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# Thermal analysis in cultural heritage safeguard: an application

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## Abstract

Damage layer formation on buildings is due to the deposition of atmospheric pollutants and their interaction with the underlying materials. The composition of black crusts is therefore closely related to the characteristics and levels of pollution in the surrounding environment. Thus, the study of its constituents is of fundamental importance in planning strategies for the protection and conservation of monuments and historic buildings. Damage layers have been shown to be primarily composed of carbonaceous particles embedded in gypsum, pointing to the overwhelming role of combustion-derived air pollution in their formation. The identification and evaluation of elemental carbon and other carbon species constituting the non-carbonate fraction of total carbon is required in investigating the damage on historic buildings in urban areas. The removal of organic carbon is a critical step in the analytical methodologies used for the measurement of elemental carbon. The paper describes a study performed on black crust samples from historic buildings of two Italian towns, on which the carbon compound discrimination was achieved by applying an analytical methodology based on thermal analysis.

*Keywords:* Combustion analysis; Carbon speciation; Elemental carbon; Material damage; Cultural heritage

## 1. Introduction

It is well known that atmospheric pollution is the main agent responsible for the damage encountered on calcareous buildings located in urban areas [1]. On sheltered surfaces, the weathering of stones and mortars leads to the formation of damage layers which commonly present a characteristic dark colour [2]. This phenomenon causes serious stone decay processes, especially on carbonate matrices, and appears to have accelerated over the past 50 years, as can be easily inferred from the continual blackening and repeated restoration of historic buildings and monuments currently occurring in European cities.

Black crusts have been found to be primarily composed of carbonaceous particles embedded in gypsum [3], and since they originate from combustion processes, their presence testifies to the overwhelming role of combustion-derived air pollution in the formation of the damage layers [4].

Over recent decades the degradation of stones and other structural components used in ancient and modern masonry has been extensively studied, with particular attention focused on the sulphation process occurring on carbonate materials. However, only a few recent works report measurements on the atmospheric content of carbonaceous particles, addressing the issue of their possible role in gypsum formation [5–7].

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In the atmosphere, carbonaceous particles primarily derived from various combustion processes, and over the last century their concentration in urban areas has undergone a drastic, quasi-exponential increase. All combustion processes produce abundant amounts of carbonaceous species that contain organic and elemental carbon [8]. While the atmospheric concentrations of sulphur dioxide (the first pollutant responsible for sulphation) have been drastically reduced in recent years, the air contents of carbonaceous particles has continued to rise.

Because combustion is a ubiquitous pollution source, carbonaceous particles are observed in damage layers in all environments. The few existing data on the speciation and measurement of carbon material show that non-carbonate carbon is, after sulphur, the main element originating from atmospheric deposition [9].

The carbon found in black crusts may have different origins, such as (a) calcium carbonate, basically due to the underlying material [10]; (b) deposition of atmospheric particles from multipollutant sources [11–13]; (c) biological weathering due to organisms that produce, among their metabolic secretions, formic, acetic and oxalic acids [14–17]; (d) treatments with organic materials used in the past to preserve monuments and buildings [18].

The total carbon (TC) present in damage layers on stones and mortars is composed of three main fractions:

$$\mathrm{TC} = \mathrm{CC} + \mathrm{OC} + \mathrm{EC}$$

where CC is carbonate carbon, nearly all of which originates from the stone or mortar constituting the monument or building; OC is the organic carbon of both biological and anthropic origin, linked to the action of micro-organisms on surfaces and to the deposition of primary and secondary pollutants; and EC is elemental carbon, mainly due to the aerosol emitted by combustion processes and, therefore, a quantitative index of the carbonaceous particles embedded in the black crusts [19]. Together; OC and EC constitute the non-carbonate fraction of total carbon (NCC).

Since EC and many of the components of OC are tracers of specific anthropic sources typical of urban areas, such as vehicle exhaust, road dust, industrial combustion and domestic heating systems [20,21], the measurement of non-carbonate carbon, the discrimination of EC and OC and the characterisation of the organic fraction, are all essential for a complete identification of the main components of the damage layers on monuments, and for the characterisation of sources.

The availability of a correct, accurate and reproducible analytical method for a complete carbon balance in black crusts is of major importance in studying the effects of the interaction between atmospheric pollutants and the environment, including those on human health and the conservation of cultural heritage [22].

The literature contains a wide variety of carbon speciations in complex carbon compound materials on atmospheric samples, performed by means of several different techniques. However, the analytical procedures adopted in such studies make their results unsuitable for comparison. In fact, the critical step in common to all the procedures is the removal of organic carbon.

Furthermore, information regarding the carbonaceous components in black crusts on buildings and the carbonaceous particles in damage layers is generally limited to the identification of the different types of embedded particles, on the basis of their morphology and elemental composition by optical microscopy and scanning electron microscopy [23,24]. Finally, data on elemental and organic carbon in black crusts are extremely rare [25].

Since buildings and outdoor statues and monuments act as repositories of airborne pollutants, the chemical composition of black crusts directly reflects the surrounding atmospheric environment [26]. The characterisation and evaluation of carbon compounds in damage layers on monuments are necessary for a correct partitioning of pollutant sources and identification of the threshold levels required for a sustainable protection and conservation of cultural heritage.

We present below a study carried out on the carbonaceous material in damage layers on monuments of two Italian cities, where carbon speciations were obtained by applying a methodology based on thermal analysis preceded by specific chemical treatments.

## 2. Experimental

Samples were collected from the black damage layer (Fig. 1) on monuments and buildings located in

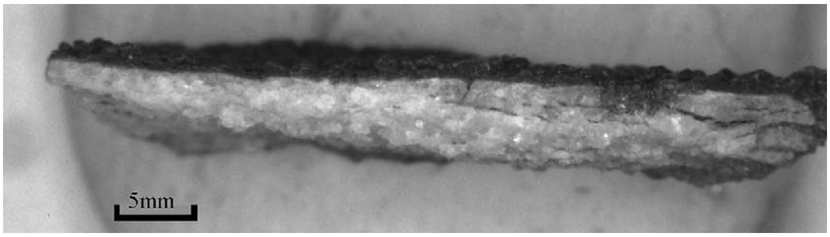


Fig. 1. Stereomicrograph of a damage stone specimen from the Rasponi Palace (Ravenna) showing at the surface the black crust formation.

Table 1
Samples collected and characteristics of their sampling position

| Sample | City | Monument | Characteristics |
|---|---|---|---|
| PT | Pisa | Leaning Tower | Black crust of the entrance door in the external trodden of the fifth order path, sector west |
| PB1 | Pisa | Baptistery | Black crust sampled on the 19th century capital, east sector on the right of the entrance |
| PB2 | Pisa | Baptistery | Black crust of the arch between the column on the right of the entrance and the column of PB1 sample |
| RC | Ravenna | S. Francesco Church | Black crust of the column basements of the lodge on the right side of the façade |
| RP1 | Ravenna | Rasponi Palace | Black crust of the column surfaces of the balcony at the first floor of the front façade |
| RP2 | Ravenna | Rasponi Palace | Black crust of the back part of the palace, at 1 m above ground level |

the centre of two major historic cities in Italy: Pisa and Ravenna. The towns in question are similar in urban extension, population, level of industrialisation and geographic position. Pisa lies about 8 km from the Tyrrhenian Sea, and Ravenna about 7 km from the Adriatic.

Samplings were performed on two monuments in Pisa's Piazza dei Miracoli, i.e. the Leaning Tower and the Baptistery (Fig. 2), and on Ravenna's Rasponi Palace (main building of the university) and S. Francesco Church. All of these important masonry works are built in low porous carbonate stones, materials in which the black crust and undamaged stone can be easily distinguished thanks to a well-defined interface. The specimens and sampling characteristics are listed in Table 1.

After collection, the samples were dried and stored at 20 °C in a nitrogen environment, until the time of analysis.

With the purpose of identifying the atmospheric carbonaceous particles deposited and embedded in the gypsum crystals, scanning electron microscopy was carried out, using a Philips XL 20 equipped with a dispersive energy microanalyser (SEM–EDX).

Fig. 2. Capital of the Baptistery of Piazza dei Miracoli in Pisa where black crusts are clearly evident.

In order to quantify the gypsum, the main product of stone degradation, differential and gravimetric thermal analysis (DTA–TGA) by Netzsch STM was performed after the specimens were ground in an agate mortar.

Subsequently, to discriminate and evaluate the carbon fractions, the powder specimens underwent the analytical procedure [19], previously set up and tested on standards of similar composition to black crusts. All the experimental measurements of carbon were carried out by means of thermal analysis (CHNSO) using a Carlo Erba Analyzer.

The analytical procedure consists of three fundamental steps, each performed on a different part of the same damage layer specimen:

(a) thermal analysis on one part of the bulk sample to obtain the TC value;
(b) prior to thermal analysis, a second part is treated with HCl vapours in order to eliminate the CC and measure non-carbonate carbon (OC + EC). The procedure adopted, described in detail in a previous paper [27], requires the decomposition of carbonates and the complete removal of $CO_2$;
(c) a third part undergoes thermal analysis, after the elimination of the inorganic matrix and organic species, for the determination of the residual EC. The procedure for this stage involves the following steps: (i) elimination of carbonates using a hydrochloric acid treatment; (ii) dissolution of basic organic materials and breaking up of silicates by treatment of the residue with HCl 37% in an air-tight tube at 140 °C, followed by centrifugation and rinsing; (iii) solubilisation of the most insoluble salts using an $Na_2CO_3$ saturated solution and, subsequently, elimination of carbonates, as described above; (iv) dissolution of acidic organic materials, of quartz and amorphous silica derived from HCl treatments of silicates, and completion of the previously begun solubilisation using concentrated hydrochloric acid, submitting the residual samples to five alternate treatments at 140 °C, in an air-tight glass tube, with KOH 30% and HCl 37%, each followed by centrifugation and rinsing; (v) desiccation of the residue at 180 °C, until constant weight is attained; (vi) analysis by combustion of the remaining sample to evaluate the elemental carbon content.

After the measurement of TC, NCC and EC in the three steps using CHNSO combustion analysis, CC and OC are calculated.

Finally, the organic fraction was investigated by ion chromatography (IC) to evaluate the formate, acetate and oxalate content, these anions being important tracers of specific biologic and anthropic sources [28–30]. The simultaneous quantification of water-soluble organic and inorganic anions is carried out using a Dionex Ion Chromatograph (model 4500i), equipped with conductivity detector (Dionex CDII), adopting the methodology reported in the literature [31].

## 3. Results and discussion

SEM–EDX analyses evidence the formation of gypsum crystals with the typical laminar structure [32], due to the mineralogical transformation of the carbonate matrix into sulphate [33–35], alongside the presence of carbonaceous particles deposited on the stone surfaces and embedded within the crust during its growth (Fig. 3).

The DTA and TGA data indicate a gypsum mean concentration of 57.33% in Pisa and 73.66% in Ravenna. Carbonates, expressed as $CaCO_3$, show a very different concentration in the Pisa samples, with a mean value of 22.33%, while all the specimens from Ravenna present a similar content, with a mean amount of 3.79%. Because the carbonates in damage layers derived almost exclusively from the underlying material, their presence due to atmospheric deposition being negligible, where the sampling was carried out with a small quantity of substrate, calcium carbonate shows low and similar values. Fig. 4 shows the differential and thermogravimetric (DTA–TGA) analyses curves of a black crust sampled in Pisa.

Using the analytical methodology based on the combustion analyses described above, the discrimination and measurement of the different carbon components was performed. The values of TC, CC, NCC, OC, EC and OC/EC ratio are given in Table 2.

The total carbon concentration, referring to the bulk sample weight, ranges between 6.79 and 1.33% in Pisa and between 3.09 and 1.78% in Ravenna. The TC values measured are typical of specimens collected on stone monuments in urban areas [36].

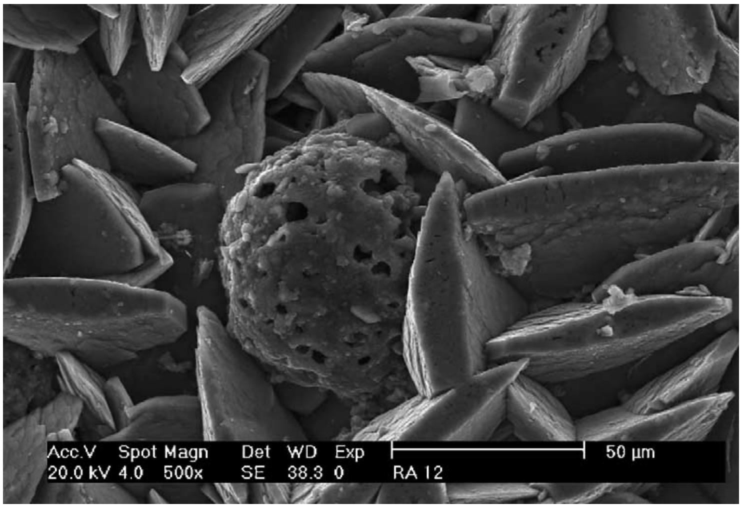
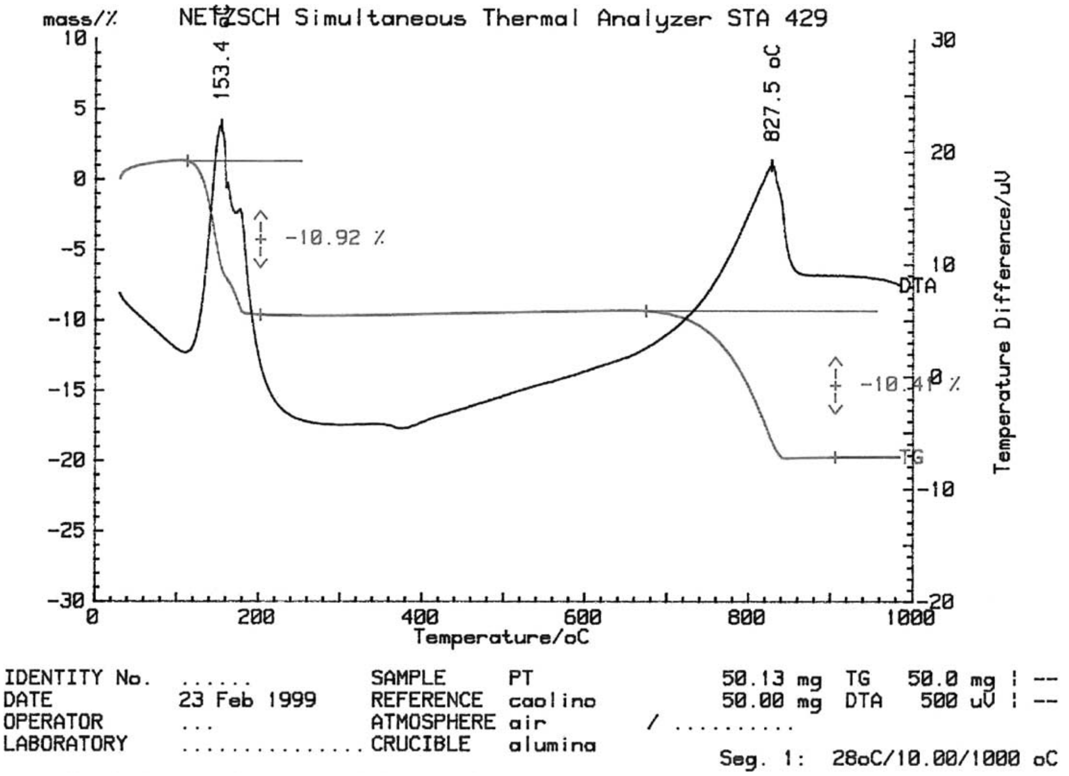


Fig. 3. Scanning electron micrograph of a damage layer showing gypsum crystals with lamellar habit which embed a spongy carbonaceous particle.



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IDENTITY No.  ......            SAMPLE      PT              50.13 mg  TG    50.0 mg ! --
DATE          23 Feb 1999       REFERENCE   caolino         50.00 mg  DTA   500 uV  ! --
OPERATOR      ...               ATMOSPHERE  air         / .........
LABORATORY    ...............   CRUCIBLE    alumina
                                                            Seg. 1:  28oC/10.00/1000 oC
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Fig. 4. Differential and thermogravimetric analysis (DTA–TGA) curves of a black crust sampled on the Leaning Tower of Pisa showing the percentage concentrations of gypsum and carbonates.

Table 2
Total carbon (TC), non-carbonate carbon (NCC), elemental carbon (EC) concentrations (%) measured in black crusts by combustion analysis (CHNSO) and carbonate carbon (CC), organic carbon (OC), OC/EC ratio calculated

| Sample | TC | CC | NCC | OC | EC | OC/EC |
|---|---|---|---|---|---|---|
| Pisa | | | | | | |
| PT | 6.79 | 5.43 | 1.36 | 0.80 | 0.56 | 1.43 |
| PB1 | 1.33 | 0.14 | 1.19 | 0.60 | 0.59 | 1.02 |
| PB2 | 4.12 | 3.09 | 1.03 | 0.67 | 0.36 | 1.86 |
| Ravenna | | | | | | |
| RC | 1.78 | 0.22 | 1.56 | 1.20 | 0.36 | 3.33 |
| RP1 | 3.09 | 1.64 | 1.45 | 0.67 | 0.78 | 0.86 |
| RP2 | 2.69 | 0.18 | 2.51 | 1.64 | 0.87 | 1.89 |

The results obtained analysing the specimens collected in the two cities reveal a marked difference in the carbonate carbon contents, especially in the black crusts from Pisa. The high variability in the percentage of CC with respect to TC is due to the presence of calcite fragments embedded within the damage patina, or scraped from the underlying stone during sampling. This observation highlights the necessity of measuring and eliminating the CC fraction when carbon of atmospheric origin must be discriminated and quantified.

Non-carbonate carbon, ranging between 1.36 and 1.03% in Pisa, and 2.51 and 1.45% in Ravenna, represents on average 29.17 and 73.02% of total carbon, respectively. In the two cities the percentage of NCC with respect to TC is very different depending on the different CC content, while the variability of the individual NCC percentage values is reasonably low when related to the total mass, evidencing how the fraction of TC not deriving from the stone has a common origin.

The data for OC contents of the Pisa and Ravenna samples, with mean values of 0.69 and 1.17%, respectively, show that the organic fraction represents, on average, 57.98 and 63.59% of NCC, respectively. These results confirm that there is a wide range of possible OC sources, and that the measurement of organic carbon is of great importance in order to evaluate the

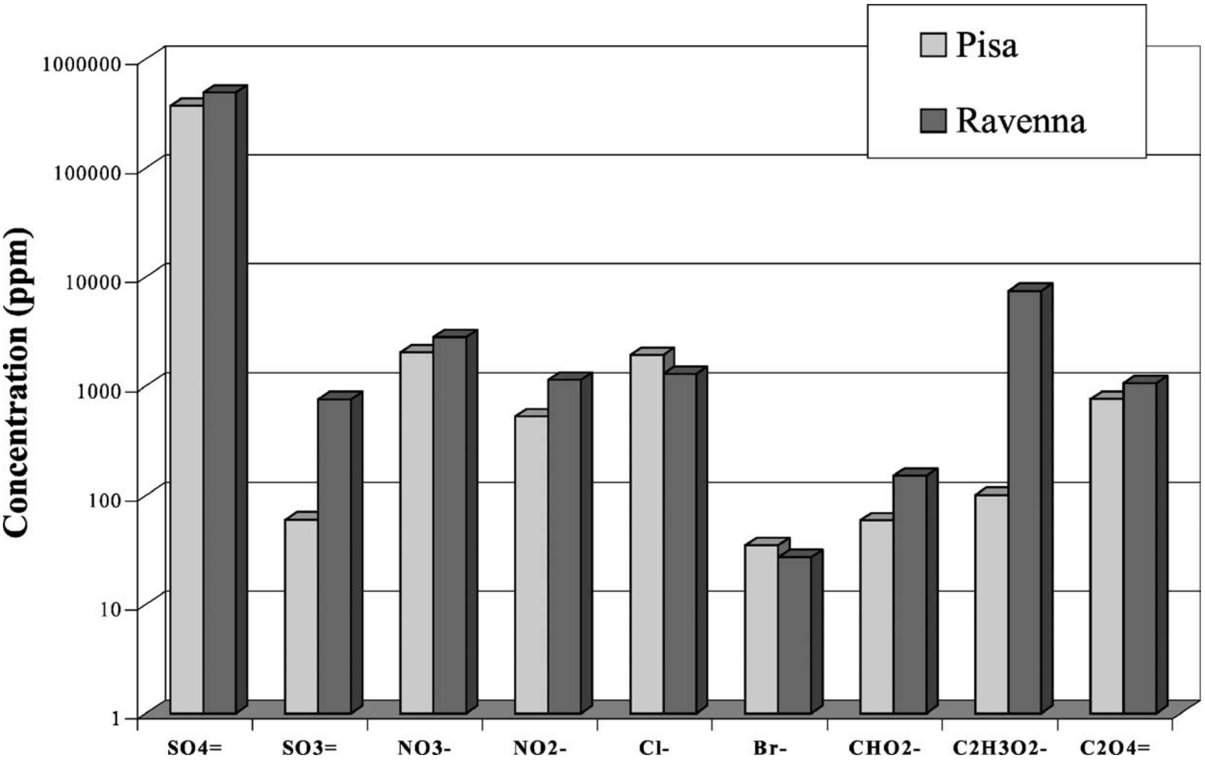

Fig. 5. Mean anion concentrations measured by IC in the black crusts sampled.

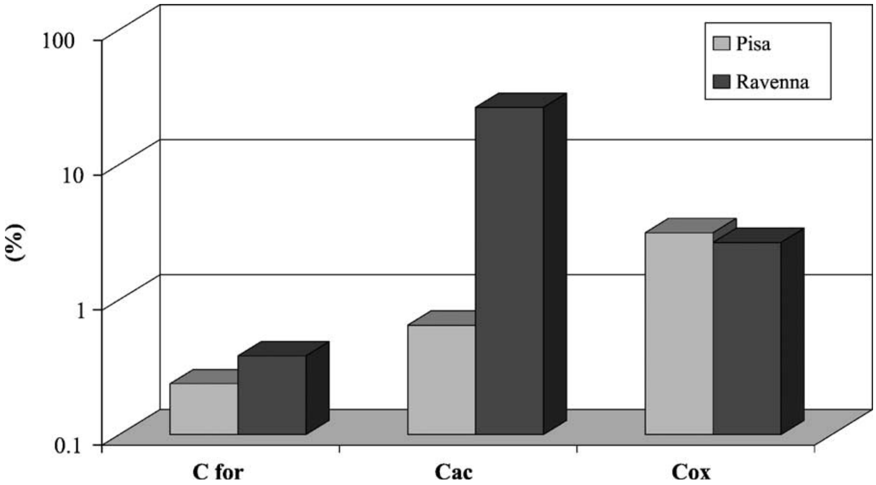

Fig. 6. Relative mean percentage of carbon due to formate (Cfor), acetate (Cac) and oxalate (Cox) anions with respect to the OC concentration in Pisa and Ravenna samples.

contribution of atmospheric deposition and establish the pollutant sources responsible for the formation of the deterioration layers.

Elemental carbon has similar mean values in Pisa (0.50 ± 0.1%) and Ravenna (0.67 ± 0.3%) and represents 42.02 and 36.41% of non-carbonate carbon, respectively. Since EC is almost exclusively a product of combustion processes and a good marker for combustion-generated aerosol deposited on stone surfaces, these results indicate a significant pollution level in the areas around the towns in question. Moreover, since the EC in black crusts is mainly due to the deposition of atmospheric carbonaceous particles, elemental carbon constitutes a quantitative index of their abundance. Both sites reveal similar characteristics with regard to the organic and elemental carbon content. The reasonably low variability in the OC and EC data obtained by thermal analyses suggests that the carbon fraction deriving from atmospheric deposition has a common origin in the two cities.

The ratio between the OC and EC contents is quite homogeneous in Pisa, while presenting a marked variability in Ravenna, a difference which may indicate that the organic fraction at the latter site is not exclusively attributable to combustion emissions [13].

The IC data (Fig. 5) reveal the presence of sulphates with the highest mean concentration in both cities, confirming gypsum as the main constituent of black crust, followed by nitrates, chlorides, nitrites, sulphites and bromides. Many of these anions are essentially due to human activities. With the exception of chloride and bromide, all the anions detected are present in slightly greater quantities in Ravenna than in Pisa. The IC results also show the constant presence of formates, acetates and oxalates, the organic anionic tracers of specific natural and anthropic sources [14,37,38]. Fig. 6 reports the relative mean percentage of organic carbon due to formate (Cfor), acetate (Cac) and oxalate (Cox) anions in Pisa and Ravenna samples.

In Ravenna, acetates are the organic anions measured in the highest concentration and account, on average, for more than 60% of organic carbon.

## 4. Conclusions

The carbon content in black crusts sampled on monuments and historic buildings has been studied. A thermal analytical methodology was used with the aim of distinguishing carbonate, non-carbonate, organic and elemental carbon in total carbon, and quantifying the amounts present.

The methodology comprises three steps of carbon thermal analysis. The first, using the bulk sample, provides the TC measure. The second permits the quantitative determination of NCC by analysing the specimen after the elimination of carbonates by treatment with HCl vapours. Finally, the EC content is obtained by submitting the sample to a preliminary chemical treatment bringing about the elimination of carbonates, inorganic matrix and organic material. Carbonate and organic carbon are then evaluated.

The results obtained indicate that thermal analysis distinguishes satisfactorily between carbonate, organic and elemental carbon and allows a reliable evaluation of their quantities, crucial data for a complete carbon balance in black damage crusts on historical stones. In this context, the identification of carbon compounds is important for obtaining information on weathering processes and on the typology of carbonaceous particles embedded in damage layers.

The innovative thermal analysis applied here turns out to be suitable for the discrimination and measurement of the carbon fraction in damage layers on buildings, where carbonate carbon accounts for 40–50% of the total carbon, unlike the case of atmospheric aerosol, where CC is almost negligible. In fact, the analytic methodology generally used for carbon analysis in atmospheric particles is not suitable for application to black crusts, since total carbon is limited to OC and EC quantification.

Our data show that, after sulphur, total carbon is the main anthropogenic component of atmospheric deposition present in damage layers on buildings, and that in all the samples analyzed the OC fraction is always greater than the elemental one, except in the RP1 specimen from Ravenna. The predominance of OC over EC highlights the important role played by vehicular traffic and other organic sources in the pollution of cities.

The values of anion concentrations, obtained by ion chromatography analysis, reveal the presence of sulphate with the highest mean concentration, confirming that external masonry undergoes a sulphation process, the transformation of $CaCO_3$ into gypsum. Formate, acetate and oxalate, the organic anions also measured with the IC technique, are found to be constantly present in both Pisa and Ravenna samples, with the highest concentration in the latter.

The availability of suitable analytic methodologies is important both in damage assessment of monument and historical buildings in urban areas and in defining a sustainable protection and maintenance of the cultural heritage.

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