, i.e. gypsum and residual and/or reprecipitated calcite (Del Monte *et al*., 1981; Camuffo *et al*., 1982). Their presence has been reported by various authors (Camuffo *et al*., 1983; Leysen *et al*., 1989; Ausset *et al*., 1991) and plays an important role in the overall deterioration process. Firstly, carbonaceous particles are responsible for the blackening of the patina, which seriously impairs the appearance of monuments (Fig. 1). They also contribute to the sulphation of calcite into gypsum due to their sulphur content and the presence of heavy metals, which act as catalysts in deterioration processes. Finally, it has been suggested that carbonaceous particles themselves, especially due to their high specific surface, act as a catalytic support to the heterogeneous oxidation of SO_2 (Benner *et al*., 1982).

In the literature relating to building stone damage much attention has been focused on the effects of atmospheric deposition of gaseous pollutants, mainly SO_2 and NO_2 (Gauri and Gwinn, 1982; Johansson *et al*., 1988), and acid precipitation (Baer *et al*., 1991). However, the atmospheric aerosol embedded in the damaged layers has never been systematically studied. Thus, as part of our investigations into the deterioration mechanisms affecting stone monuments, carried out over several years, our group has devoted attention also to the evaluation of carbonaceous particles in the alteration patinas.

The aim of the present work is the quantitative determination of the carbonaceous particles present in black and white areas and their correlation with the main components of damaged surfaces.

1.1. *Carbon in the damaged patina*

Within the damaged layers of monuments in marble and limestone exposed to urban atmosphere, carbon can be of three different origins: (i) calcium carbonate deriving from the underlying rock; (ii) deposition of atmospheric particles; (iii) biological weathering, where calcium oxalate monohydrate and dihydrate, whewellite and weddellite, have been indicated as major products (Jones and Wilson, 1985; Del Monte *et al*., 1987).

Due to the high concentration of calcium carbonate present in the damaged layers, the measurement of total carbon is evidently not sufficient to quantify the carbon of atmospheric origin.

Total carbon (C_t) can be considered to be composed of two fractions:

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

where C_c is the carbonate carbon originating from the carbonates both in the stone and aerosol deposition, and C_{nc} is the non-carbonate carbon which contains other forms of carbon, both elemental and organic. Since the C_c due to atmospheric deposition is negligible (Tomadin *et al*., 1984; Pie, 1987), it is reasonable to suppose that C_c is derived from the rock (mainly calcite). C_{nc} is composed of the carbon content of: (a) the atmospheric aerosol embedded in the crust,

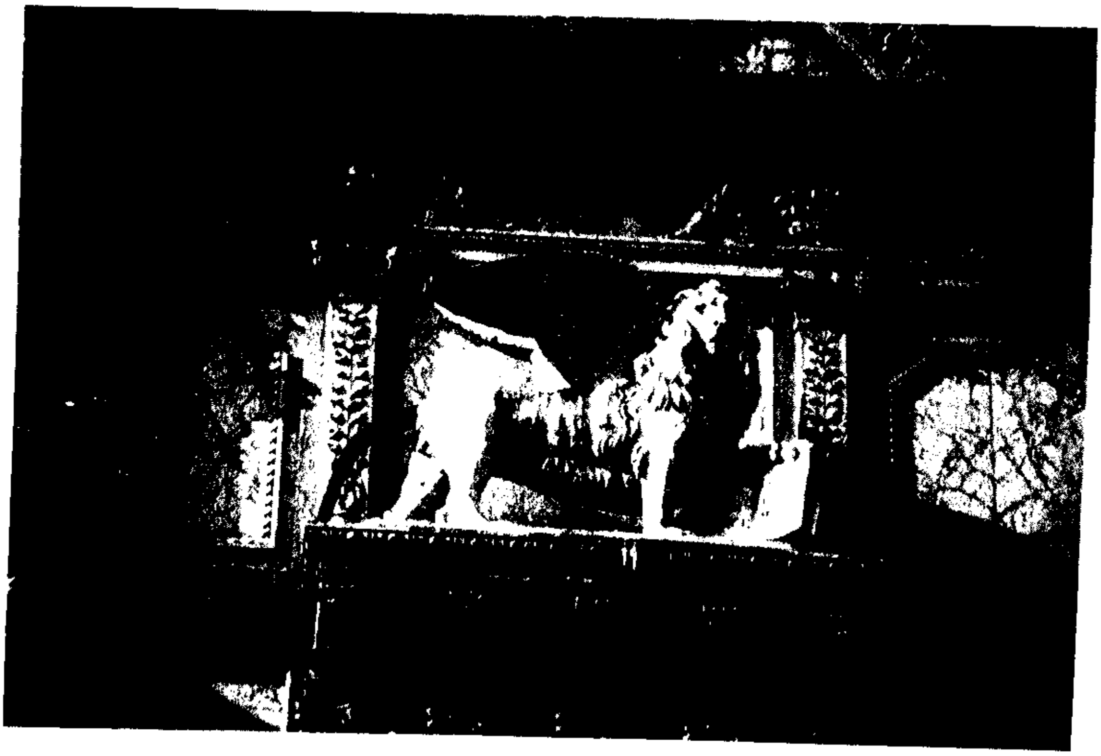

Fig. 1. Monument showing the characteristic white areas (surfaces exposed to intense rain wash-out) and black crusts (sheltered to wash-out), which are the areas where the atmospheric deposition and the products of chemical reactions accumulate. (Detail of the Ospedale Civile in Venice.)

(b) any non-carbonate carbon present in the underlying rock, and/or (c) the products of biological weathering.

2. EXPERIMENTAL SECTION

2.1. *Sampling*

Samples of the black alteration patinas and white areas were collected from marble and limestone monuments of different historical periods, situated in nine towns of northern and central Italy. Most of the samples originate from the historic centre of Bologna, since this town was chosen to be representative of an urban centre of average size and medium level of industrialization. By way of comparison, samples were also collected from centres (Fig. 2) which are larger (Rome and Milan), smaller (Trento and Verona), more highly industrialized (Milan and Ravenna) and on the coast (Venice, La Spezia and Ancona).

Where the deterioration patina was of sufficient thickness, the material was scraped away in three subsequent layers: the surface deterioration layer (A), the underlying deterioration layer (B) and the unaltered rock layer (C).

2.2. *Analyses*

Once collected, the samples were dried, ground and preserved at a temperature of 20°C in an inert environment (N_2).

Fig. 2. Location of the sites where the carbon content was measured in the damaged layers of monuments.

In order to determine the C_{nc} content of our samples, we developed a specific methodology which was controlled on the basis of preliminary analyses performed on specially prepared standard samples; this technique involves the elimination of carbonates and the subsequent determination of the residual non-carbonate carbon by means of combustion. This procedure was followed for all samples: 100 mg of ground sample was placed for 48 h in an atmosphere saturated in 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

Table 1. Non-carbonate carbon (C_{nc}), gypsum and carbonate concentrations in black and white area samples

Sites	C_{nc} (mg g^{-1})	C_c (mg g^{-1})	C_t* (mg g^{-1})	Gypsum† (%)	Carbonates‡ (%)	Others (%)
Bologna	19.65	8.56	28.21	75.6	7.1	15.3
Milan	16.02	1.68	17.70	78.4	1.4	18.6
Venice	15.99	Traces	15.99	86.6	Traces	11.8
Rome	19.50	23.54	43.04	71.0	19.6	7.4
Ravenna	28.50	7.81	36.31	56.5	6.5	34.1
Verona	23.70	9.85	33.55	66.9	8.2	22.5
Trento	14.00	21.86	35.86	57.3	18.2	23.1
La Spezia	15.10	23.18	38.28	64.0	19.3	15.2
Ancona	25.50	2.16	27.66	76.5	1.8	19.1
Black areas						
Mean	19.77	10.95	30.73	70.3	9.1	18.6
White areas						
Mean	3.97	112.90	116.87	1.1	93.2	5.3

* $C_t = C_c + C_{nc}$.
† Calculated as $CaSO_4 \cdot 2H_2O$.
‡ Calculated as $CaCO_3$.

combustion and IR spectroscopy (LECO apparatus Mod. CS-44) of the treated sample provide the C_{nc} value.

To evaluate the amount of carbon of biological origin, the ion oxalate $(COO)_2^{2-}$ was quantified by means of ionic chromatography (HPLC, Dionex 4500).

With the purpose of establishing the correlation between C_{nc} and the other components of the alteration patinas, the gypsum and carbonate content of the samples was quantified by Differential Thermal Analysis (DTA) and Thermal Gravimetric Analysis (TGA). DTA and TGA were simultaneously performed with Netzsch Simultane Thermoanalyse STM Mod. 429 apparatus, under air flow at a heating rate of 10°C min^{-1}. Finally, elemental analyses were performed by Inductively Coupled Plasma Spectroscopy (ICP Perkin-Elmer 5500), through the digestion of samples in Teflon vessels with a $HF-HNO_3$ mixture at 120°C.

3. RESULTS AND DISCUSSION

Table 1 shows the mean values of C_{nc}, gypsum and carbonates for the black patinas divided according to site, together with the overall mean values for the white areas. The mean C_{nc} concentration is 19.77 mg g^{-1}, with values ranging from a minimum of 14.00 to a maximum of 28.50 mg g^{-1}.

Table 2 reports the C_{nc} measured in the samples of layers A, B and C for the black and white areas. The data show that the C_{nc} concentration decreases from the external surface towards the internal layers and that the C_{nc} concentration in the underlying rock (layer C) is approximately two orders of magnitude lower than that measured at the surface. Thus, the stone can be considered to give a negligible contribution to the C_{nc} value of damaged layers.

Moreover, HPLC analysis indicates that the ion oxalate $(COO)_2^{2-}$ is present in the black layers in amounts varying from 0.049 to 0.209 mg g^{-1}, with an average value of 0.134 mg g^{-1}, corresponding to a carbon concentration of 0.037 mg g^{-1}. These data prove that even biological weathering makes a negligible contribution to the C_{nc} value of patina.

Table 2. Stratigraphic concentrations of C_{nc} in black and white area samples

Samples		Layer A (mg g^{-1})	Layer B (mg g^{-1})	Layer C (rock) (mg g^{-1})
Black areas	1	25.30	1.68	0.18
	2	19.77	8.60	0.15
	3	40.62	30.89	0.28
White areas	1	8.33	5.42	0.22
	2	8.68	3.00	0.10
	3	8.92	2.92	0.03

Therefore, the C_{nc} must be considered as being entirely due to the deposition of atmospheric particles and, as such, constitutes a quantitative index of the carbonaceous particles embedded in our crusts. From these data, it should be possible to calculate the total mass of carbonaceous particles present in our samples. In the literature some papers report the carbon concentration measured in the aerosol at atmospheric emission sources. Unfortunately the data are highly scattered owing to both the difficulty in performing the analyses and the heterogeneity of the emission sources (Goldberg, 1985; Masuda and Takahashi, 1990). Although a quantitative evaluation of the carbonaceous particles within our samples is not possible, a direct quantitative relationship exists with C_{nc}, which must be considered the lower limit of their concentration within our samples. Carbonaceous particles are in fact a complex system consisting of elemental carbon (black carbon), organic compounds (primary and secondary), sulphur (oxides, sulphates and organic compounds) and small quantities of diverse elements including heavy metals, such as Fe, Ni and V (Goldberg, 1985). Finally, in evaluating the importance of the C_{nc} concentration, it must be remembered that the characteristics and properties of the particles (high specific surface, catalytic properties) are such that their effect is considerable even in the case of very low concentrations.

The data for gypsum and carbonates in the black patinas (Table 1) show gypsum to be the most abundant species, with values of between 56.5 and 86.6%. This finding confirms that the main deterioration reaction on stone monuments is the surface transformation of calcium carbonate (calcite) into gypsum. The carbonate content varies from 0 up to a maximum of 19.6%. The presence of carbonates should be attributed to fragments of calcite of the stone embedded within the patina and to calcite due to *in-situ* reprecipitation (Del Monte and Sabbioni, 1986).

The white area samples naturally present very different results (Table 1): the species with the highest concentration is carbonate, with a mean value of 93.2%, followed by gypsum with 1.1%. The white areas correspond to those areas of the monument which are unsheltered and therefore subject to intensive rain water wash-out. The white eroded surface, coupled with the presence of small amounts of gypsum and of C_{nc} in quantities at least one order of magnitude greater than in the underlying rock (Table 2) suggests that, alongside the wash-out process, the white areas also undergo acid attack due to a dry deposition similar to that affecting the black areas. The fact that a patina is missing must be attributed to the rain water wash-out which gives rise to solubilization and/or the removal of most of the dry deposition as well as reaction products.

The distribution of gypsum and calcite values as a function of C_{nc}, as shown in Fig. 3, shows that in the black areas the higher gypsum values correspond to the maximum C_{nc} concentrations, while for the white areas, lower values of gypsum correspond to lower C_{nc} values. Calcite, on the other hand, reveals an inverse correlation for both white and black areas. Thus, the gypsum–black particle correlation turns out to be proved by the experimental results.

Finally, elemental analyses of the black patinas (Fig. 4) show that the remaining 18.6%, indicated in Table 1 under the heading "others", is mainly composed of Si, Al, Cl and Na (in order of abundance), which are characteristic components of soil dust and

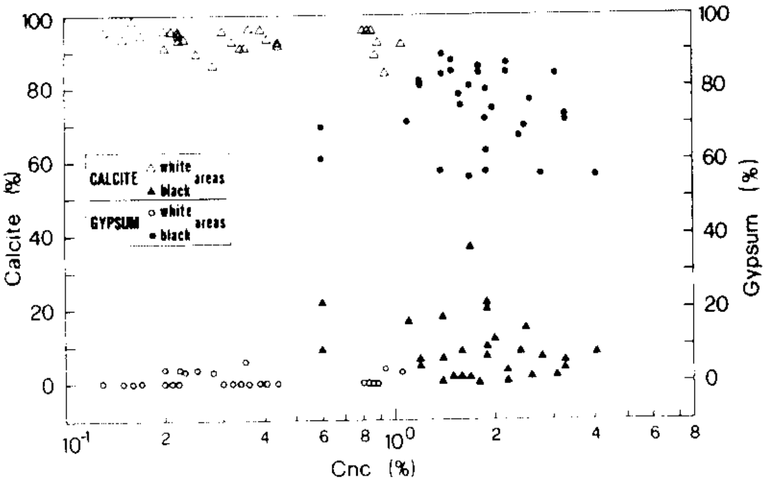

Fig. 3. Non-carbonate carbon (C_{nc}) as a function of gypsum and calcite concentration measured in the black and white areas.

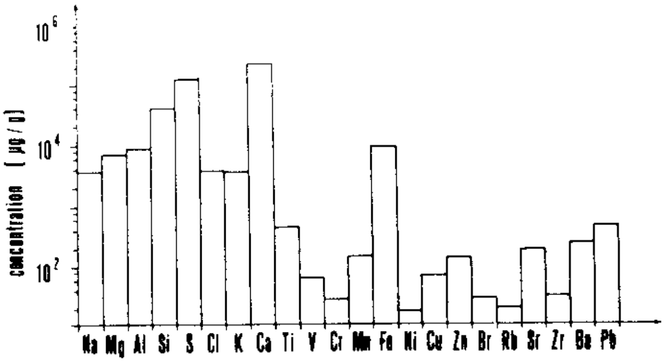

Fig. 4. Mean elemental concentrations measured in the black crusts.

sea spray of natural origin, and of heavy metals. The fraction of heavy metals (1.1%) is comprised of 10 metals: Fe, Ti, Pb, Mn, Zn, Cu, V, Cr, Zr and Ni in order of abundance. The presence, albeit in tiny quantities, of such elements is highly significant since they are efficient catalysts of surface deterioration reactions.

4. CONCLUDING REMARKS

The carbon associated with the black and white areas of a wide series of monuments in different sites of Italy was studied.

A methodology was developed with the aim of distinguishing carbonate carbon (due to the underlying rock) from the other carbon species. A quantitative index was identified for the carbonaceous particles embedded in the damaged layers in the form of non-carbonate carbon (C_{nc}). Therefore, our data show that, after sulphur, the non-carbonate carbon is the main anthropogenic component of atmospheric deposition contributing to black crust formation in urban areas.

White areas were also found to contain C_{nc}, albeit in modest concentrations.

Finally, the C_{nc} values reveal a direct correlation with the gypsum concentration and an inverse correlation with the calcite content.

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