Natural and anthropogenic sources of total suspended particulate and their contribution to the formation of black crusts on building stone materials of Catania (Sicily)

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ORIGINAL ARTICLE

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Giuseppe Montana · Luciana Randazzo · Paolo Mazzoleni

Abstract Blackening and disaggregation of exposed surfaces of stone monuments are well-known effects of stone decay taking place in polluted urban environments all over the world. This paper aims to assess the contribution of natural and anthropogenic sources of total suspended particulate (TSP) causing permanent damage (black crusts) to the stone monuments of Catania (Sicily), one of the most popular "cities of art" of southern Italy. Atmospheric pollution of Catania, a typical Mediterranean coastal town, is mainly contributed by vehicle exhaust emissions rather than industrial ones. Episodically, the city also suffers gaseous and ash emissions (plumes) from the nearby Mount Etna volcano. Thus, to discriminate between natural and anthropogenic contributions to stone decay on Catania monuments, black crusts and TSP were sampled within the urban area and subjected to specific analytical procedures (optical microscopy, X-ray powder diffraction, Fourier transformed infrared spectroscopy, scanning electron microscopy equipped with energy dispersive spectrometry, ionic chromatography and dual inlet mass spectrometry). Mineralogical, chemical and isotopic characterization of black crusts and TSP provided new insights concerning the partition of sulfate sources in this particular urban context. The influence of Mount Etna emissions on both TSP and black crusts compositions was shown. Nevertheless, the key role of anthropogenic sources in the total sulfate budget was confirmed, while sea spray and volcanic emissions were found to make subordinate contributions. Quantitative data useful for the identification of the threshold pollution levels for preventive conservation of Catania monuments were obtained.

Keywords Total suspended particulate · Black crusts · Chemical analyses · Isotopic analysis · Catania (Sicily)

Introduction

The deterioration of stone materials used in historic buildings that, on the whole, represent the cultural heritage of a "city of art" can be considered a relevant phenomenon for both its scientific and socioeconomic impact. In the last few decades, the development of human activities, industrialization and urbanization with the release into the atmosphere of several products and substances constitutes a risk to the integrity of historic building materials that are subject to alteration phenomena due to the interaction with environmental agents (Realini et al. 1995; Rodriguez Navarro and Sebastian 1996; Lefèvre and Ausset 2002; Schiavon et al. 2004). Weathering has been considered a natural step in the "life cycle" of rocks since the pioneering papers in this field (Honeyborne and Harris 1958; Robinson and Baker 1975). However, it can be strongly accelerated by the action of acid substances derived from several combustion processes (Fassina et al. 1976; Del Monte et al. 1984; Ausset et al. 1999; Esbert et al. 2000; Delalieux et al. 2001; McAlister et al. 2006). Compositional and textural features of stone materials are acknowledged to be determining factors in the efficiency of the response offered against attack by aggressive environmental agents. In particular, mineralogical and chemical

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composition, grain size distribution and porosity all represent important properties that control, on the whole, the kinetics of degradation processes and the durability of stone materials (Winkler 1982; Amoroso and Fassina 1983; Camuffo 1986; Theoulakis and Moropoulou 1999; Moropoulou et al. 2001; Benavente et al. 2004; Cardell et al. 2008).

Especially since the second half of the 1970s, committees of European experts have started to develop a systematic scientific approach concerning different topics related to stone deterioration and conservation. In this context, for example, the contributions of RILEM (Réunion Internationale des Laboratoires et Experts des Matériaux, Systèmes de Construction et Ouvrages, established in 1947), ICCROM (International Centre for the Study of the Preservation and Restoration of the Cultural Property, established by UNESCO in 1956) and, in Italy, the "NorMal" Commission (Commissione Normalizzazione Materiali Lapidei, established in 1977) can be cited.

At present, the most common mechanisms of stone decay (blackening and crust formation, powdering due to cyclical salt crystallization, frost damage, differential erosion, etc.) can be considered to be rather exhaustively studied (Fitzner and Heinrichs 2002; Bonazza et al. 2005; Siegesmund et al. 2008; Toniolo et al. 2009). On the other hand, several critical revisions concerning the conservation interventions have also been made (Maxwell 1992; MacDonald et al. 1992; Moropoulou et al. 2003) since the 1990s. Moreover, the most recent research issues have been focused on new methods and materials, especially in terms of compatibility and reversibility requirements for diagnostic and restorative purposes like, for example, micro-Fourier transformed infrared spectroscopy (μ-FTIR), laser ablation inductively coupled plasma mass spectrometry (LA ICP-MS), laser beam cleaning and consolidation with nanoparticles technologies (Dei and Salvadori 2006; Chapoulie et al. 2008; Giussani et al. 2009).

The mechanisms of degradation of stone materials used in the historical buildings in Sicily have been studied since the 1990s (Alaimo et al. 1995; Cirrincione et al. 2000; Mazzoleni et al. 2003; Punturo et al. 2006; Montana et al. 2008). In Catania, one of the most popular "cities of art" of southern Italy, the modern intensification of air pollution has caused rapid damage to ancient monuments. The economy of the city is primarily based on cultural tourism, light industry and handicrafts, the tertiary sector and agriculture. Catania is a typical coastal town where atmospheric pollution is mainly contributed by vehicle exhaust emissions rather than industrial ones. Episodically, it also suffers gaseous and ash emissions (plumes) from the nearby Mount Etna, which is the largest active volcano in Europe, whose most recent activity was characterized by permanent open-conduit passive degassing interrupted by

eruptive paroxysms (Branca and Del Carlo 2005). Volatile species such as S, Cl, F and trace metals, together with major compounds (H_2O and CO_2), are thus continuously released in the volcano's plume. It must be underlined that the calculated yearly SO_2 fluxes in the Etna plume (1.2 Mt/a) represent approximately 10% of global terrestrial volcanic emissions (Allard 1997). Recent ash emissions by the Etna volcano (i.e., 2001, 2003, 2005, 2006–2007, 2008) blanketed the city, leading to severe risks to people's health as well as to monuments, infrastructures, agriculture and so on (Barsotti et al. 2010), with variable strength mainly depending on the dominant wind direction and speed.

This paper deals with the discrimination between natural and anthropogenic sources of total suspended particulate (TSP) in the urban area of Catania (Sicily). The study will determine the role played by TSP in blackening and thickening of stone surfaces of monuments. To identify the sources of dry solid pollutants, specimens of black crusts developed on different stone substrates were collected from ancient buildings situated in the old city area. At the same time, TSP was sampled in the urban atmosphere using low and high flow-rate vacuum pumps and analyzed. The results are expected to clarify the cause–effect mechanisms of stone decay and could also facilitate the creation of deterioration models that will represent a novel quantitative data set useful for decision-making procedures for preventive conservation in this city.

Sampling and analytical methods

Black crusts developed on stone surfaces were sampled, taking into account several characteristics: orientation of architectural elements, intensity of washout action, linear distance from the shoreline, height above ground level, level of road traffic and rock types (petrographic classification). Therefore, a total of 18 representative black crust samples were collected from the same number of significant historical buildings, all located in the ancient heart of Catania according to the indication of UNI-NORMAL 3/80 (Fig. 1).

TSP sampling was done by constant flow portable sampler (TCR Tecora Bravo H2) and by a high volume sampler (Staplex Model TF-1A). Two sampling points were chosen, both located in the city center and characterized by intense vehicle traffic. They were chosen on the basis of dominant wind flow regime, distance from localized dust sources (like unpaved streets, building demolition and construction activity or nearby industrial plants with dust emissions), relative closeness to the sea and proximity to emission sources represented only by vehicle traffic on roadways. The first was located at 18 m above ground level (Site 1: Corso Italia, 55), while the second was sited at
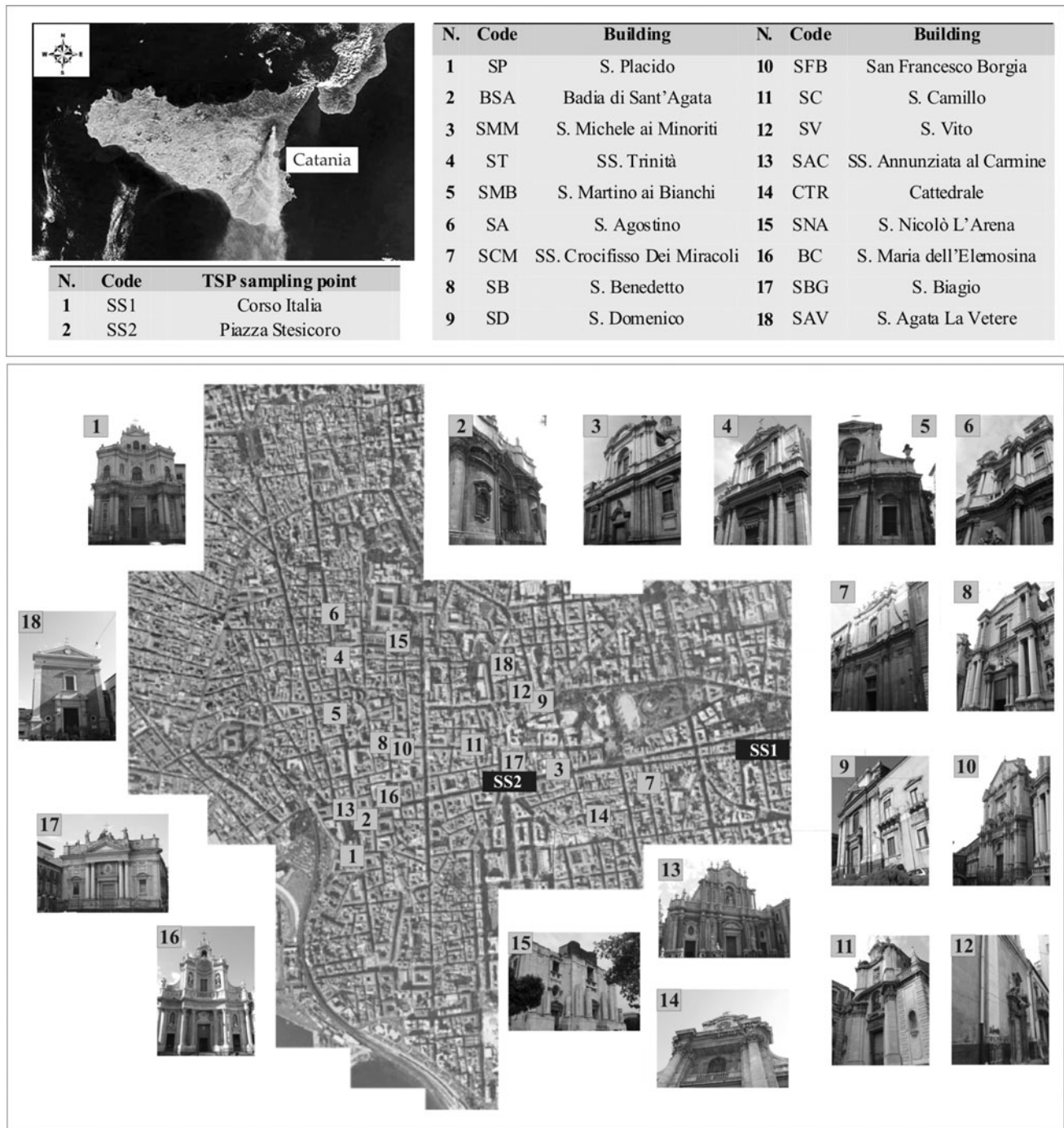
N.	Code	TSP sampling point
1	SS1	Corso Italia
2	SS2	Piazza Stesicoro

N.	Code	Building	N.	Code	Building
1	SP	S. Placido	10	SFB	San Francesco Borgia
2	BSA	Badia di Sant'Agata	11	SC	S. Camillo
3	SMM	S. Michele ai Minoriti	12	SV	S. Vito
4	ST	SS. Trinità	13	SAC	SS. Annunziata al Carmine
5	SMB	S. Martino ai Bianchi	14	CTR	Cattedrale
6	SA	S. Agostino	15	SNA	S. Nicolò L'Arena
7	SCM	SS. Crocifisso Dei Miracoli	16	BC	S. Maria dell'Elemosina
8	SB	S. Benedetto	17	SBG	S. Biagio
9	SD	S. Domenico	18	SAV	S. Agata La Vetere

Fig. 1 Position of TSP and black crusts sampling sites

ground level (Site 2: Piazza Stesicoro, 21). Three TSP samples (filters) per month were collected at each site from January to September 2008, giving a total of 54 TSP samples; each sample was collected over a 24-h period. Local meteorological data (wind speed and direction, temperature, relative humidity) and concentrations of the most important pollutants (SO_2, NO_x, CO, CO_2, PM_{10}) during the same time interval were obtained from the SIAS (Servizio Informativo Agrometeorologico Siciliano) and the civic monitoring network of Catania, respectively.

Black crust specimens were examined by means of the following procedures and analytical methods: petrographic characterization of thin sections by transmitted polarized light microscope observation; mineralogical analysis by X-ray powder diffraction (XRD) and Fourier transformed infrared spectroscopy (FTIR); micro-morphological and

qualitative chemical analysis through scanning electron microscopy (SEM–EDS); dosing of soluble salts by liquid chromatography (IC); and measurements of $^{34}S/^{32}S$ ratio by dual inlet mass spectrometry.

Thin sections were observed by means of optical microscopy (OM) using a Leica DM LSP polarizing microscope equipped with digital camera (Leica DC200). XRD analyses were performed on fine powdered samples by a Philips X'Pert Pro diffractometer with the following conditions: generator settings 40 kV and 40 mA; radiation CuKα ($\lambda = 1.5418$ Å); graphite monochromator; continuous scan $= 1°$ min^{-1}; and scan range 2–60°θ. Infrared spectroscopy was performed with a TENSOR 27 FT-IR spectrometer equipped with a HYPERION 1000 FT-IR microscope in the region 4,000–400 cm^{-1} using the ATR (attenuated total reflectance) method. Liquid chromatography was carried out by a Dionex DX120 system according to the procedure reported in the current Italian standards (UNI 11087:2003). An LEO 440 scanning electron microscope equipped with a Link Analytical ISIS energy dispersive spectrometer was used for morphological and qualitative microchemical analysis. Measurements of the $^{34}S/^{32}S$ ratio of black crust samples were obtained by dual inlet mass spectrometry. The conversion of gypsum to barium sulfate was obtained according to routine procedures (Grinenko 1962; Coleman and Moore 1978). Sulfate was extracted from the concentrates by leaching with distilled and degassed water. The sulfate solutions were separated and acidified, and BaSO$_4$ was precipitated. The dried BaSO$_4$ precipitate was loaded into a 5-cm-long, 6-mm-diameter quartz tube and dropped into a 9-mm-diameter quartz tube, the system was evacuated, and the sample was heated to 1,170°C. The gaseous products were passed over a hot copper plug (750°C) and separated cryogenically. The volume of SO$_2$ was measured and transferred to a suitable bottle for mass spectrometry. Prepared gases were analyzed on a mass spectrometer SIRA-II (VG-Isotech) in dual inlet mode. As a dual inlet system, sample gases are analyzed against an internal working SO$_2$ gas. This gas is calibrated to the CDT (Canyon Diablo Troilite) scale by analysis of at least three international reference materials: NZ-1 (IAEA-S-1), S° (IAEA-S-4), NBS-122, NBS-123 and NBS-127. Sulfur isotope results are reported as $\delta^{34}S‰$ on the VCDT (Vienna-Canyon Diablo Troilite) scale. The overall analytical reproducibility was 0.2‰. Isotopic results are presented as averages of duplicate analyses. It should be noted that only the black crust samples showing relatively more elevated concentrations of sulfate ions after liquid chromatography runs were selected for isotopic measurement.

TSP samples were weighed for mass measurements (gravimetric analysis). The net mass of TSP was obtained by weighing the preconditioned filter under a controlled environment (temperature $20 \pm 5°C$; relative humidity $50 \pm 5\%$ for 48 h) before and after sampling. Filter and field blanks were prepared following the same procedures and the obtained mass values were routinely subtracted.

Morphological and qualitative/quantitative microchemical analyses using SEM–EDS (LEO 440 equipped with Link Analytical ISIS energy dispersive spectrometer) were also carried out on TSP samples. To have statistically representative measurements, five portions approximately 1 cm^2 (area) were cut from each filter (giving a total of 270 subsamples) and analyzed independently and up to ten single quantitative analytical runs were performed on each portion by a reduced raster of 100 μm^2. Operating conditions for quantitative analysis were: 20 kV accelerating voltage, 600 pA beam current and 100 s live-time. ZAF correction of matrix effects was routinely applied. Natural mineral standards were used to calibrate quantitative analyses. The EDS elemental detection limit is estimated to be between 0.5 and 0.1 wt% according to Buseck and Bradley (1982), thus affecting the detectability of several trace elements (essentially metals) linked with anthropogenic air pollution. However, SEM–EDS requires a transcurable pre-treatment of the sample and, at the same time, several diagnostic major elements useful for differentiating between the most common sources of TSP can be quantified. Measurements of the $^{34}S/^{32}S$ ratio of TSP samples were performed following the operative conditions already described in the case of black crusts. However, in this case, the minimum amount of barium sulfate required for the analytical procedure followed (20 mg) was reached only for a very restricted number of samples (3 samples from a total of 54).

Results and discussion

Black crusts

Black crusts collected from the external walls of several historic buildings located in the center of Catania (see Fig. 1) were first subjected to thin-section petrographic characterization by optical microscopy. The sampled monuments of the city were frequently built from a combination of basaltic lava ashlars (locally quarried) and calcareous ones (calcarenites imported from the Hyblean Plateau, mainly from Syracuse area). The latter were mostly represented by red algae boundstone (Fig. 2a) belonging to the Mount Climiti Formation (Oligocene–Miocene) or by well-cemented fossiliferous packstone (Middle–Upper Pleistocene). It is interesting to note that black crusts were exclusively developed on calcareous substrates. The black crusts, generally adhering well to the lithic base and stratified, showed a relevant level of
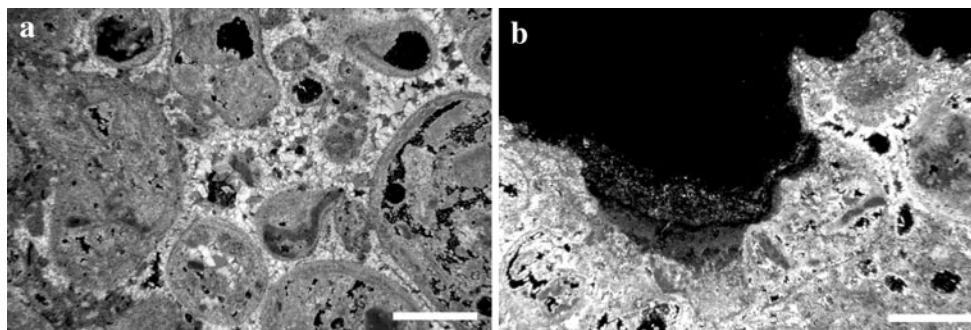
Fig. 2 Thin section microphotographs: **a** microscopic features of stone substrates; **b** microscopic characteristics of black crusts and their relations with stone substrate (crossed Nicol; *scale bar* 0.5 mm)

penetration along textural discontinuities (Fig. 2b). Their thickness was rather variable, usually ranging from a few tenths of microns up to 2 mm.

They presented a similar mineralogical composition, confirmed by XRD patterns and by infrared spectra, with gypsum and calcite being the prevalent mineralogical phases with traces of quartz, plagioclase, and more rarely weddellite (dihydrate calcium oxalate). Calcite can be considered a residual phase from the lithic substratum. Quartz and plagioclase in all probability derive from dust deposition, while both gypsum and weddellite are neo-formed alteration phases. Weddellite is reported predominantly as a product of the reaction between organic compounds and calcium carbonate (AA.VV. 1996).

The SEM–EDS analysis revealed the microstructure of black crusts, which were found to be composed of chaotic aggregates of gypsum crystals with lamellar habit and size up to 30 μm (Fig. 3a). Concerning bulk chemical composition, these layers show that S and Ca are by far the main components followed by smaller amounts of Mg, Al, Si and Fe, which are certainly related to the deposition of particulate matter (Fig. 3b). The presence of subspherical fly ash particles composed of Si, Al, Fe and S was also observed (Fig. 3c, d). Superficial absorption of SO_2 by these kinds of particles was strongly indicated to play a significant catalytic role in black crust formation (Hutchinson et al. 1992).

Liquid chromatography revealed analogous tendencies in terms of SO_4^{2-}, Ca^{2+}, Na^+ and Cl^- concentrations in all the analyzed black crusts (Table 1). The variability recorded for NO_3^- is likely to be correlated with more or less intense influences of various anthropogenic sources at the specific sampling points. HCO_3^- concentration reflects the variable contribution of the calcareous substrate to black crust formation. Mg^{2+} is poorly correlated with SO_4^{2-} ($R^2 = 0.19$) and not correlated with Ca^{2+} ($R^2 = 0.09$). These results suggest that their concentrations were controlled by different sources. However, the sum of these ions ($Mg^{2+} + Ca^{2+}$) shows an elevated positive correlation

with sulfate ions ($R^2 = 0.99$) suggesting that both are present in the form of sulfate salts in the black crusts. In any case, the abundance of magnesium could likely be ascribed to natural sources. The SO_4^{2-} anion was found to be the prevailing ionic species (average value 225.94 mg/l), confirming that sulfation was the most important process in their formation. In Fig. 4a, a linear diagram shows the variation in Cl^- and SO_4^{2-} concentrations measured in the studied samples. An outstanding enrichment in sulfate with respect to the seawater can be observed, which is indicative of additional sulfate sources, while chlorine concentration is lower. A good correlation between Ca^{++} and SO_4^{2-} in black crust samples ($R^2 = 0.97$) was also evident (Fig. 4b). Concerning the relative abundances of Na^+ and Cl^- (Fig. 4c), together with a good enough correlation ($R^2 = 0.83$), the black crust samples showed an average Na/Cl ratio equal to 0.75, which is slightly lower than the one known for Mediterranean seawater (0.86). These data suggest a relative surplus of chlorine with respect to sodium. In general, these results put forward achievable sources of sulfate and chlorine in the decay process of Catania monuments that could be agreeably explained considering also the role played by the emissions from the Mount Etna volcano. These considerations are also supported by the presence of neoformed mineralogical phases such as syngenite $K_2Ca(SO_4)_2 \cdot 2H_2O$, thenardite Na_2SO_4 and aphthitalite $K_3Na(SO_4)_2$ which were revealed by XRD and SEM–EDS of local black crusts in a previous work (Alaimo et al. 1995). Alkali metals (Na and K) can be originated straightforwardly by hydrolysis and dissolution reactions of feldspars and amorphous silica (glass), which are the main components of volcanic ash deposited at the stone surfaces.

Total suspended particulate

Figure 5 shows the results of gravimetric analysis of TSP focusing on the correlation between temperature, wind speed, wind direction and particulate abundances at the
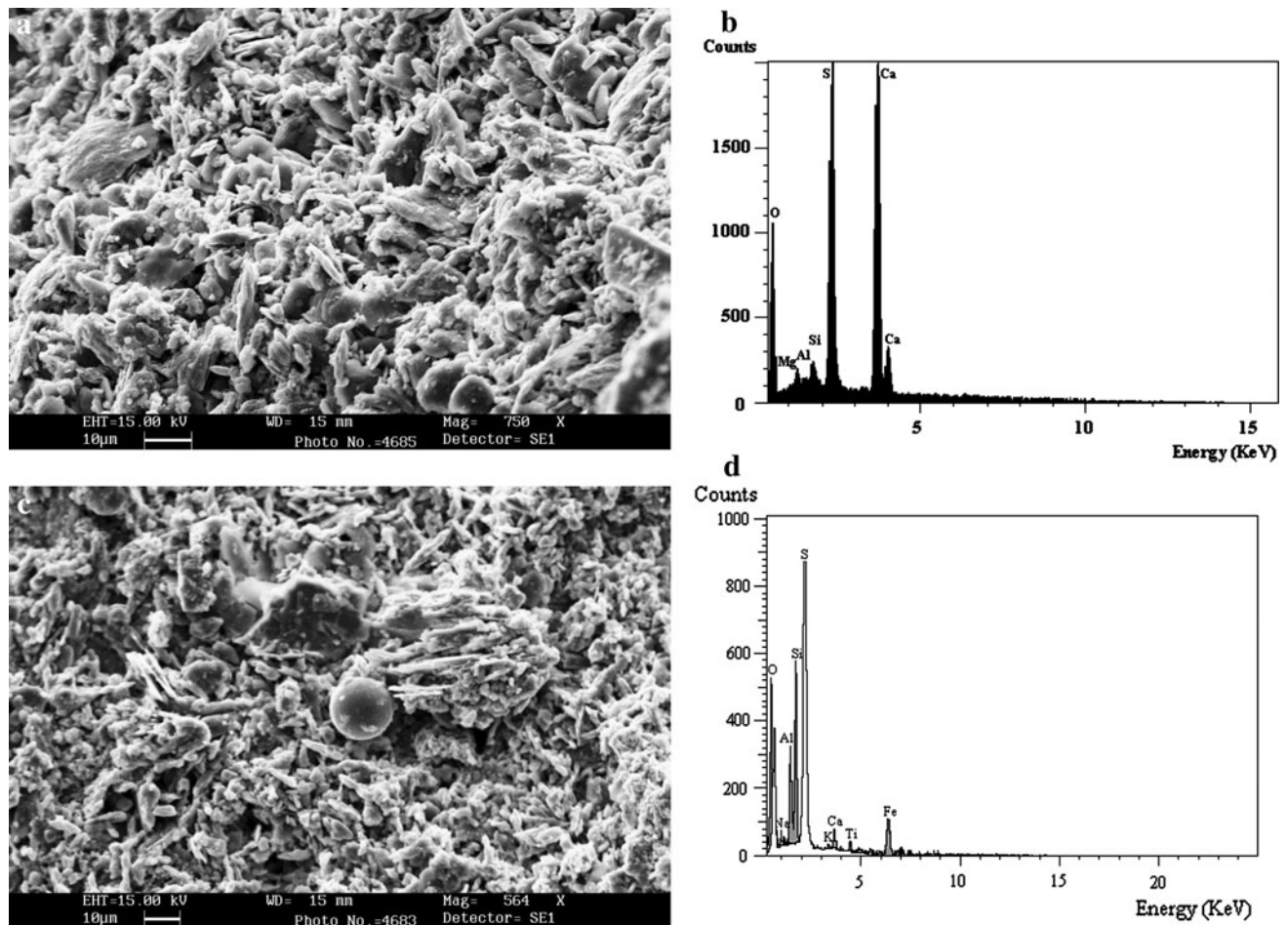
Fig. 3 SEM images of black crust samples and correspondent EDS spectra

studied sampling points. It should be noted that TSP abundances could vary significantly even within intervals of a few days. When observing TSP weights, a contrariwise trend with wind speed was evident that could be explicated considering that elevated wind speed causes a higher dispersion of solid particulate in the atmosphere (Fig. 5a). It is also well known that temperatures directly affect the force of vertical air convection, causing a negative correlation with concentration of TSP (Hussein et al. 2006). In this study, however, this effect was not particularly clear during the whole period of sampling. On the contrary, TSP concentrations were observed to be notably affected by the height above ground level of the selected measurement site. In fact, a relatively lower TSP abundance was measured at sampling site 1 (18 m above ground level) with respect to site 2 (ground level). A single exception to this trend was documented in the sample collected on 10 January 2008 at SS1, which showed a remarkable TSP abundance (327 $\mu g/m^3$). However, on the same date, a discontinuous explosion occurred at the southeast crater of Mount Etna volcano, as documented in a report by the

Istituto Nazionale di Geofisica e Vulcanologia (Neri and Cascone 2008), and the ash particles moved from NNW to SSE direction to the city of Catania as also testified by the TSP sample collected.

To obtain a realistic representation of the various sources of inorganic TSP in the urban area of Catania, several filters collected by high volume sampler were analyzed by SEM–EDS. With this technique, particle sizes and micromorphology were investigated by secondary electron (SE) imaging. Afterward, qualitative and quantitative EDS analyses were carried out to acquire elemental compositions. As a result, different clusters of particles can be discriminated on the basis of morphology and/or composition (Table 2).

Silicate particles exhibit a variety of forms, but are mostly irregular in shape. They are commonly represented by 3–10 μm granules or even submicrometric particles forming chaotic aggregates with overall size ranging from 5 to 20 μm, made of iron, alkaline metals and alkaline earth metals (Fig. 6a, b). Carbonate particles ordinarily show irregular shape, their size being quite varied

Table 1 Results obtained by ion chromatography analysis (values in mg/l)

Sample code	Na$^+$	K$^+$	Mg^{++}	Ca^{++}	Cl$^-$	NO$_3^-$	SO$_4^-$	HCO$_3^-$
BC	2.83	4.76	5.72	102.69	6.50	17.23	232.42	32.93
SCM	3.08	5.15	3.45	77.69	7.05	9.80	172.82	28.73
CTR	2.80	5.62	5.93	58.07	7.05	25.49	140.65	6.90
SAC	2.92	3.71	9.91	89.65	5.88	40.27	219.73	7.38
SB	3.54	3.31	2.56	93.77	6.33	2.39	203.13	41.61
SC	3.84	3.86	1.76	53.62	7.05	4.91	117.18	22.51
SMB	3.16	4.95	8.83	87.27	7.00	35.76	211.08	10.75
SNA	2.57	5.80	0.72	151.70	6.90	10.31	316.93	56.73
SSB	2.60	5.17	9.44	99.93	6.51	36.66	239.44	15.20
SV	2.50	4.89	10.13	140.04	6.20	33.84	324.94	34.76
SAV	2.97	4.18	3.94	53.25	6.26	15.61	123.86	12.84
SA	6.14	6.01	5.36	77.69	11.16	22.01	179.37	20.40
SBG	2.93	4.50	7.64	99.95	6.43	27.40	233.30	23.05
SD	3.03	4.47	15.07	179.91	6.53	53.07	424.45	35.76
SMM	3.60	4.27	9.96	140.03	7.05	33.45	324.31	35.51
SP	5.41	5.69	1.72	75.44	10.10	3.13	162.25	34.97
ST	3.60	3.06	10.26	97.70	6.24	41.03	237.62	10.38
SFB	3.37	4.09	13.47	47.00	6.66	0.27	143.48	32.07
Mean	3.42	4.69	6.87	98.01	7.12	22.12	226.65	27.33

(0.5–10 μm) as well. Sulfate particles (originating from both alkali-earth and alkaline metals) are mostly composed of crystals with columnar habit and sized 1–10 μm. Aggregates of tiny prismatic crystals are common (Fig. 6c, d). Sea salts consist essentially of NaCl crystals with common cubic habit and mean dimension around 5–10 μm. Finally, metal oxides particles fall into the finer fractions (1–3 μm) and usually present subspherical shape.

Quantitative chemical analysis done on the filters collected at the two sampling sites (SS1 and SS2) allowed the concentration of elements detectable by SEM–EDS to be estimated. Enrichment factors (EFs) were calculated on the set of chemical data according to the equation of Puckett and Finegan (1980) using literature data concerning the average elemental composition of the upper continental crust (Mason and Moore 1982). The obtained results are plotted in the variation diagram of Fig. 7 considering both crustal and marine enrichment. It can be noted that Si, Mg, K, Ca and Fe showed relatively lower enrichment factors with respect to the composition of the Earth's crust, while, on the contrary, very high EFs with respect to the seawater composition were recorded. The most likely sources of these elements are thus the crustal materials like soil dust or road dust (re-suspension). The EF values of elements like Na and S were found to be much higher than unity, clearly indicating non-crustal sources (sea salts, volcanic ash emission and car exhausts).

With the aim of evaluating the possibility of classifying the TSP particles into different "chemical groups", a hierarchical cluster analysis (HCA) was performed on the set of quantitative chemical data acquired by SEM–EDS, using Ward's method with squared Euclidean measure. The procedure described carefully in the section on analytical methods was followed with the aim of obtaining a statistically representative data set (in total, 2,700 spot or reduced raster EDS quantitative analytical runs were elaborated). After this statistical treatment, the TSP particles appear to gather into different chemical groups, which correspond to dendrogram clusters having acceptable levels of similarity in terms of bulk elemental composition. Figure 8 shows the dendrogram obtained from the EDS analysis of the filters collected at SS2 (Piazza Stesicoro); nevertheless, an identical trend was obtained for filters collected at SS1 (Corso Italia). Group 1 of Fig. 8 (representing 24% of the TSP filters) gathers together the particles composed of Si, Al, Ca, Fe, K and Na (elements primarily of crustal origin), most likely deriving from the soil erosion of the volcanic soil of the Catania plain. Group 2 (24%) is yet again characterized by Si-rich particles that, however, also contain amounts of Na, Al, S, Ca and Fe. Regarding group 2, the presence of sulfur puts forward a possible origin directly linked to the ash emissions of the Etna volcano. Group 3 (13%), which is characterized by S, Ca, Na and K, could be considered representative of the euhedral or subhedral crystals of sulfate salts identified by the SEM (gypsum, thenardite and syngenite) whose origin might be correlated with natural or anthropogenic S as well. Group 4 (9%), characterized by Na and Cl, chiefly represents particles derived from the seawater aerosol (sea spray). Group 5 (14%) gathers together the Ca-rich
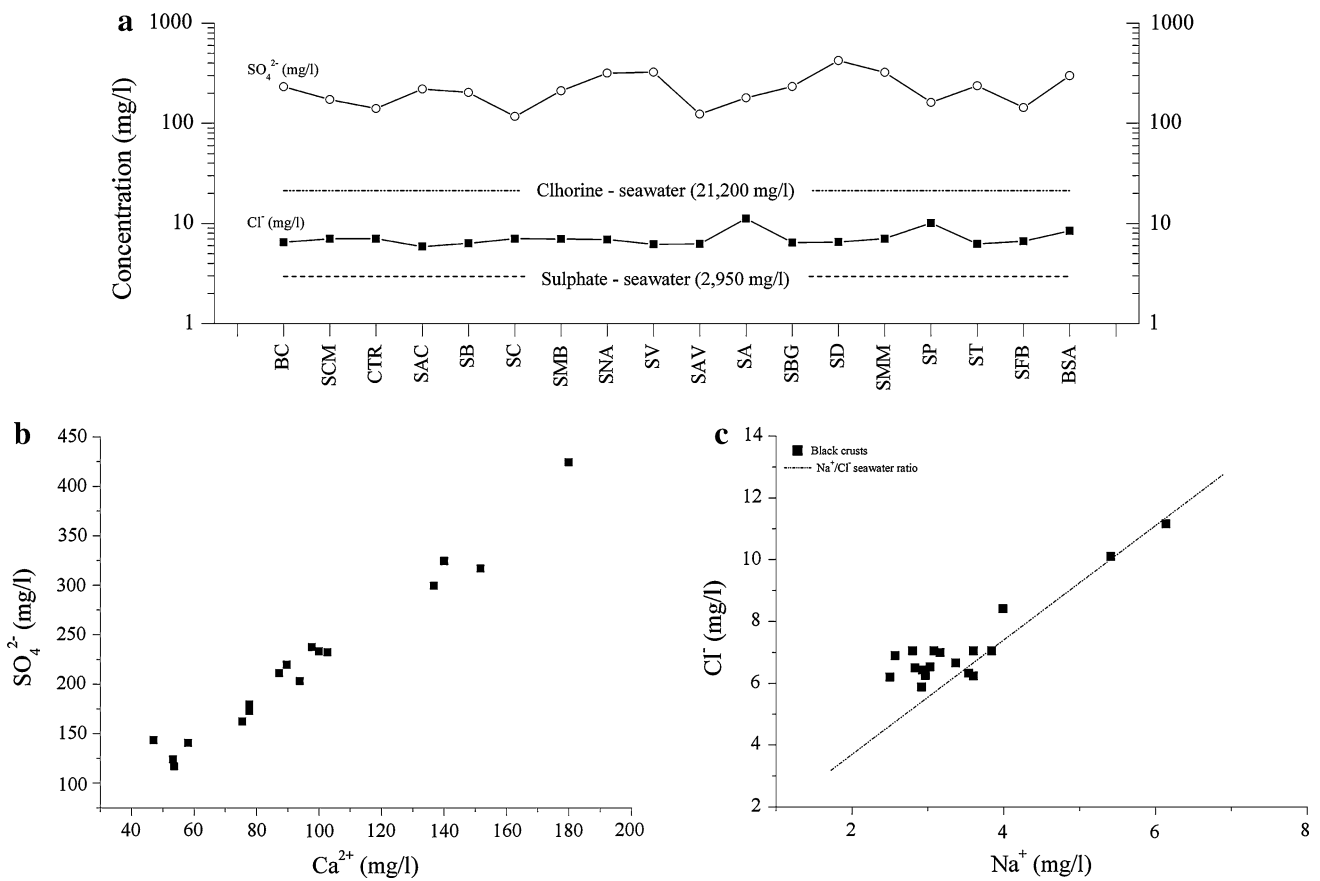
Fig. 4 **a** Variation diagram showing Cl^- and SO_4^{2-} concentrations in the studied samples (equivalent values in seawater after Cotruvo 2005). **b** Correlation between Ca^{++} and SO_4^{2-} in black crust samples. **c** Na^+–Cl^- in the black crusts of Catania monuments and buildings compared with the same ratios in seawater (Korzh 1976)

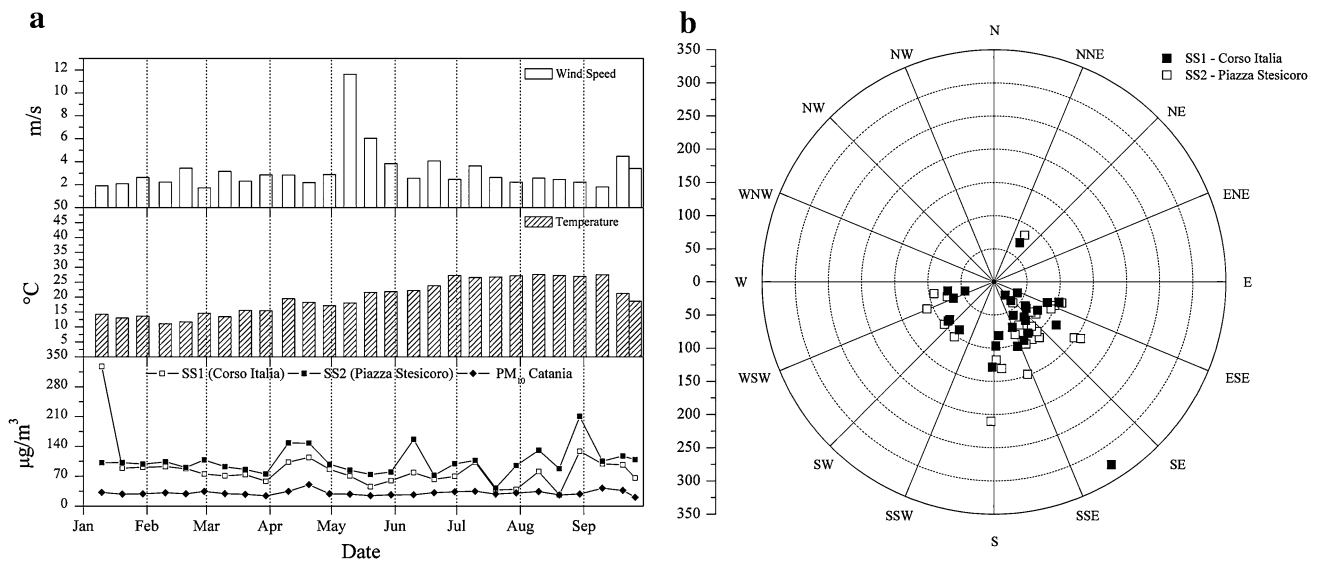**Fig. 5** Results of gravimetric analysis in terms of TSP concentration and relationship between TSP concentration, wind speed and temperature (**a**) or wind direction (**b**)

Table 2 Schematic description of the different categories of TSP particles identified in the urban area of Catania

Elemental composition	Particles categories	Typical morphology
Si(Al)–O or Si(Al)–O–X where X = Na, Mg, K, Ca, Fe	Silicates	Irregular shape
Ca–O or Ca–Mg–O or Mg–Ca–O	Carbonates	Irregular shape
Ca–S–O	Gypsum	Lamellar and/or prismatic habit
S–O–X where X = Na, K, Mg or associations	Other sulfates	Prismatic habit
NaCl, S	Sea salts	Cubic habit
X–O where X = Fe, Ti, V, Cu, Zn, Cr	Metal oxides	Subspherical shape
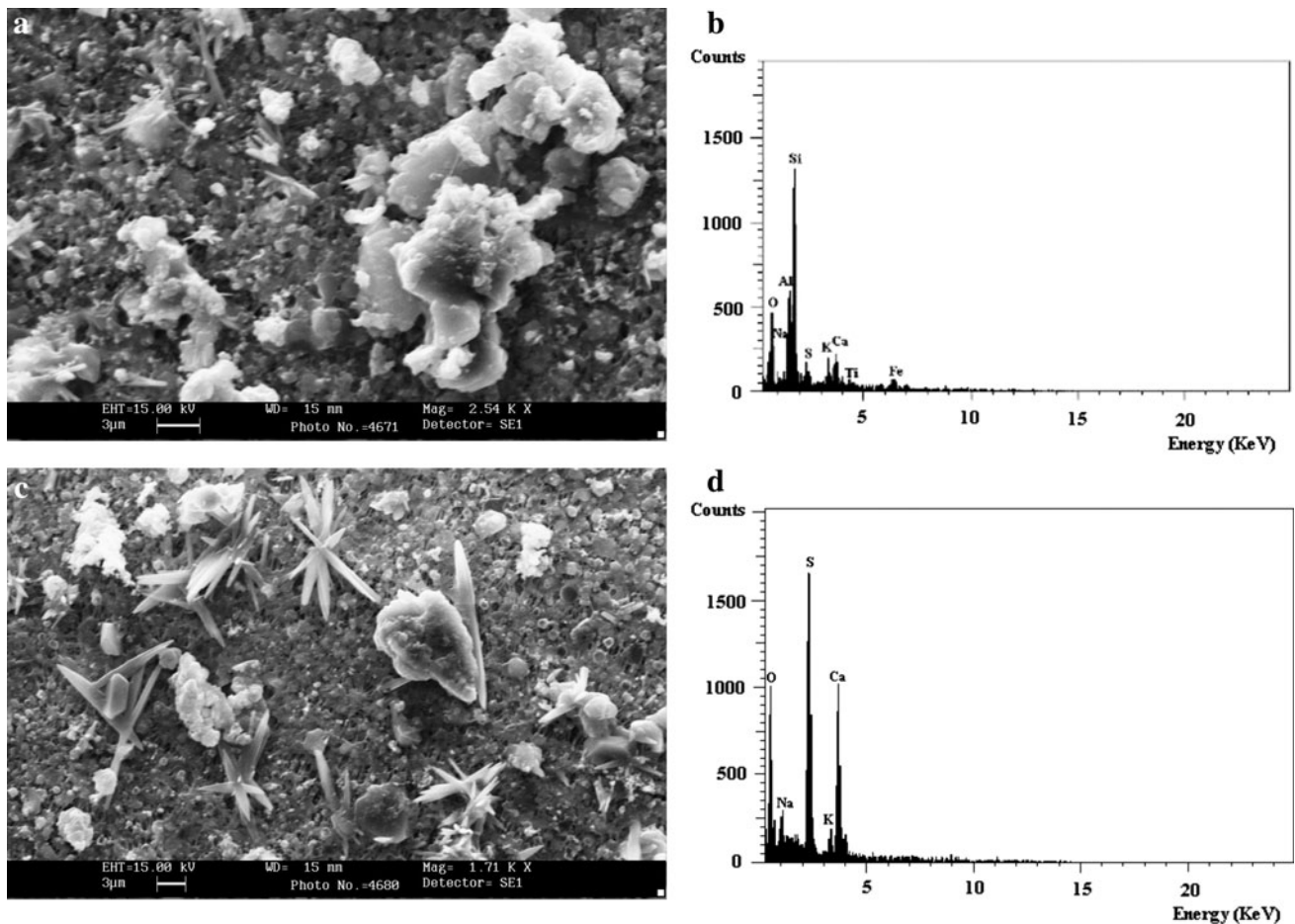
Fig. 6 SE images and relative EDS spectra of various TSP filters sampled in Catania: aggregate of aluminosilicate particles (**a**, **b**) and sulfate crystals with prismatic habit (**c**, **d**)

soil-related particles also containing minor quantities of Mg. These particles, representing the most common carbonate minerals, calcite and dolomite, are ordinary constituents of soils not far from the plain of Catania (about 30 km to the south). Group 6 (16%) comprises the subrounded Fe-rich particles documented by the SEM and most likely derived from the combustion of fossil fuels.

Sulfur stable isotope ratios in black crusts and total suspended particulate

Gypsum ($CaSO_4^{2-} \cdot 2H_2O$) has been definitely acknowledged to be the main mineral component of black crusts for almost 50 years (Winkler 1966; Winkler 1973). In fact, it derives from the reaction between Ca^{2+} generally
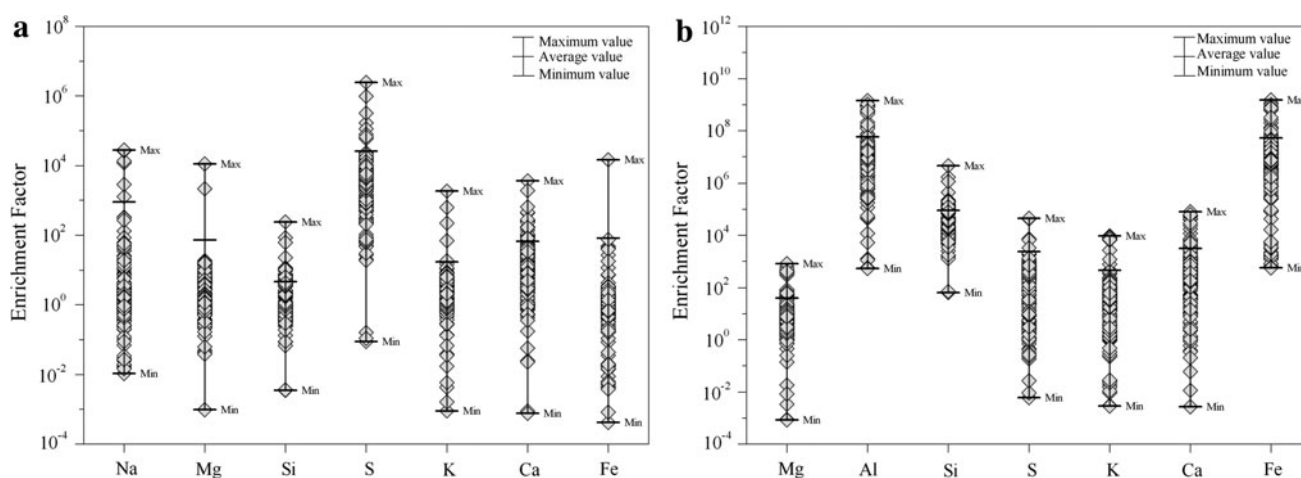
Fig. 7 Enrichment factors of major elements in Catania TSP samples with respect to the Earth's crust (**a**) and seawater composition (**b**). Aluminum and sodium were used as the normalizing elements
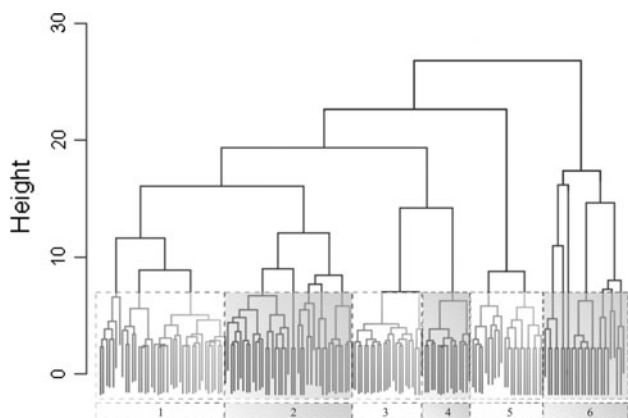

Fig. 8 Dendrogram resulting from hierarchical cluster analysis of TSP samples from Catania corresponding to 135 individual filter portions collected at SS2 (Piazza Stesicoro)

Table 3 $^{34}S/^{32}S$ ratios measured in black crust and total suspended particulate (TSP) (analytical uncertainty ±0.2‰)

Sample code	$\delta^{34}S$ (‰)
Black crusts	
BC	+2.3
CTR	+2.6
SAC	+5.4
SC	+3.1
SA	+3.1
SP	+9.6
ST	+2.3
BSA	+2
TSP	
P1	+0.3
P2	+4.4
P3	+4.3

dissolved from the stone substrate and atmospheric SO_2, which in turn is oxidized to SO_4^{2-} and set down on monument surfaces through dry and/or wet deposition mechanisms (Amoroso and Fassina 1983).

The isotopic compositions of sulfur-bearing minerals in black crusts were previously successfully used for discriminating between natural and anthropogenic sources of SO_2. The isotopic ratio $^{34}S/^{32}S$ has been applied since the end of the 1970s to individuate the various sources of atmospheric sulfur even if with different aims (Longinelli and Bartelloni 1978; Buzek and Sramek 1985; Pye and Schiavon 1989; Thorfs and Van Grieken 1997; Zhao et al. 1998). A correspondent analytical approach was used here for the black crusts and the TSP samples collected in Catania. The results of the isotopic analyses are summarized in Table 3.

The $\delta^{34}S$ observed in the black crust was found to vary from a minimum value of +2‰ (sample BSA) up to a

maximum value of +9.6‰ (sample SP). However, apart from the sample coded SAC, which also shows a rather positive $^{34}S/^{32}S$ ratio (+5.4‰), the analyzed samples on the whole have ratios between +2‰ and +3.1‰. These values seem to be in satisfactory agreement with the ones recorded in other Italian and European cities: the $\delta^{34}S$ characterizing the black crusts of Venice ranges between +4.6‰ and +5.6 ‰ (Longinelli and Bartelloni 1978); the $\delta^{34}S$ of black crusts in Prague varies between +1.8‰ and +4.5‰ (Buzek and Sramek 1985); the ratio was found to be relatively more negative in Antwerp, ranging between –8‰ and +1‰ (Thorfs and Van Grieken 1997); the $\delta^{34}S$ of black crusts of Dresden is evidently positive and constrained within +5.7‰ and +10.1‰ (Klemm and Siedel 2002); in Palermo, the only existing Sicilian term of comparison (Montana et al. 2008), $\delta^{34}S$ ranges between slightly negative (−0.5‰) and quite positive values (+5‰).
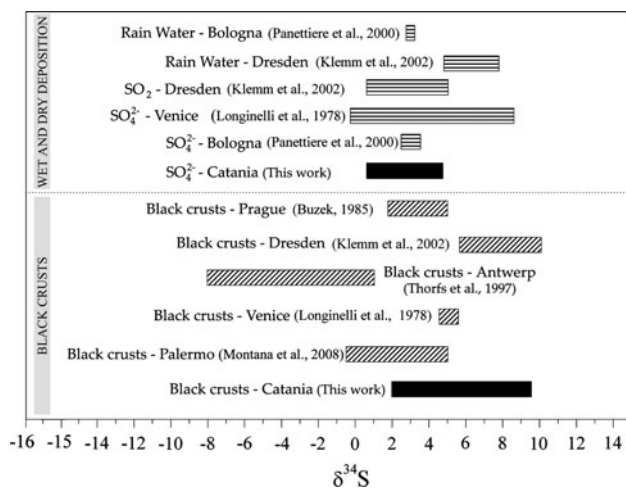
Fig. 9 Comparison between sulfur isotopic composition of wet/dry depositions and black crusts measured in different European urban areas (literature data) and the values found in this work

The $\delta^{34}S$ value found in the samples P1, P2, and P3 was considered as a representative isotopic marker for the TSP of the urban area of Catania even if with caution as a consequence of the difficulties in collecting measurable particulate specimens (in terms of sulfate content). The lowest value recorded (+0.3‰) belongs to sample P1, which was collected during the already cited ash explosion of the Mount Etna volcano that occurred on 10 January 2008. This relatively less positive $\delta^{34}S$ value confirms the predominant role played by volcanic SO_2 in this odd case, being also fully consistent with the data reported by Allard (1983), who previously analyzed the isotopic composition of the SO_2 emitted by the Mount Etna volcano revealing $\delta^{34}S$ ratios between +0.2‰ and +2.2‰.

In Fig. 9, the existing literature data for $\delta^{34}S$ isotopic ratios measured in other cities in Italy and Europe concerning both wet and dry depositions are compared with those found in TSP and black crusts of Catania. In all the reported case studies, the isotopic compositions of sulfur were interpreted as being predominantly contributed by anthropogenic sources with only subordinate influence of natural emissions. The correspondent isotopic values measured in TSP and black crusts of Catania seem to agree with the literature data, being chiefly controlled by anthropogenic S, which is considered to be in general depleted in ^{34}S.

An additional confirmation of the incidence of anthropogenic sulfur comes from the examination of the binary correlation diagram involving chloride and sulfate concentration in the analyzed black crust samples. In Fig. 10, the bold gray line (SW) indicates the Cl/SO_4 ratio in the Mediterranean Sea, while the hatched area represents the range of variation of the same ratio found in the plume of

the Mount Etna volcano (data by Aiuppa et al. 2001). It is worth noting that Cl/SO_4 ratios in black crust samples do not match typical ratios reported for Etna's plume or for seawater, which, consequently, seem to be somewhat less important sources of SO_4. For that reason, the origin of sulfate in the black crusts in Catania can be considered principally correlated to anthropogenic sources.

Concluding remarks

Chemical and isotopic characterization of black crusts and TSP has provided new insights concerning the partition of sulfate sources in Catania (Italy).

The results of the analyses of $\delta^{34}S$ ratios carried out on black crusts deposited on stone monuments of Catania as well as on TSP allowed us to determine that in the studied urban area, air pollution deriving from vehicle exhausts can be considered a main contributor to black crust formation together with a minor impact of marine salts and volcanic emissions. Therefore, isotope ratio measurements have proven to be a good tool for clarifying the origin of black crusts on monuments.

However, the contribution of Mount Etna emissions to both TSP composition and, consequently, black crusts has been pointed out clearly in this work. The occurrence of volcanic plagioclase was documented by XRD on black crusts of exposed stone surfaces; moreover, secondary mineral phases (Na and K sulfates), derived from alteration of volcanic minerals/glass, were also found to be a significant component of sampled TSP (average frequency 13%). The input of Etna volcano was also confirmed by the average Na/Cl ratio (0.74) found in the analyzed samples, which is somewhat lower than that of seawater (0.86), suggesting the presence of chlorine of volcanic origin in black crusts. Sulfate ions, which are the main component of black crusts, are certainly also derived, to some extent, from the emissions of the Etna volcano.

Nevertheless, considering the above hypothesis, the theoretical comprehensive contributions of marine and volcanic sulfate were not able to explain the measured amount in the studied black crusts. Therefore, an important contribution of anthropogenic sources to the total sulfate budget should be realistically considered. In this connection, the isotopic data seem to suggest that sulfur is chiefly sourced from vehicle exhausts and, in contrast, both sea spray and volcanic emissions contribute to a less important extent. However, at present it is still difficult to assess quantitatively the volcanic supply due to the numerous variables influencing the isotopic composition of individual sulfur compounds (i.e., stage of activity, type of eruption, temperature, kinetic isotope effects, exchange during redox reactions, etc.).

Fig. 10 Cl⁻/SO₄²⁻ ratios for all analyzed black crust samples compared with the corresponding values found in the Mediterranean sea and in the Mount Etna plume (after Aiuppa et al. 2001)
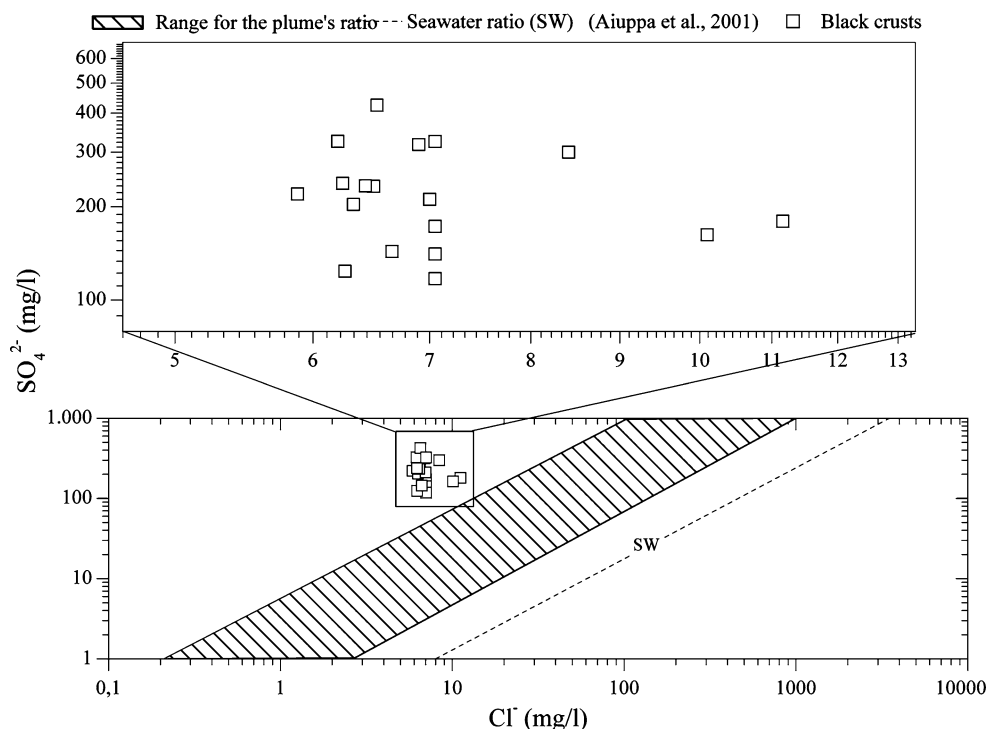
Further studies should investigate more closely the isotopic composition of volcanic sulfate aerosols in Catania to obtain a more detailed knowledge of this sulfur source. Additionally, the combination of other stable isotopes (above all oxygen) could increase the discriminatory power of isotope studies with respect to contaminant sources in this peculiar urban context.

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