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Isotopic analysis of black crust samples from the Monza Cathedral (Italy): a preliminary study

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Abstract – **The degradation of historical buildings surfaces through the formation of black crusts is a process mainly related to air pollution. The origin of air pollutants can be determined by measuring the stable isotope ratio of their main elements. In this study, the results obtained from the isotopic analysis of BCs taken from the historical Monza cathedral, an important monument placed in Monza, a highly polluted city of Northen Italy, are discussed. In particular, stable isotope ratios of carbon, sulphur and oxygen of two black crust samples (namely MD and MS) were measured by Isotope Ratio Mass Spectroscopy. The obtained δ^{13}C, δ^{34}S and δ^{18}O values suggest that anthropogenic pollution is responsible for the formation of black crusts on the façade of this cathedral.**

I. INTRODUCTION

The degradation of cultural heritage caused by exposure to atmospheric pollutants is a growing concern, especially for buildings and monuments located in the historic centres of large cities [1–8]. The chemical interaction of stone surfaces of historical buildings with atmospheric pollutants such as sulphur dioxide (SO_2) can originate dark-coloured deposits called black crusts (BCs) [9]. BCs are referred to the areas where atmospheric deposition accumulates together with the products of the chemical transformation of materials, and their formation is one of the most dangerous phenomena that occurs in architectural heritage. Different pollutants can be detected on BCs, including organic matter, metals and polycyclic aromatic hydrocarbons [10–13].

To characterize the nature and sources of degradation products is an important aspect to identify proper strategies to prevent damaging of cultural heritage. In this context, stable isotope ratio is a valuable tool to assess the origin and sources of pollutants, and it is employed in several fields of environmental science [14–18].

For instance, carbon stable isotope ratio (δ^{13}C) allows to discriminate between anthropogenic and biogenic origin of carbon dioxide: characteristic values of δ^{13}C for atmospheric CO_2 are observed depending on the type of environment (from −27 to −18.5 ‰ in rural areas, from −35 to −25.6 ‰ in urban environments and from −45 to −40 ‰ in house kitchens). Moreover, variations in the value of δ^{13}C were correlated with increasing or decreasing visitor presence or varying air pollution level, proving that this parameter can be used for air quality assessment in cultural heritage sites [19].

Sulphur isotope ratio, expressed as δ^{34}S, has been already used for the identification of the source of sulphur in black crusts and efflorescences formed on stone surfaces of monuments and buildings [20–22]. Generally, the most important source of sulphur is SO_2 emissions from fossil fuels combustion by road vehicles and factories (δ^{34}S ranges from -5 to +10 ‰), although other sources such as marine and/or biological ones (δ^{34}S ~ +20 ‰) and construction materials (δ^{34}S ranges from +12 to +22 ‰) cannot be overlooked [21]. Moreover, the stable isotope ratio of oxygen (δ^{18}O) in sulphate contributes to the identification of the primary or secondary origin of the sulphate in BC samples [23,24]. In fact, the oxygen in the gypsum formed in the black crust can be derived either from atmospheric oxygen or from oxygen already present in SO_2. Only one example of stable carbon isotope ratio analysis of BCs is reported in the literature [25]. Nevertheless, the determination of this parameter can give very important information regarding the origin of the organic portion of the black crust. No literature papers report the simultaneous measurement of all three of these stable isotope ratios ($\delta^{13}C$, $\delta^{34}S$ and $\delta^{18}O$) for black crust samples.

In this study, the results of isotopic analysis on BCs samples collected from the historical Monza cathedral are reported. These BC samples have been previously characterized and they contemplate an accumulation of pollutants ranging from 280 to 650 years [26–28]. This makes it very interesting to study the sources of pollutants that over the years have contributed to the formation of black crusts and thus to the degradation of the materials of which the cathedral façade is made. Consequently, the aim of this study is the evaluation of the sources of air pollutants responsible for the formation of BCs, through the analysis of stable isotope ratio of carbon ($\delta^{13}C$), sulphur ($\delta^{34}S$) and oxygen ($\delta^{18}O$).

A. Case study: The Monza Cathedral (Monza, Italy)

Monza cathedral (Figure 1), officially the minor Basilica of San Giovanni Battista, is situated in the centre of the homonymous city, in the Lombardy region (Northen Italy).

Fig. 1. Photograph of the façade of the Monza cathedral (Monza, Italy).

The city is the third largest city in the Lombardy region and is characterized by high anthropogenic pollution (vehicular traffic, domestic heating, industrial and agricultural activities). The building was constructed under the supervision of the architect and sculptor Matteo da Campione between 1300 and 1350 AD, and it is characterized by alternating dark and white-coloured rows of stone blocks. The façade of this cathedral is a significant example of the 15th century architecture. Several restoration works were carried out from 1700 to 1900, and the last restoration took place in 2017.

II. MATHERIALS AND METHODS

Two samples of BCs developed onto marble stones were taken from the façade of the Monza cathedral (Figure 2), one on the right (MD) and one on the left (MS).

For these samples, years of pollution accumulation range from 280 (MS) to 650 (MD), depending on the height of the sample.

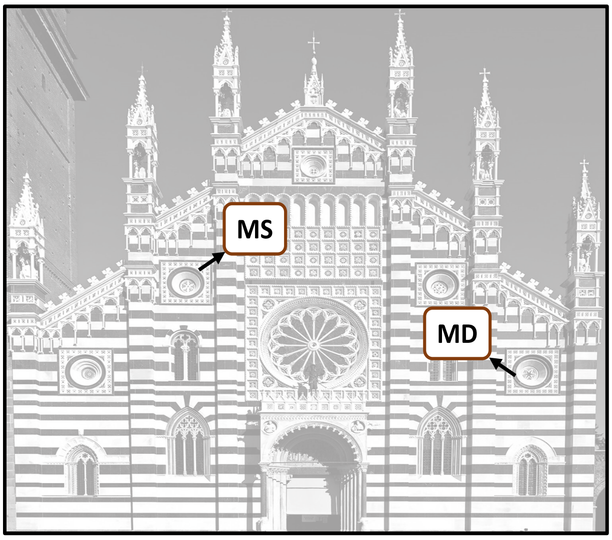

Fig. 2. Map of the position of BC samples analyzed.

The BCs were first reduced to powder with a mortar in order to obtain homogeneous samples for isotopic analysis.

A Delta Plus V isotope ratio mass spectrometer (IRMS) equipped with a Flash EA 1112 Elemental Analyzer (Thermo) was used to measure $\delta^{13}C$, $\delta^{34}S$ and $\delta^{18}O$ of BC samples. The stable isotope ratios were calculated according to the following equations:

$$\delta^{13}C = \frac{(R^{C}_{Sample} - R^{C}_{Reference})}{R^{C}_{Reference}} \tag{1}$$

$$\delta^{34}S = \frac{(R^{S}_{Sample} - R^{S}_{Reference})}{R^{S}_{Reference}} \tag{2}$$

$$\delta^{18}O = \frac{(R^{O}_{Sample} - R^{O}_{Reference})}{R^{O}_{Reference}} \tag{3}$$

-R_{Sample} is the isotope ratio of the sample (the number of atoms of the heavier isotope divided by the number of atoms of the lighter isotope of the same element, i.e. $^{13}C/^{12}C$, $^{34}S/^{32}S$ and $^{18}O/^{16}O$ ratio);
-$R_{Reference}$ is the isotope ratio of the reference material.
The delta values are multiplied by 1000 and expressed in units "per mil" (‰), against these international standards:
- Vienna Pee Dee Belemnite (V-PDB) for $\delta^{13}C$;
- Vienna Canyon Diablo Troilite (V-CDT) for $\delta^{34}S$;
- Vienna Standard Mean Ocean Water (V-SMOW) for $\delta^{18}O$.

The precision of measurement, expressed as one standard deviation, was 0.1‰.

III. RESULTS AND DISCUSSIONS

BCs from the Monza cathedral have already been characterized in term of the mineralogical and the carbonaceous fraction [26], and content of heavy metals and ions [27]. X-ray diffraction and Fourier Transform-Infrared spectroscopy analyses have pointed out that these BCs are mainly composed of gypsum, with some traces of oxalate and quartz. Types of metal detected (lead, zinc, copper and vanadium) and their concentration, represent the fingerprint of air pollution occurred in the different years of deposition in the considered BCs.

Firstly, elemental analysis (Table 1) reveals that the two samples have similar composition in terms of carbon (9.7-10.1 %), sulphur (2.0-2.3 %) and oxygen (34.1-35.5 %).

Table 1. Results of elemental analyses (% of C, S and O) with standard deviation.

Sample	% C	% S	% O
MD	9.7±0.5	2.3±0.9	35.5±0.9
MS	10.1±0.6	2.0±0.8	34.1±0.8

These values are greatly affected by the composition of the crust matrix, which is mainly carbonate. The low % of sulphur reflects the low amount of sulphates for these crusts, which, as previously reported, are developed over a very long time resulting in lower porosity and less interaction with surrounding air pollution [26].

The results of stable isotope ratio of carbon ($\delta^{13}C$), sulphur ($\delta^{34}S$) and oxygen ($\delta^{18}O$) are reported in Table 2. It is important to note that measured δ values are in general interpreted as mixed values from several environmental influences.

Table 2. Results of IRMS analyses (δ of C, S and O) with standard deviation.

Sample	$\delta^{13}C$ (‰)	$\delta^{34}S$ (‰)	$\delta^{18}O$ (‰)
MD	-1.1±0.2	-3.0±0.4	18.9±0.6
MS	-0.7±0.2	-2.6±0.3	19.1±0.5

In our case, the values of $\delta^{13}C$ (-1.1±0.2 ‰ for MD and -0.7±0.2 ‰ for MS) are derived from the contributions of both organic pollutants on the crust and the carbonate matrix. The same thing is observed in the case of oxygen, where the $\delta^{18}O$ values obtained (18.9±0.6 ‰ for MD and 19.1±0.5 ‰ for MS) are intermediate between the $\delta^{18}O$ of the carbonate matrix (20-27 ‰) and those of sulphate originated in the crust formation process (5-11 ‰). In the case of sulphur, instead, the measured $\delta^{34}S$ values (-3.0±0.4 ‰ for MD and -2.6±0.3 ‰ for MS) are typical of sulphates originated by interaction of stone materials with sulphur dioxide emitted from fossil fuels combustion by road vehicles and factories ($\delta^{34}S$ from -5 to +10 ‰).

In this context, it is of interest to identify the sources of local pollutants that result in the degradation of the work of arts. Several strategies can be employed for this purpose, such as continuous monitoring of air concentrations of pollutants by passive sampling systems and the use of smart monitoring stations [29]. In the last case, monitoring over even very long periods of time can be carried out in a straightforward manner, which is essential for studying degradation processes that occur over very long time frames such as the formation of black crusts.

The findings of this study confirm what has already been seen in previous works [26,27]: anthropogenic pollution from the industrial activities, as well as from vehicular traffic, is the main responsible for the formation of BCs on the façade of the Monza cathedral.

IV. CONCLUSIONS

In this study, stable isotope ratios of carbon, sulphur and oxygen of two BC samples from the historical Monza cathedral, are reported. These BCs are mainly composed of gypsum, with some traces of oxalate and quartz. Elemental analysis reveals that the two samples have similar composition in terms of % of carbon, sulphur and oxygen. The results of the IRMS measurements ($\delta^{13}C$ from -1.1 to -0.7‰, $\delta^{34}S$ from -3.0 to -2.6‰ and $\delta^{18}O$ from 18.9 to 19.1‰) highlight that anthropogenic pollution is the main responsible for the formation of BCs on the façade of this cathedral, confirming what has already been seen in previous works. This is only a preliminary study and further investigations should be performed to identify more specific sources of air pollution on BC samples.

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