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A multi-analytical approach for the identification of pollutant sources on black crust samples: Stable isotope ratio of carbon, sulphur, and oxygen

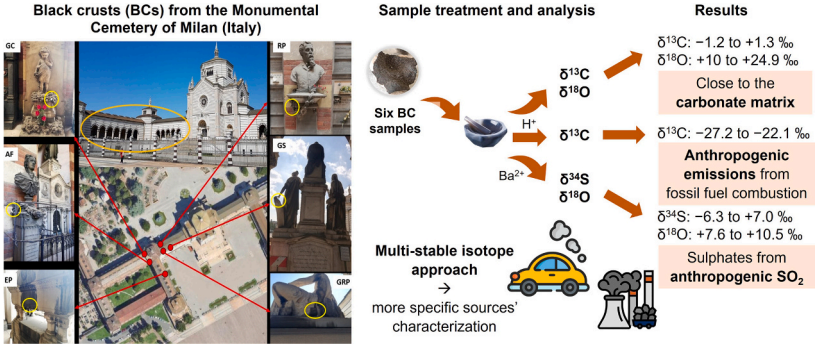
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HIGHLIGHTS

- C, S and O isotopes were combined to assess pollutant sources on black crust samples.
- Carbon, sulphur and oxygen stable isotope ratios were determined by IRMS.
- $\delta^{13}C$ values are in line with anthropogenic emissions from fossil fuel combustion.
- $\delta^{34}S$ and $\delta^{18}O$ values suggest sulphates formation from anthropogenic SO_2.
- Multi-stable isotope approach allows a more specific characterization of sources.

GRAPHICAL ABSTRACT



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ABSTRACT

This study is focused on the identification of pollutant sources on black crust (BC) samples from the Monumental Cemetery of Milan (Italy), through a multi-analytical approach based on the determination of stable isotope ratios of carbon, sulphur, and oxygen. Six black crust samples, mainly developed on marble sculptures over a time span of 100–150 years, were analysed.

For the first time, $\delta^{13}C$ was measured for BC samples: $\delta^{13}C$ values of the pulverized samples (from −1.2 to +1.3 ‰) are very close to the values obtained from the carbonate matrix, whereas after the removal of the matrix through acidification, $\delta^{13}C$ values of BC samples from Milan range from −27.2 to −22.1 ‰, with no significant variation between samples with different ratios of organic carbon to elemental carbon. In sum, the $\delta^{13}C$ values obtained for all BC samples fall within the range of anthropogenic emissions such as vehicle traffic, coal combustion and industrial emissions.

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$\delta^{34}S$ and $\delta^{18}O$ values of sulphate from BC samples range from −6.3 to +7.0 ‰ and from +7.6 to +10.5 ‰, respectively. Coupling the analysis of the oxygen isotope ratio with that of sulphur enables a more precise identification of the origin of sulphates: the observed isotopic composition falls in the range typical for anthropogenic emission of sulphur dioxide.

Overall, in this study, C, S and O isotopes were combined for the first time to assess pollutant sources on black crust samples: this multi-stable isotope approach allowed to show that the BC formation on monuments from the Monumental Cemetery of Milan mostly results from anthropogenic emissions from fossil fuels combustion by road vehicles and factories, as well as domestic heating.

1. Introduction

It is well known that air pollution is one of the main causes of the degradation of stone materials in urban settings (Comite et al., 2017; Pironti et al., 2023). In fact, the interaction of specific atmospheric pollutants (e.g. sulphur dioxide, particulate matter etc) with stone materials generates dark-coloured deposits called black crusts (BCs) (Belfiore et al., 2013; Comite et al., 2020b; Fermo et al., 2018; Pozo-Antonio et al., 2017). Identifying the origin of the pollutants that caused the formation of black crusts is of particular importance in preventing their formation on historical monuments. In this context, stable isotope ratios are valuable tools to assess origins and sources of different type of samples (Pironti et al., 2017; Zanasi et al., 2006), being employed in several fields of environmental science, e.g. atmospheric pollution (Aguilera and Whigham, 2018; Genot et al., 2020; Gong et al., 2024; Guo et al., 2021; Jung et al., 2022; Motta et al., 2022; Négrel et al., 2012; Pironti et al., 2022; Proto et al., 2014; Xing et al., 2023; Zhao et al., 2021), water pollution (Peters et al., 2019; Ricciardi et al., 2022), commercial products (e.g. food) authentication (Camin et al., 2016; Pironti et al., 2021, 2020, 2016) and medicine (Motta et al., 2009).

Sulphur stable isotope ratio, expressed as $\delta^{34}S$, has been already employed to identify the sources of sulphur in BCs formed on stone surfaces of monuments and buildings (Aroskay et al., 2021; Buzek and Šrámek, 1985; Klemm and Siedel, 2002; Kloppmann et al., 2014, 2011; Kramar et al., 2011; Longinelli and Bartelloni, 1978; Přikryl et al., 2004; Rivas et al., 2014; Torfs et al., 1997; Vallet et al., 2006) and in other types of stone degradation related to soluble salts (e.g. efflorescences, subflorescences and powdering) (Kloppmann et al., 2014, 2011; Kramar et al., 2011). The emission of sulphur dioxide from fossil fuels combustion by road vehicles and factories ($\delta^{34}S$ from −5 to +10 ‰) is considered the most important source of sulphur. Other minor sources are gypsum plaster ($\delta^{34}S$ from +12 to +22 ‰) and marine and/or biological ones ($\delta^{34}S \sim +20$ ‰) (Aroskay et al., 2021). Generally, the measurement of the sulphur stable isotope ratio in sulphates is combined with the measurement of the oxygen stable isotope ratio ($\delta^{18}O$). In fact, the determination of $\delta^{18}O$ contributes to the identification of the primary or secondary origin of the sulphate in BC samples: the oxygen in the gypsum can be derived either from atmospheric oxygen, atmospheric water or from oxygen already present in sulphur dioxide (Kloppmann et al., 2014, 2011; Kramar et al., 2011).

At the best of authors' knowledge, only one study concerning carbon isotope ratio analysis of black crust samples is reported in the literature: a $\delta^{13}C_{V\text{-}PDB}$ value of −20.1 ‰ was observed for a black deposit associated with pictographs at Little Lost River Cave, Idaho, suggesting an origin from animal tissue (cooking residue) (Steelman et al., 2002). On the contrary, several studies are reported regarding the use of $\delta^{13}C$ analysis to characterize the emission sources of airborne particulate matter (Aguilera and Whigham, 2018; Fisseha et al., 2009; Ho et al., 2006; Huang et al., 2006; Morera-Gómez et al., 2021; Singh et al., 2023; Widory et al., 2004; Zenker et al., 2020). In fact, the carbon stable isotope analysis of particulate matter is useful for understanding the sources of pollutants and distinguishing between vehicle emissions ($\delta^{13}C$ values from −28.3 to −24.5 ‰) and biomass burning ($\delta^{13}C$ values from −34.7 to −25.4 ‰ for C3 plants and from −22.2 to −13.0 ‰ for C4 plants) (Aguilera and Whigham, 2018). A wider range of $\delta^{13}C$ values has been observed for non-vehicle anthropogenic emissions, such as combustion of coal, charcoal, and fireplace (−30.1 to −23.4 ‰) (Aguilera and Whigham, 2018). It should always be considered that samples from mixed sources have $\delta^{13}C$ values averaged between those of the individual origins. The carbonaceous fraction in the aerosol particulate matter, besides inorganic carbon (carbonate), mostly consists of elemental carbon (EC) and organic carbon (OC), the sum of which is referred to as total carbon (TC) (Fermo et al., 2020; Huang et al., 2006; Morera-Gómez et al., 2021). In this context, most of the investigation on carbon stable isotope ratio regard $\delta^{13}C$ composition of TC to perform source apportionment studies (Aguilera and Whigham, 2018; Górka et al., 2012; Kunwar et al., 2016; Masalaite et al., 2015; Widory et al., 2004). Only few studies report the separate measurement of the $\delta^{13}C$ in the EC and OC components, which would allow a more precise source apportionment, offering the possibility of studying aerosol transformation processes in the atmosphere (Cao et al., 2011; Fisseha et al., 2009; Ho et al., 2006; Huang et al., 2006; Morera-Gómez et al., 2021; Zenker et al., 2020). However, no significant differences between $\delta^{13}C$ values of EC and OC are usually observed, due to the homogeneity of the anthropogenic sources, and the efficiency of the combustion (Huang et al., 2006).

Definitely, 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. Consequently, the aim of this study is the evaluation of the sources of air pollutants responsible for the formation of BCs collected from the Monumental Cemetery of Milan (Northern Italy), through the analysis of stable isotope ratios of carbon ($\delta^{13}C$), sulphur ($\delta^{34}S$) and oxygen ($\delta^{18}O$).

2. Materials and methods

2.1. Materials

All the chemicals used for the measurements (hydrochloric acid 37 %, barium chloride dihydrate ≥99 %, dichloromethane and pentane HPLC grade) were purchased from Sigma-Aldrich (St. Louis, MO, USA).

2.2. Sampling points

The Monumental Cemetery of Milan is the oldest city cemetery design by architect Carlo Maciachini (1818–1899), built from 1864 onwards in an eclectic style and located nearby the centre of the city. It has now become an important tourist destination for its cultural interest as it houses a large number of burials monuments in some cases realized by famous artists.

Six fragments (referred to as GS, AF, GRP, RP, GC and EP) fallen from some of the monuments in the Western Gallery of the Monumental Cemetery of Milan (Fig. 1) were sampled between 2019 and 2020. About 1 g of each sample were placed in plastic bags, and stored refrigerated, avoiding the exposure to light, until the analysis was performed. A detailed description of all BC samples is reported in Table 1 (description and history of the works of art, the main material and the year of construction). Since the sculptures considered in this study are works of art dedicated to the memory of deceased members of wealthy Milanese families, they do not have proper names, but are identified with an

abbreviation containing only the initials of the name and surname of the deceased. The exposure context is a semi-confined outdoor type, as the artworks are located in one of the galleries of the Monumental Cemetery, which are outdoor areas with an arcade structure. Two sculptures (AF and GC) are located in a more sheltered area of the Western Gallery, while the other four (GS, GRP, RP and EP) are in more open parts of the Western Gallery.

2.3. Samples' treatments

BC samples were finely pulverized in a mortar and firstly analysed as they are. Three different treatments were then carried out on the pulverized samples.

To remove the organic matter, a Soxhlet extraction was carried out on a weighted amount of sample (about 0.2 g) using a mixture of dichloromethane/pentane:1/1 *v*/v for 12 h. Solids were recovered by filtration and dried at 100 °C for at least one night.

To remove the carbonate matrix, BC samples were acidified according to the following procedure. A weighted amount of pulverized BC sample (about 0.2 g) was treated with HCl 10 % to volatilize carbonate carbon; after the complete evolution of CO_2, sample was filtered and dried at 60 °C for at least one night.

To recover pure sulphates, sulphate minerals were dissolved in water and subsequently precipitated as $BaSO_4$, following a literature procedure (Kloppmann et al., 2011). A weighted amount of pulverized BC sample (0.05–0.5 g) was acidified with HCl 10 % to dissolve the carbonates, filtered, and then an excess of $BaCl_2$ (solution at 10 %) was added. The precipitate of $BaSO_4$ was then recovered on a 0.45 μm filter, washed with MilliQ water and dried at 60 °C for at least one night.

A summary of the analytical determinations carried out on the samples after the various treatments is given in Table 2.

2.4. Determination of sulphate (%) on pulverized samples

Sulphate content of pulverized samples was measured by ion chromatography (Dionex ICS- 1000 HPLC system equipped with a conductivity system detector, Thermo Fisher Scientific) following a literature procedure (La Russa et al., 2017): a weighted amount of pulverized BC sample (about 2–3 mg) was treated with 10 mL of MilliQ water and put in an ultrasonic bath for 1 h, then centrifuged to obtain the solution for IC analysis. The analysis was carried out with an Ion Pac AS14A column using 8 mM Na_2CO_3/1 mM $NaHCO_3$, a flow rate of 1 mL/min and a conductivity system detector working with an anion self-regenerating suppressor ULTRA (ASRS-ULTRA) suppression mode.

2.5. Isotope ratio mass spectrometry (IRMS) measurements

$\delta^{13}C$, $\delta^{34}S$ and $\delta^{18}O$ of BC samples were obtained through IRMS measurements following the instrumental conditions reported in this paragraph.

The samples were weighed in tin (around 2 mg for $^{13}C/^{12}C$ and $^{34}S/^{32}S$) or silver capsules (0.25 mg for $^{18}O/^{16}O$) on a microbalance. The



Fig. 1. In the central part, at the top, is shown the front view of the Monumental Cemetery of Milan (orange circle indicate the location of the Western Gallery), while at the bottom is shown the top view with the indication in red of the position within the Western Gallery of the sampled sculptures. The side parts show photos of the sculptures, where the yellow circle indicates the exact sampling point of the black crusts.

Table 1
Detailed description of the BC samples from the Monumental Cemetery (Milan, Italy).

Sculpture identifier	Description	Year of monument construction / Years of pollutants accumulation*	Main material
GS	Dedicated to the memory of engineer Giulio Sarti, GS, (1796–1866), the creator of the Milan-Monza railway line. Sculptor: Giovanni Stazza (Milan, 1818–1875). Pyramid-shaped honorary monument: on the highest point of the plinth is the remarkable life-size portrait of Sarti, depicted in a sitting position and intent on studying; next to him, two fine female figures act as allegories of work and science. The BC sample comes from the support behind the female figure.	1870 / 149	Carrara marble
AF	Dedicated to the memory of an adult woman (AF). Sculptor: unknown The artwork is a bust of a lady wearing a necklace and mantle, with a wreath of fruit and flowers at the base. The BC sample comes from the wreath of fruit and flowers.	1875 / 144	Marble
GRP	Dedicated to the memory of an adult man (GRP). Sculptor: unknown The artwork consists of a sarcophagus on which is placed a man sitting on a rock. The BC sample comes from the lower part of the seat.	1900 / 119	Marble
RP	Dedicated to the memory of an adult man (RP). Sculptor: unknown The artwork consists of an upper-class gentleman's bust with beard and shirt, presents a wreath of fruit and flowers. The BC sample comes from the wreath of fruit and flowers.	1884 / 136	Marble
GC	Dedicated to the memory of a little girl (GC). Sculptor: unknown The artwork is a bust of a lost little girl with her finger in her mouth on a throne of flowers, i.e. lilies. The BC sample comes from one of the flowers at lower right).	1906 / 114	Marble
EP	Dedicated to the memory of an adult man (EP). Sculptor: unknown The work of art consists of a sarcophagus without human representation, resting on small columns and on a plinth embroidered with ovules at the top. The BC sample comes from the lower part of the plinth.	1922 / 98	Calcarenite

* Difference between year of sample collection and year of monument construction.

Table 2
Summary of the analytical determinations performed after the various treatments.

Sample Treatment	Analytic determinations
Pulverized	% of C, S, O and SO_4^{2-}, $\delta^{13}C$, $\delta^{18}O$
Pulverized + acidified	$\delta^{13}C$
Pulverized + Soxhlet extracted + acidified	$\delta^{13}C$
Pulverized + acidified + $BaCl_2$ (recovered as $BaSO_4$)	$\delta^{34}S$, $\delta^{18}O$

$^{13}C/^{12}C$ and $^{34}S/^{32}S$ isotope ratios were measured using an isotope ratio mass spectrometer (Vision, Elementar, Langenselbold, Germany) connected with a continuous flow inlet system to a Vario Isotope Cube Elemental Analyser (Elementar, Germany). The $^{18}O/^{16}O$ isotope ratio was analysed using an isotope ratio mass spectrometer (Finnigan DELTA XP, Thermo Scientific, Bremen, Germany) after complete pyrolysis in an elemental analyser (Finningan DELTA TC/EA, high-temperature conversion elemental analyser, Thermo Fisher Scientific).

The stable isotope composition of a substance is typically expressed using the delta (δ) notation, with units in either parts per thousand (per mil, ‰) or in the SI unit Urey (mUr is equivalent to ‰), as recommended by IUPAC (Brand and Coplen, 2012). Specifically, stable isotope compositions are reported as variations of the molar ratio, R, of the heavy (^{i}E) to light (^{j}E) isotope of an element E or of a rare to common stable isotope (such as $^{13}C/^{12}C$ or $^{15}N/^{14}N$) relative to a reference standard (Skrzypek et al., 2022), according to the following equation:

$$\frac{\delta^{i}E_{sample/standard} = R\left(^{i}E/^{j}E\right)_{sample}}{R\left(^{i}E/^{j}E\right)_{standard} - 1} \quad (1)$$

The delta values are multiplied by 1000 and expressed in units per mil, ‰. The standard is an internationally recognized reference material, as is the Vienna Pee Dee Belemnite (VPDB) for carbon, the Vienna Standard Mean Ocean Water (VSMOW) for oxygen and hydrogen, and the Vienna-Canyon Diablo Troilite (VCDT) for sulphur. The isotopic values were calculated against two standards through the creation of a linear equation. Two internal working standards calibrated using international reference materials were used for $^{13}C/^{12}C$: fuel oil NBS22 ($\delta^{13}C = -30.03 \pm 0.05$ ‰), sucrose IAEA-CH-6 ($\delta^{13}C = -10.45 \pm 0.03$ ‰) (IAEA, International Atomic Energy Agency, Vienna, Austria). USGS 90 (Millet flour from Tuscany $\delta^{18}O = +35.90 \pm 0.29$ ‰) and NBS 127 (barium sulphate $\delta^{18}O = +9.3 \pm 0.4$ ‰) from the U.S. Geological Survey and IAEA were used to normalize the $^{18}O/^{16}O$ values. Barium sulphates IAEA-SO-5 and NBS 127 (IAEA) were applied for $^{34}S/^{32}S$ calibration. Each reference material was measured in duplicate at the start and end of the analytical run and each sample was also analysed in duplicate. The precision of measurement, expressed as one standard deviation, were 0.3 ‰ for $\delta^{13}C$ and $\delta^{34}S$, 0.5 ‰ for $\delta^{18}O$.

Thanks to the presence of the Elemental Analyser, it was also possible to obtain the elemental composition (in terms of % of C, O and S) of the pulverized samples from these analyses.

2.6. Statistical analysis

Statistical analysis, two-way ANOVA (analysis of variance), was performed using Origin 2018 software. In particular, the statistical differences between the $\delta^{13}C_{V\text{-}PDB}$ (‰) values of BC samples pre- and post-extraction of organic matter were evaluated. The null hypotheses for the ANOVA analysis were that there are no differences between the samples. The significance level was $\alpha = 0.05$.

3. Results and discussion

3.1. Carbon and oxygen stable isotope ratio of pulverized BC samples

The BC samples from the monumental Cemetery of Milan contemplate an accumulation of pollutants ranging from 98 to 149 years (Table 1) and have been already characterized in terms of their main components, as reported in (Comite et al., 2020a). Briefly, Scanning Electron Microscopy/Energy-Dispersive X-Ray Spectroscopy and Fourier-transform infrared spectroscopy with attenuated total reflection analyses showed that almost all the BC samples are made of gypsum, calcium carbonate derived from the matrix together with carbon substances, i.e. organic carbon and elemental carbon.

Firstly, BC samples were finely pulverized in a mortar, to obtain homogeneous samples for the analyses. In Table 3 the % of C, O and S obtained by the Elemental Analyser (coupled with the IRMS instrument), sulphate % determined by IC, and $\delta^{13}C_{V\text{-}PDB}$ (‰) and $\delta^{18}O_{V\text{-}SMOW}$ (‰) measured by IRMS are reported. It is worth to note that there is a very good accordance as regards S concentrations between the two techniques. As we can see from Table 3, most of the samples contain not negligible amount of carbon and oxygen derived from the carbonate matrix, except for the GRP sample, which contains >40 % of sulphates.

Consequently, the $\delta^{13}C_{V\text{-}PDB}$ (‰) and $\delta^{18}O_{V\text{-}SMOW}$ (‰) of the pulverized BC samples (Table 3 and Fig. 2) are very close to the values obtained from the carbonate matrix (1.5 ± 0.3 for $\delta^{13}C_{V\text{-}PDB}$, and 28.8 ± 0.6 for $\delta^{18}O_{V\text{-}SMOW}$, in line with literature data for calcites (Guo et al., 2018)). As previously observed (Ricciardi et al., 2023), the presence of a relatively large amount of carbonate matrix in the simply pulverized samples, causes an isotopic ratio value for both carbon and oxygen close to that of the matrix itself, making the influence of the organic carbon part (for $\delta^{13}C$) of the black crust, as well as sulphate (for $\delta^{18}O$), unappreciable. Only for the GRP sample the values are significantly different from the matrix, as only a small part of the matrix is present in this sample, as can be seen from the % of C, S and O.

3.2. Carbon stable isotope ratio of acidified BC samples vs elemental and organic carbon

As discussed above, only one literature study reported the carbon isotope ratio analysis of a black crust sample. In particular, a $\delta^{13}C_{V\text{-}PDB}$ value of −20.1 ‰ was observed for a black deposit associated with pictographs at Little Lost River Cave, Idaho (Steelman et al., 2002). Different studies are instead reported concerning the $\delta^{13}C$ analysis of particulate matter to characterize its emission sources (Aguilera and Whigham, 2018). The difference in the ranges of $\delta^{13}C$ values observed makes the distinction between biomass combustion and vehicular emission easier than distinguishing between vehicular emission and other anthropogenic emissions, such as coal combustion and industrial emissions, due to the closer ranges of $\delta^{13}C$ values. Likewise, the distinction in terms of $\delta^{13}C$ between the sources of OC and EC is complicated (Huang et al., 2006).

In this study, for the first time, $\delta^{13}C_{V\text{-}PDB}$ of six BC samples, from the monumental Cemetery of Milan, was measured using IRMS. An acid treatment was performed to remove the carbonate matrix: the obtained $\delta^{13}C_{V\text{-}PDB}$ (‰) are reported in Table 4. Moreover, we compare these data with the $\delta^{13}C_{V\text{-}PDB}$ (‰) values obtained after the extraction of organic matter and acidification (Table 4).

$\delta^{13}C_{V\text{-}PDB}$ values for the majority of samples ranges from −27.2 to −22.1 ‰, only for EP a very different value was observed (−1.8 ± 0.8 ‰). After the removal of organic matter, a narrower range of values was obtained (from −26.4 to −23.7 ‰). Statistical differences between the $\delta^{13}C_{V\text{-}PDB}$ (‰) values of BC samples pre- and post-extraction of organic matter are observed only for samples AF (*p-value* of $9*10^{-3}$) and EP (*p-value* of $4*10^{-22}$). The very strange value for the EP sample seems to derive from a different composition of the matrix of this sample, that comes from a calcarenite sculpture, and not from a marble sculpture like all the other samples. The acid treatment carried out on EP sample as it was, simply pulverized, did not allow all the carbonate matrix to be removed, still returning a $\delta^{13}C_{V\text{-}PDB}$ value intermediate between the crust and the matrix. After the removal of the organic matter by extraction with organic solvents, the $\delta^{13}C$ value for this sample (−23.7 ± 0.9 ‰) realigns to that of the other BC samples analysed. Most probably, the removal of the organic matter made it possible to completely remove the carbonate matrix with the acid treatment, allowing the value of the black crust part of EP to be observed. In sum, the values obtained for all BC samples fall within the range of anthropogenic emissions such as vehicle traffic ($\delta^{13}C$ from −28.3 to −24.5 ‰), as well as coal combustion and industrial emissions ($\delta^{13}C$ from −30.1 to −23.4 ‰). Indeed, nowadays the city of Milan suffers from high

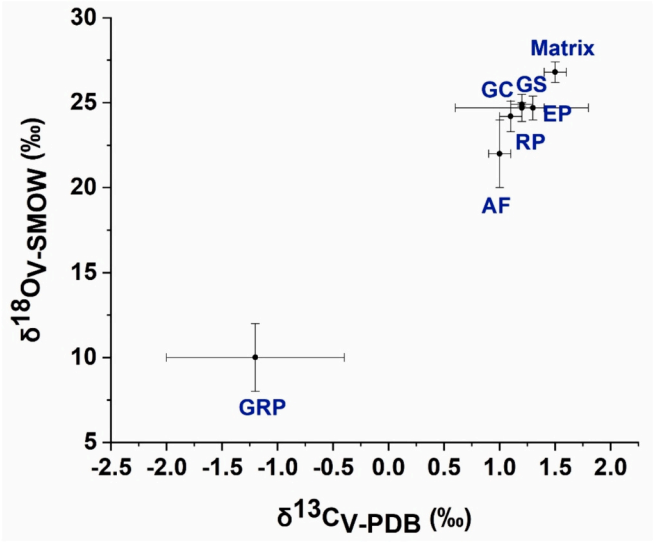


Fig. 2. $\delta^{18}O_{V\text{-}SMOW}$ (‰) vs $\delta^{13}C_{V\text{-}PDB}$ (‰) for the pulverized BC samples, with their standard errors. As can be seen from these data, sample processing to remove the carbonate matrix is necessary to obtain stable carbon isotope ratios only relative to the black crust.

Table 3
Amount (%) of carbon, oxygen, sulphur and sulphates, and $\delta^{13}C_{V\text{-}PDB}$ (‰) and $\delta^{18}O_{V\text{-}SMOW}$ (‰) of pulverized BC samples, with their standard errors.

Sample	C (%)	O (%)	S (%)	SO_4^{2-} (%)	$\delta^{13}C_{V\text{-}PDB}$ (‰)	$\delta^{18}O_{V\text{-}SMOW}$ (‰)
GS	11.0 ± 0.4	28 ± 7	1.2 ± 0.1	3.3 ± 0.2	1.2 ± 0.6	24.7 ± 0.8
AF	10.3 ± 0.3	33.6 ± 0.6	2.1 ± 0.2	5.9 ± 0.5	1.0 ± 0.2	20.4 ± 0.6
GRP	3.2 ± 0.2	39.1 ± 0.7	15 ± 1	41 ± 2	−1.2 ± 0.8	10 ± 2
RP	11.4 ± 0.7	32 ± 1	1.5 ± 0.1	4.2 ± 0.3	1.2 ± 0.2	24.9 ± 0.3
GC	11.1 ± 0.1	28 ± 3	1.5 ± 0.1	4.1 ± 0.3	1.1 ± 0.2	24.2 ± 0.9
EP	10.0 ± 0.6	34.4 ± 0.9	2.7 ± 0.2	7.8 ± 0.6	1.3 ± 0.2	24.7 ± 0.7

Table 4
$\delta^{13}C_{V\text{-}PDB}$ (‰) for all the black crusts analysed, with their standard errors.

Sample	$\delta^{13}C_{V\text{-}PDB}$ (‰)	$\delta^{13}C_{V\text{-}PDB}$ (‰) after organic matter extraction
GS	−27.2 ± 0.5	−26.0 ± 0.8
AF	−22.1 ± 0.9	−24.4 ± 0.5
GRP	−25.2 ± 0.3	−26.4 ± 0.6
RP	−26.7 ± 0.4	−25.9 ± 0.7
GC	−24.2 ± 0.3	−25.0 ± 0.6
EP	−1.8 ± 0.8	−23.7 ± 0.9

pollution produced by the intense vehicular traffic, from the high use of domestic heating, as well as from the pollution produced by the industrial sector and agricultural activities located in the Po valley. However, variations between sources of carbon pollutants over the broad period of development of the black crusts under study (between 100 and 150 years) must be considered. This may account for the co-presence of the different sources discussed above.

In addition, the variation of the $\delta^{13}C_{V\text{-}PDB}$ (‰) measured depending on the OC and EC values (Fig. 3), previously determined on these samples (Comite et al., 2020a), was considered.

Considering the $\delta^{13}C_{V\text{-}PDB}$ values obtained both before and after removal of soluble organic matter, there is no substantial variation in the carbon stable isotope ratio as the OC/EC ratio changes. As a matter of fact, a significant difference between $\delta^{13}C$ values of EC and OC is often not observed, especially when anthropogenic sources are homogeneous, and combustion is efficient (Huang et al., 2006). In fact, in the case of vehicular traffic emissions, the $\delta^{13}C$ value remains close to that of fuel used (e.g. −27.6 and − 26.2 ‰ for diesel and gasoline respectively). For instance, carbon stable isotope ratio of OC and EC was determined in particulate matter from fourteen cities in China, obtaining wide and overlapping ranges of $\delta^{13}C$ values (from −26.63 to −23.27 ‰, and from −26.90 to −23.08 ‰ for EC and OC respectively), probably due to the simultaneous presence of different sources (coal combustion and vehicular traffic) (Cao et al., 2011). Zenker and co-workers observed a narrower $\delta^{13}C$ interval for OC (from −28 to −26 ‰) in particulate samples from the Naples area, but the $\delta^{13}C$ values were close to those of the ambient filters (Zenker et al., 2020). On the contrary, a larger difference in the $\delta^{13}C$ values of EC (−23 ‰) and OC (−26 ‰) is noted in the case of particulate from a forest in Canada, attributed to a mixed origin of carbonaceous particles (biomass burning and background air) (Huang et al., 2006).

In this study, the values of total $\delta^{13}C$ obtained for BC samples are perfectly in line with the literature data for TC derived from anthropogenic emissions such as vehicle traffic, coal combustion and industrial emissions, with no substantial differentiation between the BC samples with different OC/EC ratios.

3.3. Sulphur and oxygen stable isotope ratio of sulphates from BC samples

Since isotopic fractionation does not significantly affect the $\delta^{34}S$ value during the formation of sulphates from gaseous sulphur species (Kramar et al., 2011), the $\delta^{34}S$ value of BCs reflects that of the sulphur present in the atmosphere at the time of their formation (Torfs et al., 1997). Thus, the study of this parameter can provide important information on the sources of air pollution at the sampled site.

$\delta^{34}S_{V\text{-}CDT}$ and $\delta^{18}O_{V\text{-}SMOW}$ values for BC samples from the Monumental Cemetery of Milan ranges from −6.3 to +7.0 ‰ and from +7.6 to +10.5 ‰ respectively (Table 5).

The S of sulphates on degraded stones can be derived from different

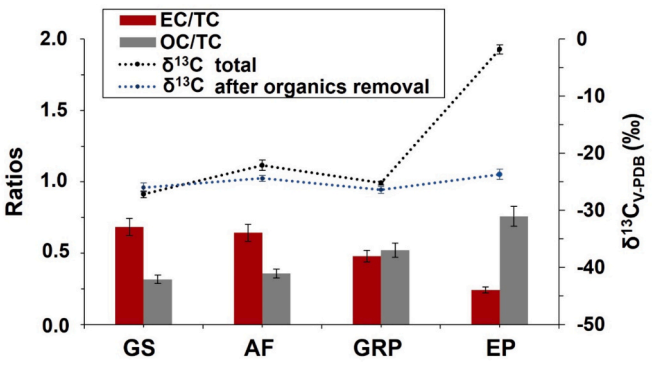


Fig. 3. $\delta^{13}C_{V\text{-}PDB}$ (‰) vs OC/TC and EC/TC for GS, AF, GRP and EP, with their standard errors.

Table 5
$\delta^{34}S_{V\text{-}CDT}$ (‰) and $\delta^{18}O_{V\text{-}SMOW}$ (‰) for all the black crusts analysed, with their standard errors.

Sample	$\delta^{34}S_{V\text{-}CDT}$ (‰)	$\delta^{18}O_{V\text{-}SMOW}$ (‰)
GS	+3.7 ± 0.7	+9.4 ± 0.3
AF	+2.0 ± 0.9	+8.3 ± 0.8
GRP	−6.3 ± 0.2	+7.6 ± 0.4
RP	+3.5 ± 0.2	+8.7 ± 0.3
GC	+7.0 ± 0.3	+10.5 ± 0.4
EP	+1.4 ± 0.2	+9.8 ± 0.6

sources: sulphur dioxide in the air and sulphate in the aerosols (mainly in the fine fraction), sulphates from rainwater and construction materials, and also pyrite oxidation (Kramar et al., 2011). Atmospheric SO_2 has a very wide range of $\delta^{34}S$ values (from −40 ‰ to +30 ‰), with negative values being associated with coal combustion and positive values with oil combustion (Newman et al., 1991). Consequently, mixed values are generally observed for anthropogenic SO_2 (from fossil fuel combustion and vehicular traffic) in urban areas (narrower range, from −5 ‰ to +10 ‰) (Torfs et al., 1997). The presence of sulphate from construction materials leads to $\delta^{34}S$ values from +12 ‰ to +21 ‰, even if values around +21 ‰ were observed also for marine origin (Montana et al., 2008), while the oxidation of sedimentary sulphides (pyrite) showed values around −12 ‰ or lower (Kloppmann et al., 2011; Kramar et al., 2011). The range of $\delta^{34}S$ values observed in this study (from −6.3 to +7.0 ‰) suggests a sulphate origin from anthropogenic SO_2.

The use of a multi-isotopic approach, which also includes the analysis of the stable isotope ratio of the oxygen present in sulphates, makes it possible to discriminate between the possible sources indicated by the sulphur isotope ratio value. Moreover, the oxygen isotope ratio makes it possible to find indications of the mechanism of sulphate formation in black crusts: the oxygen that is added to sulphur dioxide (SO_2) to form sulphates (SO_4^{2-}) may derive from atmospheric oxygen O_2 and/or from water molecules in the atmosphere (Kramar et al., 2011). Since the rate of isotope exchange between SO_2 and associated water is very high, while that between SO_4^{2-} and water is extremely low, and the $\delta^{18}O$ values of atmospheric water is generally very low (down to −50 ‰), whereas that of atmospheric oxygen is generally positive (+23.8 ‰), the value of $\delta^{18}O$ is useful in discriminating the contributions of the two mechanisms of SO_4^{2-} formation mentioned above (Holt and Kumar, 1991). Consequently, a positive $\delta^{18}O$ value of the BCs indicates a relatively greater incorporation of O_2 from the atmosphere rather than from water, on the contrary, negative values suggest a higher input due to atmospheric water. In Northern Italy the $\delta^{18}O$ values of precipitation range from −15 to −4 ‰ (Bono et al., 2005; Giustini et al., 2016; Longinelli et al., 2006). The range of $\delta^{18}O$ values obtained for the BC samples under study (from +7.6 to +10.5 ‰) shows an increased influence of atmospheric oxygen incorporation respect to oxygen from water precipitation and is perfectly in line with sulphate formation from atmospheric SO_2 (from +5 ‰ to +10 ‰) (Novák et al., 2007), allowing any other origin to be excluded (Holt and Kumar, 1991).

For comparison, the values of $\delta^{34}S_{V\text{-}CDT}$ and $\delta^{18}O_{V\text{-}SMOW}$ of BCs from the most relevant studies are also reported in Fig. 4. Most studies conducted so far on black crusts have shown that the S and O isotopic composition of this type of samples is fairly homogeneous, with some shifts towards higher $\delta^{34}S$ for coastal urban contexts due to marine inputs (Aroskay et al., 2021). The observed isotopic composition in this study falls in the range typical for air pollution derived BCs, as reported for other monuments (Aroskay et al., 2021; Chabas et al., 2022; Kloppmann et al., 2014, 2011; Rivas et al., 2014; Torfs et al., 1997). The relatively homogeneous isotopic composition of these BCs may derive from the fact that the investigated samples come from monuments located at parts of Milan's Monumental Cemetery that do not differ greatly in terms of exposure to air pollution. All sculptures are, in fact, located in the Western Gallery of the Monumental Cemetery, an outdoor area with an arcade structure. AF and GC are in a slightly more sheltered

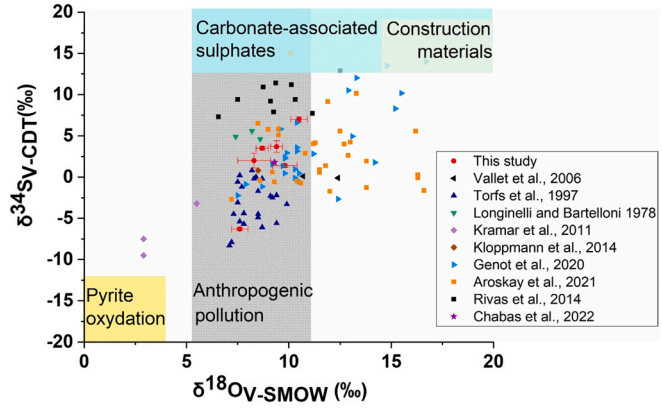


Fig. 4. $\delta^{34}S_{V\text{-}CDT}$ (‰) vs $\delta^{18}O_{V\text{-}SMOW}$ (‰) for all the black crusts analysed in this study (●), with their standard errors, and for the main studies reported in literature. The grey rectangle indicates the $\delta^{18}O$ - $\delta^{34}S$ zone of sulphates resulting from anthropogenic pollution (from Lee et al. (2002) and Faure (1986)); the other sulphates sources reported in literature are also shown in rectangles (carbonate-associated from (Rennie and Turchyn, 2014); construction material/gypsum plaster from (Kloppmann et al., 2011); oxidized pyrite from (Canfield, 2004)).

area of this Gallery, factor that does not allow discrimination between samples based on the isotope ratio values obtained.

This study shows that the BC formation on monuments from the Monumental Cemetery of Milan, a large urban area highly affected by different pollution sources, mostly results from anthropogenic SO_2 emissions from fossil fuels (coal and petroleum) combustion by factories, heating plants and vehicular traffic (Fig. 4). It is important to emphasise that today, SO_2 concentrations in the air are below the limits set by regulations because sulphur levels in fuels are very low. However, these samples account for an accumulation of pollutants over a period of >100 years, so the contribution of the fossil fuel source is evident. With regard specifically to the BC samples under study, it must be considered that these samples originated over a relatively long period of time, so the distribution between the different anthropogenic sources of SO_2 (coal and petroleum combustion etc.) may vary depending on the sample considered, reflected in the $\delta^{34}S$ and $\delta^{18}O$ values observed. By plotting the $\delta^{34}S_{V\text{-}CDT}$ (‰) and $\delta^{18}O_{V\text{-}SMOW}$ (‰) values as the years of accumulation change, some considerations can be made (Fig. 5).

No single trend in the value of sulphur and oxygen isotope ratios is observed for samples with different years of pollutants' accumulation. This may be due to the low number of samples investigated in the present study and the wide range of years considered (construction of sculptures from 1870 to 1922). Indeed, it must always be borne in mind that there was a different distribution of SO_2 sources in the years indicated. However, if only the oldest samples (GS, AF, RP and GRP) were considered, it is possible to observe a gradual decrease in both $\delta^{34}S$ and $\delta^{18}O$ values (corresponding to an enrichment in the lighter isotopes) as the years of pollutants' accumulation decrease. Turning to the two most recent crusts, GC and EP (114 and 98 years of accumulation respectively), this trend is lost for both elements (S and O). This observation can indicate a different distribution of sources and emissions after 1900, and it might be due to higher proportions of anthropogenic SO_2 emitted in recent years (Genot et al., 2020). However, these hypotheses need the analysis of a larger number of samples to be verified. Obviously, anthropogenic sources of SO_2 in a city like Milan have varied over the long period of formation of these black crusts, bearing in mind that the area under consideration is located on a road that is now heavily subject to vehicular traffic and close to a railway station, active since the early 1900s. Whereas before 1900, we can assume that the main sources of SO_2 were coal and wood combustion, there has been a shift towards a preponderance of emissions from vehicular traffic, which has been decreased in recent years due to strategies implemented to reduce air

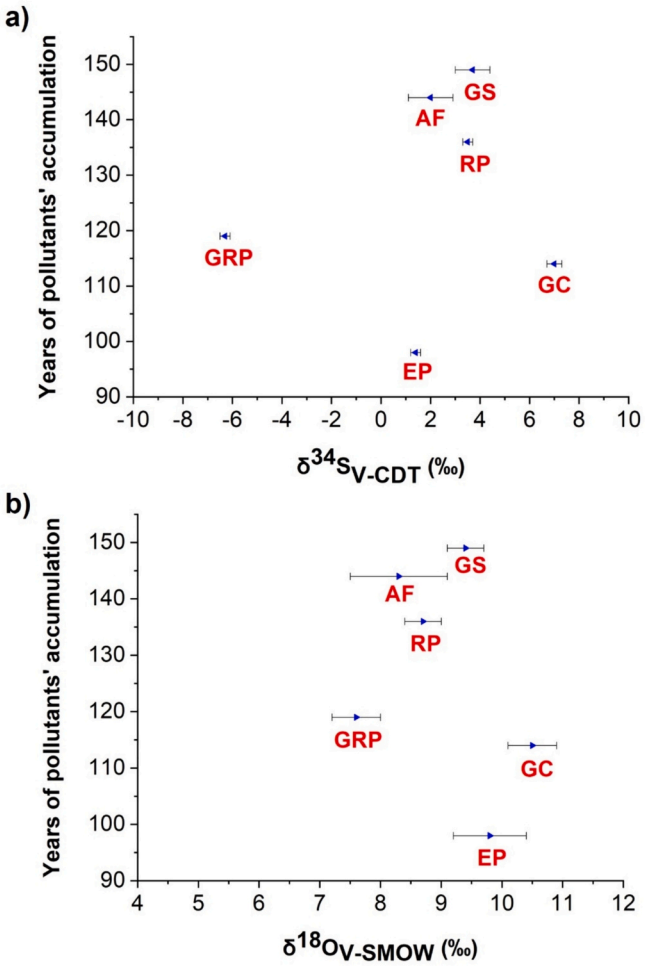


Fig. 5. Years of pollutants' accumulation vs $\delta^{34}S_{V\text{-}CDT}$ (‰) (a) and $\delta^{18}O_{V\text{-}SMOW}$ (‰) (b) for all the black crusts analysed, with their standard errors.

pollution. This accounts for the values observed for the black crusts under consideration in this study, in relation to the different periods of pollutant accumulation.

4. Conclusions

In this study, for the first time, pollutant sources on six BC samples from the Monumental Cemetery of Milan (Italy) were determined by a multi-stable isotope approach (analysis of carbon, sulphur and oxygen stable isotope ratios).

$\delta^{13}C$ values of the pulverized samples (from −1.2 to +1.3 ‰) are very close to the values obtained from the carbonate matrix. After the removal of the matrix through acidification, $\delta^{13}C$ values (from −26.4 to −23.7 ‰) are within the range of anthropogenic emissions such as vehicle traffic, coal combustion and industrial emissions. Moreover, total $\delta^{13}C$ values obtained for BC samples are perfectly in line with the literature data for total carbon derived from fossil fuels combustion, with no significant differentiation between the BC samples with different OC/EC ratios.

On the other hand, the observed isotopic composition of sulphates ($\delta^{34}S$ and $\delta^{18}O$ from −6.3 to +7.0 ‰ and from +7.6 to +10.5 ‰, respectively) falls in the range typical for air pollution derived BCs: sulphate formation is mainly due to the anthropogenic emissions of SO_2 and incorporation of atmospheric O_2.

The relatively homogeneous isotopic composition of these BCs may derive from the fact that the investigated samples come from monuments located at parts of Milan's Monumental Cemetery that do not

differ greatly in terms of exposure to air pollution.

Finally, this study shows that the formation of BCs, developed over a time span of 100–150 years, on monuments in a large urban area such as that of Milan, mostly results from anthropogenic emissions from fossil fuels combustion (petroleum and coal) by road vehicles and factories, as well as domestic heating.

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CRediT authorship contribution statement

Maria Ricciardi: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation. **Concetta Pironti:** Formal analysis, Data curation. **Valeria Comite:** Writing – review & editing, Validation, Conceptualization. **Andrea Bergomi:** Formal analysis, Data curation. **Paola Fermo:** Writing – review & editing, Validation, Supervision, Project administration, Conceptualization. **Luana Bontempo:** Writing – review & editing, Methodology, Investigation, Formal analysis, Data curation. **Federica Camin:** Visualization, Validation, Data curation. **Antonio Proto:** Validation, Supervision, Funding acquisition, Conceptualization. **Oriana Motta:** Writing – review & editing, Validation, Supervision, Project administration, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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