Geochemical study of black crusts as a diagnostic tool in cultural heritage

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Abstract This contribution focuses on spectrometric analyses carried out on crust samples covering the stone surface of the boundary walls of the Tower of London. The main goal of this research is to investigate the degradation processes related to the environmental impact on cultural heritage. Specifically, the chemical contamination of stone substrate in the Tower of London due to the crust formation was examined through laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). This technique allowed us to achieve a complete characterization of the damage layers in terms of trace elements. In addition, optical microscopy (OM), scanning electron microscopy coupled with energy-dispersive X-ray spectrometry (SEM-EDS) and infrared spectroscopic techniques (FT-IR) were also used for an exhaustive characterization of the examined samples. Results obtained demonstrated that such a geochemical approach represents a powerful diagnostic tool in the study of black crusts, since it represents a reliable indicator of the environmental pollution. The higher concentrations of most heavy metals in black crusts with respect to the underlying stone suggest that crusts were greatly influenced by atmospheric inputs in their formation, mainly represented by mobile combustion sources. In addition, the possibility of analyzing in some samples the portion of altered substrate allowed us to hypothesize that some specific heavy metals tend to migrate from the crust to the unaltered substrate over time, becoming catalysts for the formation of new crust. Therefore, this research focuses on the role of diagnostics in order to plan suitable cleaning and consolidation intervention aimed at a better protection of the monument.

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1 Introduction

Atmospheric pollution is the major agent responsible for the degradation of calcareous buildings located in urban areas [1–7]. The degradation mainly concerns those sites which are protected from washing out and leads to the formation of damage layers with a characteristic dark color, which usually give rise to a more severe decay of the stone including loss of material. The blackening of surfaces is caused by the accumulation of air pollutants produced by human activity, especially carbon particles originating from the incomplete combustion of fossil fuels [8].

Since the surfaces of buildings and monuments are the areas where air pollutants are deposited, accumulate and interact with the stone substrate, the chemical composition of crusts will reflect the change over time of the pollution sources [7–20]. To deeply understand the influence that some pollutants have on the formation of crusts, several authors [15–20] highlighted the importance of the study of

trace elements. Investigations of the geochemical composition of damage layers in the monuments can be the basis for planning suitable strategies for the protection and conservation of the built cultural heritage.

In this work, crust samples taken from the Tower of London have been investigated. This monumental complex, mostly built in the 11th century, is located in the center of London, on the banks of the River Thames, near Tower Bridge. The site is exposed to high vehicular and boat emissions, London being one of the most polluted cities in Europe. Already in the Victorian age, a high degree of pollution, mainly coming from coal combustion, concerned the city and in the last hundred years an increase in the use of petrol and diesel occurred [21, 22]. The Tower of London was chosen for its historical importance as well as for the possibility of analyzing damage layers with different macroscopic characteristics ('dendritic' black crusts and thin grey–brown crusts), for its exposure to diverse pollution sources (road traffic on the northern and eastern sides and boat traffic from the River Thames on the southern one) and for the architectural surfaces of the monumental complex being subjected to diverse deposition times of atmospheric products (∼150, 70–80 and 40–50 years) because of past restoration/cleaning carried out in different periods [23].

For an exhaustive characterization of the crusts, different and complementary techniques were used, including optical (OM) and scanning electron microscopy coupled with energy-dispersive X-ray spectrometry (SEM-EDS), Fourier transform infrared spectroscopy (FT-IR) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS).

The main goal of this study is to gain information on the chemical composition of examined crusts, with particular regard to heavy metals which can be used as indicators of the pollutants that have influenced the formation of crusts. A further purpose is to deeply investigate the alteration degree of the stone substrate, this latter exhibiting, during the sampling phase, an intense surface degradation even in areas which were restored in more recent times.

2 The Tower of London

The Tower of London is a historic castle on the north bank of the River Thames, in central London (England), which has played a prominent role in English history. The whole monumental complex consists of several buildings, including the central 'White Tower' (which gives the entire site its name), and is surrounded by a double defensive wall system and a moat.

The architectural history of the Tower appears to be very intricate and controversial. It was founded towards the end of 1066 as part of the Norman Conquest of England. Then,

in 1078, William the Conqueror commissioned the construction of the 'White Tower', with the aim of protecting the city from invasions. The fortification was then completed between 1275 and 1285 by Edward I, who created a double defensive barrier through the construction of the bailey, which entirely included the inner walls. The Tower, mainly used as a Royal residence for several centuries, has had many other uses over time, as armory, prison, treasury, menagerie, house of the Royal Mint, public records office and house of the Crown Jewels [24, 25].

More than 20 different types of stone were used for the construction of the architectural complex, which was partly damaged during the Second World War.

The Tower is located in the center of London, in an area exposed to intense road traffic on the northern side and to boat traffic from the River Thames on the southern one. The distance of the main buildings from the roads and the river is about 30–50 m. The facades of the monumental complex and the wall that face south are oriented to the prevailing winds and thus undergo to a more intense washing out by rain.

3 Sampling

Black crust samples examined in this study were collected from the Tower of London as part of the research activity carried out within the EC project CARAMEL 'CARbon content and origin of damage layers in European monuments (2001–2003)', whose aim was the discrimination and quantification of carbon fractions (organic and elemental—OC and EC) within black crusts from several European monuments [23, 26, 27].

Sampling involved some specific areas of the boundary walls of the monumental complex which are built in a local stone known as Kentish Ragstone. It is a bioclastic dark blue to green–gray sandy limestone, which was largely used in the London architecture during the Roman and Medieval ages [28].

The sampling has been made in the south, east and north–east of the Outer Curtain Wall, the Inner Curtain Wall and along the East Moat (Fig. 1). Sampling sites were chosen according to their exposure to direct sources of pollution. Specifically, southern and south-western sides overlooking the River Thames are affected by a high degree of pollution caused by the boat traffic, while the north-eastern side of the monument is exposed to intense vehicular traffic due to the presence of two roads (Tower Hill and Tower Bridge Approach). A list of examined samples, along with their location and information on past restoration works, is reported in Table 1. Figure 1 shows a plan of the Tower with the indication of sampling points and some pictures of the collected black crusts.
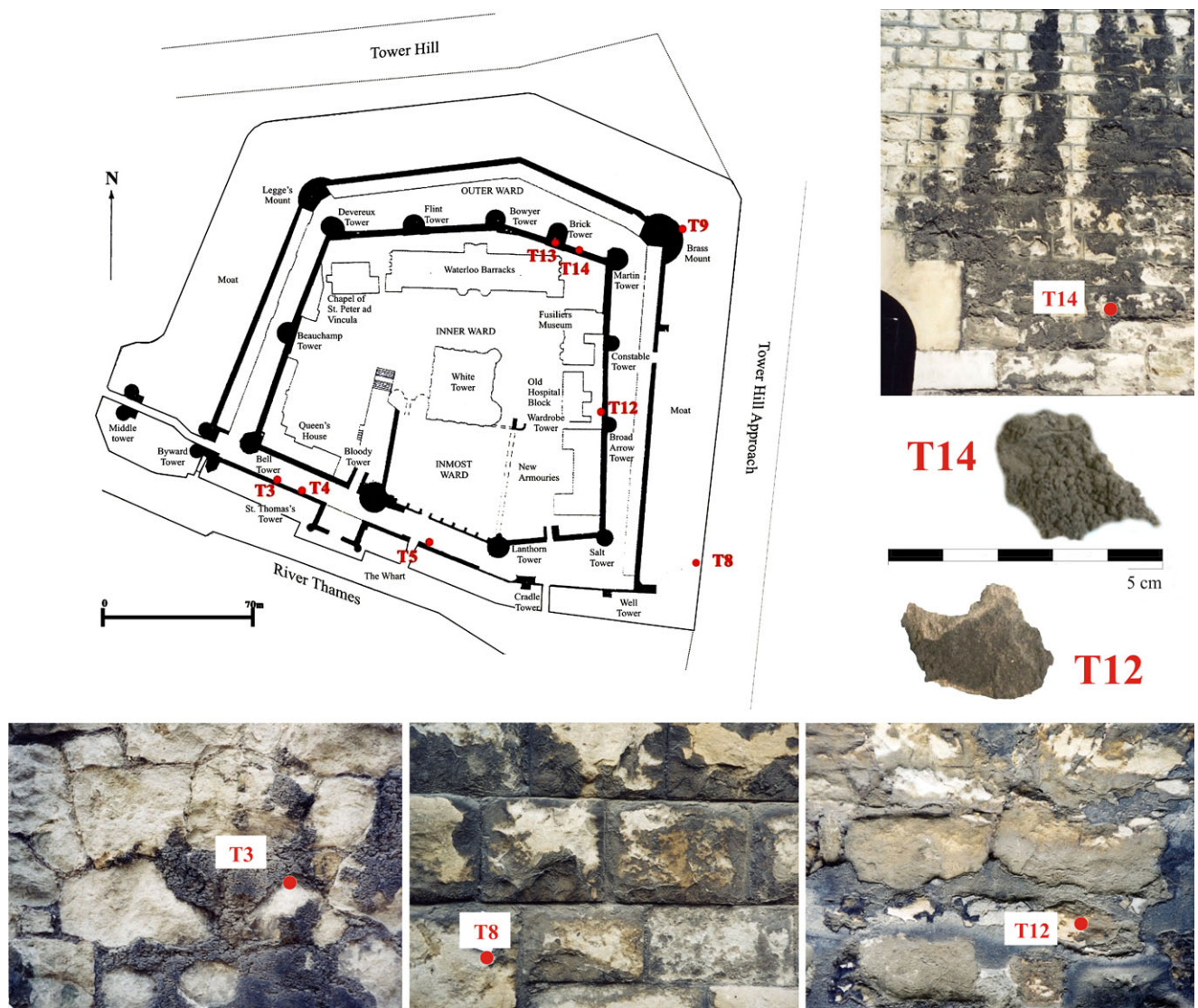
Fig. 1 General plan of the Tower of London, with the locations of sampling points, and some representative pictures of the black crusts collected (courtesy of C.M. Grossi)

Sampled black crusts show variable morphology, color and thickness, depending on their exposure to rain, deposition time and textural features of the underlying substrate, this latter exhibiting a high degree of damage and extended exfoliation phenomena. On the whole, the sampled damage layers can be divided into two typologies: (a) dendritic (tree-like) black crusts (T3, T4, T5, T13 and T14), well adherent to the substrate, showing high thickness (up to 7 mm), irregular surface and high compactness; (b) grey–brownish crusts (T8, T9 and T12), with small thickness, regular surface and good adherence to the substrate.

Dendritic black crusts are the 'oldest' among the examined ones, representing more than one century of particulate deposition, since the relevant areas of sampling were restored during the 19th century. Conversely, the grey-brownish crusts represent the 'youngest/modern' damage layers, which formed after more recent restoration works. Specifically, T8 and T9 samples were collected from areas that have been restored around the 1930s (about 70–80 years of particulate deposition), whilst the T12 sample refers to a site which underwent a cleaning work between 1960 and 1970 (about 40–50 years of deposition).

4 Analytical methods

A complete characterization of black crusts was made using different methodologies. The microscopic analysis included observations through polarized optical microscopy (OM), by using a Zeiss Axiolab microscope (equipped with a digital camera to capture images), and scanning electron microscopy coupled with energy-dispersive X-ray spectrome-

Table 1 List of samples collected from the Tower of London (see also Bonazza et al. [23]

Sample	Location	Description	Past restoration work
T3, T4	1.5 m—Outer Curtain Wall, in front of the Queen House, facing north	Dendritic black crust and underlying substrate	Restored during the 19th century, there do not appear to be any later interventions or repairs
T5	1.5 m—Outer Curtain Wall, near the gate to the Wharf, facing north	Dendritic black crust and underlying substrate	Restored during the 19th century, there do not appear to be any later interventions or repairs
T8	1.5 m—Moat, facing west. The sample has been taken between the calcareous blocks and the jointing mortars	Thin grey–brown/ black crust and underlying substrate	The area of sampling appears to have been repaired around the 1930s
T9	1.5 m—Brass Mount, north-eastern Moat, facing north	Thin grey–brown/ black crust and underlying substrate	The area of sampling appears to have been repaired around the 1930s
T12	1.5 m—Near the Broad Arrow Tower, opposite the old hospital. Eastern side, facing west	Thin 'globular' black crust and underlying substrate	Most of the surface has been repointed during the 1960s/1970s; building activity around this area during the post-war years
T13, T14	2.5 m—Inner Curtain Wall, between the Brick Tower and the Martin Tower. Northern side, facing south	Dendritic black crust and underlying substrate	Restored during the 19th century, there do not appear to be any later interventions or repairs

try (SEM-EDS), on polished cross sections. OM and SEM analyses allowed us to gain information on the micromorphological characteristics of both substrate and black crusts and the interaction between stone and damage layer, while the use of SEM-EDS permitted us to determine the chemical composition of examined crusts in terms of major elements. SEM-EDS analyses were performed by means of a Tescan Vega LMU scanning electron microscope equipped with EDAX Neptune XM4 60 microanalysis working in energy-dispersive spectrometry, with an ultra-thin Be window to ensure lower detection limits (of the order of 0.1 %) for all analyzed elements. Operating conditions were set at 20 kV accelerating voltage, 0.2 nA beam current, 100 s acquisition time and 30–35 % dead time. Analyses of the surface of crusts were performed in raster mode.

FT-IR investigations were carried out to identify the mineralogical phases constituting the examined damage layers. Analyses were performed through a Perkin Elmer Spectrum 100 spectrophotometer equipped with an ATR (attenuated total reflectance) accessory. Infrared spectra were recorded in ATR mode, in the range 500–4000 cm^{-1} at a resolution of 4 cm^{-1}.

Concentrations of trace elements in the examined samples were obtained by LA-ICP-MS (laser ablation inductively coupled plasma mass spectrometry). Analyses were carried out using an Elan DRCe instrument (Perkin Elmer/SCIEX), connected to a New Wave UP213 solid-state Nd–YAG laser probe (213 nm). Samples were ablated by a laser beam in a cell following the method tested by Gunther and Heinrich [29]. The ablation was performed with spots of 40–50 μm, with a constant laser repetition rate of 10 Hz and a fluence of ~20 J/cm^2. Calibration was achieved using NIST 612-50 ppm glass reference material as external standard [30]. Internal standardization to correct instrumental instability and drift was achieved using CaO concentrations

from SEM-EDS analyses [31]. Accuracy was evaluated on BCR 2G glass reference material and the resulting element concentrations were compared with reference values from the literature [32]. Accuracy, as the relative difference from reference values, was always better than 12 %, and most elements plotted in the range ±8 %. With the aim of better investigating the geochemical variability of black crusts from external to internal portions, analyses were performed on 100-μm-thick cross sections. A variable number of spot analyses was performed on each sample, depending on the thickness of black crusts.

5 Results and discussion

5.1 Optical microscopy analysis

A petrographic characterization through polarized optical microscopy was performed on all samples taken from the monument. The stone substrate consists of a re-crystallized biocalcarenite, showing a grain-supported texture. The allochemical component is mainly formed of bioclasts (echinoderms, bivalves, gastropods and foraminifera), associated with a silicoclastic fraction (rounded to sub-angular quartz and rounded to sub-rounded glauconite crystals). Dominant sparry cement (with crystal size >5 μm) and subordinate matrix (only in some areas) are recognized among the orthochemical component. The primary porosity is about 10–15 %. On the basis of such petrographic features, the stone can be classified as a biosparite [33] or a packstone [34]. As regards the state of conservation, the analyzed substrate appears to be highly degraded, with evidence of dissolution phenomena and numerous microfractures (secondary porosity about 30–40 %), where small gypsum crystals can be identified.

Fig. 2 Photomicrographs representative of the investigated substrate and black crust samples from the Tower of London
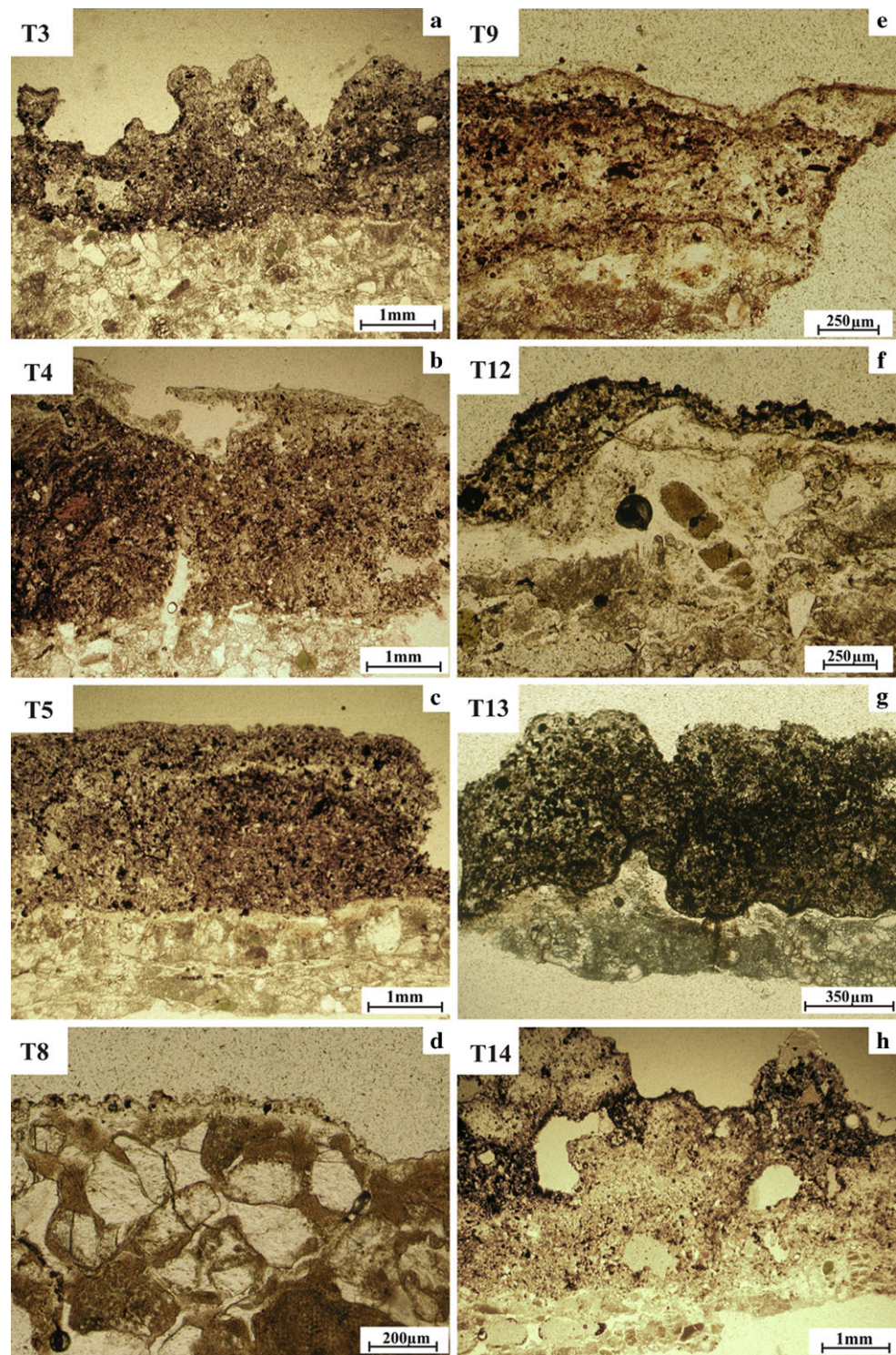
Thin-section observations of damage layers allowed us to investigate the micromorphological and textural features of the two different types of black crusts recognized during sampling (Fig. 2): (i) the first group, including the dendritic black crusts (T3, T4, T5, T13 and T14), shows a similar irregular morphology, good adherence to substrate, high thickness (up to 5 mm) and numerous particles (spherical, sub-spherical and prismatic shaped, mostly concentrated in the area in direct contact with the underlying substrate), along with red to brown oxides and hydroxides, distributed all along the damage layer. Such features give the crusts a color varying from black, in the innermost part, to dark

Fig. 3 (**a**) FT-IR spectra of crust samples from the Tower of London; (**b**) particulars of the spectra showing the characteristic absorption peaks of oxalate in samples T5, T8, T9 and T12
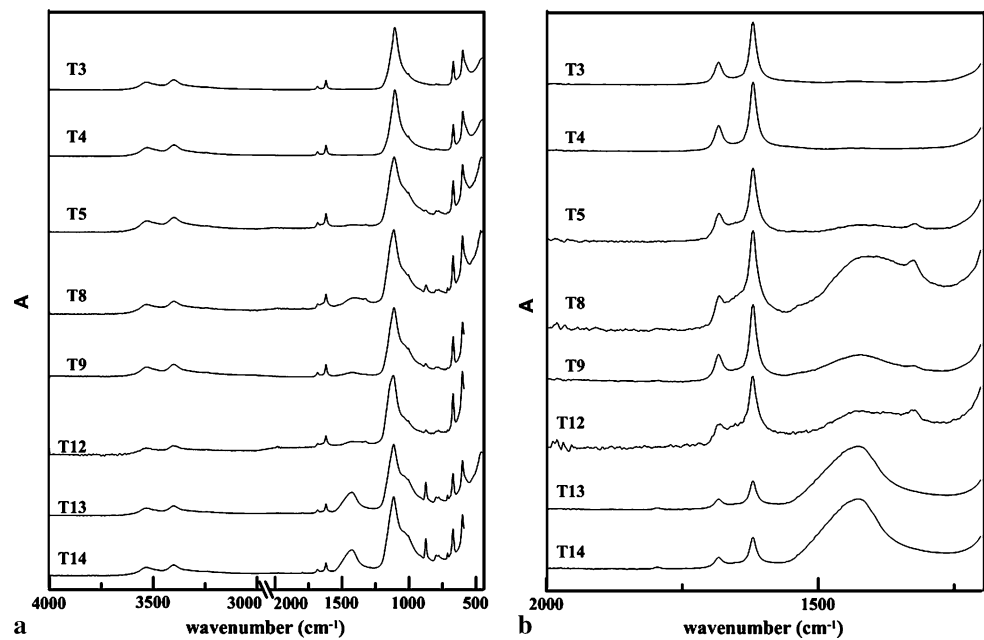
brown, in the outermost one. These crusts are made of microcrystalline gypsum, with lamellar habitus, incorporating sporadic crystals of calcite, quartz and glauconite, coming from the substrate. (ii) The second group includes the grey-brownish crusts (T8, T9 and T12), which generally exhibit a stratified morphology, reduced thickness, penetration phenomena into the substrate and the presence of a variable number of particles, variously distributed. Textural features of these crusts show some differences, which are briefly described as follows.

In the T8 sample, the crust is not continuous along all the surface of the substrate, has a very reduced thickness (30–100 μm) and is composed of two distinct layers: the innermost one, light yellow in color, has no particles and consists of microcrystalline gypsum and re-crystallized calcite; the outermost layer, made of microcrystalline gypsum, is thinner and dark-brown colored, with common particles and few oxides and hydroxides. The crust of the T9 sample, well penetrated into the substrate, shows a thickness variable from 300 to 700 μm and is composed of three layers: the innermost one, light brown, does not show any particles, oxides or hydroxides and is given by microcrystalline gypsum and re-crystallized calcite; the intermediate layer is grey–brown colored, with common particles, oxides and hydroxides which are heterogeneously distributed and is made of microcrystalline gypsum; the outermost layer is given by gypsum with acicular habitus (growing perpendicularly to the stratification of the crust) and few particles, oxides and hydroxides that make the layer light brown in color. Finally, thin-section analysis of T12 crust revealed a thickness ranging from 100 to 350 μm (700 μm in some portions) and the presence of two distinct layers: the one in direct contact with the substrate has a light-brown color (due to the presence of

particles, oxides and hydroxides) and is made of microcrystalline gypsum and re-crystallized calcite; the external layer, dark brown, exhibits common particles, oxides and hydroxides and is made only by microcrystalline gypsum.

Such a variable distribution of the particles which characterizes each single layer identified can be due to the variation over time of polluting substances, which probably have been responsible for the formation of examined damaged layers.

5.2 FT-IR analysis

As regards the mineralogical composition of analyzed damage layers, the infrared spectra of all black crust samples (Fig. 3a) show the same characteristic absorption peaks of gypsum, centered at 1109, 667 and 596 cm^{-1}, as well as the O–H stretching and bending vibrations of the calcium carbonate, with peaks at 1409, 871 and 710 cm^{-1}. Only in T9, T13 and T14 samples have bands of quartz, with distinctive peaks at 799 and 779 cm^{-1}, been identified, whereas in T5, T8, T9 and T12 (Fig. 3b) the presence of oxalate, with peaks at 1630, 1320 and 780 cm^{-1}, was observed. Peaks of calcite and quartz can be certainly ascribable to the underlying substrate, while the presence of oxalate in samples T8, T9 and T12 can be due to restoration works carried out in the past in the Tower of London or the activity of microorganism colonies [35–41].

5.3 SEM-EDS analysis

The micromorphological and chemical characterization through SEM-EDS was performed on five samples, selected as representative of the entire suite (T3, T14 among the 'old'

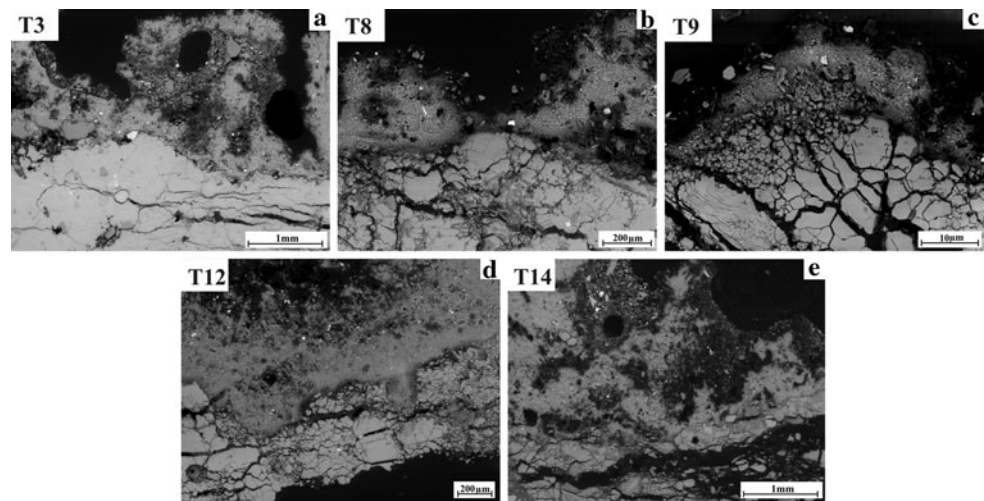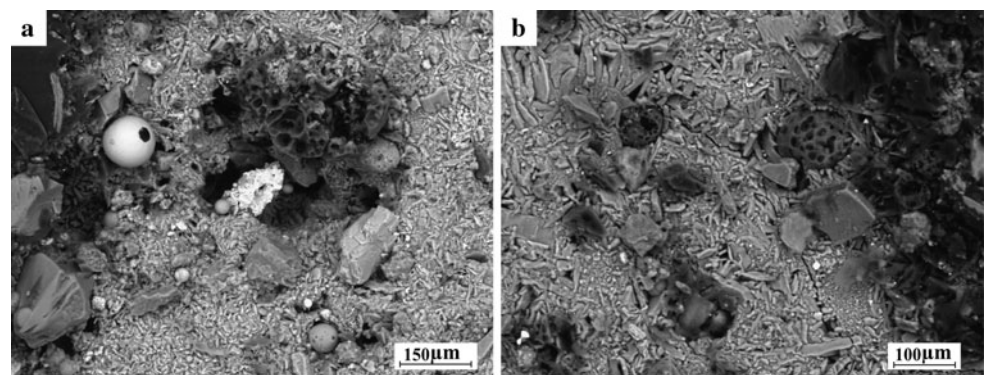**Fig. 4** BSE-SEM (Back Scattered Electron) images of examined samples

Fig. 5 BSE-SEM (Back Scattered Electron) images of the *fly ash* with different morphology and shape observed in the crust of samples T3 (**a**) and T9 (**b**)

crusts, T8, T9, T12 among the 'recent/modern' ones). The use of this methodology allowed obtaining detailed information on the morphology of crusts and their interaction with the substrate, as well as on the chemical composition in terms of major elements of the damaged layers. Specifically, as regards the oldest dendritic crusts, both samples T3 and T14 show an irregular morphology and a high thickness, up to 4 mm (Fig. 4a–e). Both crusts are rather heterogeneous, being characterized by alternating dark and light areas, where it is possible to identify acicular, lamellar and pseudo-lamellar gypsum crystals. Several *fly ash* particles (Fig. 5), with different surface morphology (smooth or microporous), shape (spherical, sub-spherical and irregular) and size (from 10 to 150 μm), were also identified in both samples.

Regarding the 'recent' crusts (Fig. 4b–d), all three analyzed samples exhibit a reduced thickness with respect to the dendritic ones, variable depending on the sample (30–300 μm in T8, 50–100 μm in T9 and 500–900 μm in T12). The morphology is regular in T9 and T12, irregular in T8. In addition, crusts of T8 and T12 samples display an alternation of dark and light areas, these latter being characterized by lamellar and pseudo-lamellar gypsum crystals. *Fly ash* particles, in variable amounts in the three examined sam-

ples and characterized by both sub-spherical microporous and spherical with smooth surface morphologies, were also observed.

The EDS analysis carried out on the same samples showed that the examined crusts are mainly composed of CaO and SO_3, followed by SiO_2, Al_2O_3, Fe_2O_3 and lesser amounts of MgO, K_2O and Na_2O. CaO and SO_3 can be certainly ascribed to gypsum, which is the main component of the crusts, while aluminum, silicon and iron can be attributed to atmospheric particulates.

5.4 LA-ICP-MS analysis

A full geochemical characterization of black crusts and substrates in terms of trace elements was obtained through LA-ICP-MS investigations. Analyses were performed on the same representative five samples (T3, T8, T9, T12 and T14) on cross sections with the aim of investigating the possible migration of trace elements from the crust to the substrate and evaluating the state of conservation of the latter. The average concentrations (in ppm) of trace elements and relative standard deviations for all examined crusts and substrates are available as electronic supplementary material (ESM).

On the whole, results show a quite different chemical behavior between black crusts, unaltered substrate and altered

portion of the substrate, this latter being analyzed only in samples T8, T9 and T14, where it was observed.

As regards the crusts, both analyzed types (old and recent) result to be enriched in some trace elements with respect to substrate. Specifically, these elements include As, Cd, Cr, Cu, Ni, Pb, Sb, Sn, V and Zn, whose maximum (max) and minimum (min) average concentrations (in ppm) are reported as follows: As (max 96.3 in T3 and min 10.7 in T12), Cd (max 8.43 in T14 and min 0.75 in T12), Cr (max 79.0 in T14 and min 9.65 in T12), Cu (max 318 in T14 and min 66.5 in T12), Ni (max 98.6 in T14 and min 12.3 in T12), Pb (max 1765 in T14 and min 307 in T12), Sb (max 33.1 in T14 and min 2.11 in T12), Sn (max 68.7 in T14 and min 4.87 in T12), V (max 251 in T14 and min 20.1 in T12) and Zn (max 734 in T14 and 121 in T12).

The same elements in the altered substrate of samples T8, T9 and T14 show the following average concentrations: As (6.27 in T8, 4.25 in T9, 33.5 in T14), Cd (0.57 in T8, 0.82 in T9, 7.32 in T14), Cr (26.7 in T8, 16.4 in T9, 39.6 in T14), Cu (77.5 in T8, 145 in T9, 560 in T14), Ni (49.4 in T8, 23.7 in T9, 208 in T14), Pb (120 in T8, 147 in T9, 809 in T14), Sb (2.87 in T8, 3.56 in T9, 12.3 in T14), Sn (6.15 in T8, 1.54 in T9, 16.9 in T14), V (51.6 in T8, 50.9 in T9, 75.8 in T14) and Zn (272 in T8, 237 in T9, 6184 in T14).

Finally, in the unaltered substrate the average concentrations were: 2.00 for As, 0.53 for Cd, 3.87 for Cr, 13.5 for Cu, 7.22 for Ni, 47.8 for Pb, 0.64 for Sb, 0.52 for Sn, 21.8 for V and 106 for Zn.

To display compositional differences between crusts, altered substrate and unaltered substrate, some of the most significant binary diagrams (As vs. Pb, Cu vs. Zn and Ni vs. V) are shown in Fig. 6a–c, where all crust samples exhibit a general enrichment in heavy metals with respect to the substrate. In particular, the higher concentrations are referred to the oldest crusts (T3 and T14) and the lower to the more recent ones (T8, T9 and T12). It is worth noting that Zn, Ni and Cu contents in the altered portion of the substrate in T14 are higher than in the crust of the same sample. In addition, all heavy metals in the crust of T12 show the lowest concentrations among the five analyzed samples.

In the histograms of Fig. 7 (where the average concentrations of trace elements in black crusts, altered substrate and unaltered substrate are grouped on the basis of their abundances) and in the spider diagrams of Fig. 8 (where the average concentrations of each element in crusts and altered substrate are normalized with respect to those in the unaltered stone), the degree of enrichment of trace elements in black crusts can be better evaluated.

Both figures show that among the oldest dendritic crusts (Fig. 8a), sample T14 exhibits higher concentrations of heavy metals and higher enrichment factors (EFs) with respect to T3. Conversely, as regards the samples belonging to
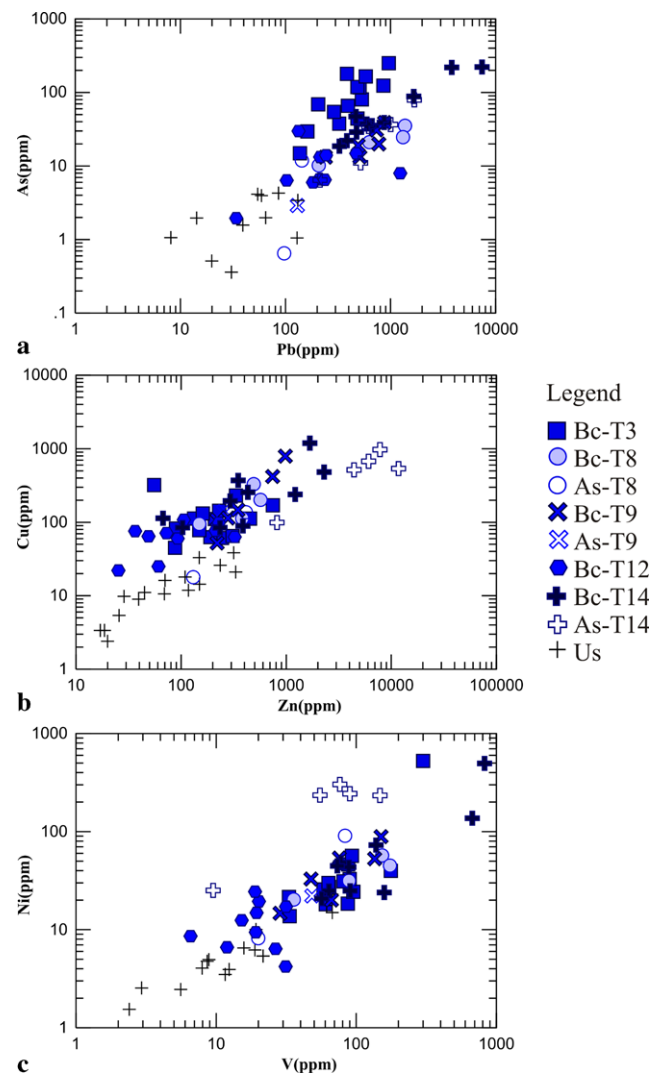

Fig. 6 As vs. Pb (**a**), Cu vs. Zn (**b**) and Ni vs. V (**c**) binary diagrams for black crusts (Bc), altered substrate (As) and unaltered substrate (Us) of all samples analyzed by LA-ICP-MS

the recent grey-brownish crusts (Fig. 8b), appreciable concentrations of all heavy metals (but lower than in the previous type) and moderate EF values were observed.

Although a contribution from several industries (manufacturing, extraction and working of iron, steel and nonferrous metals) in the neighboring areas, that release high quantities of As, Cd, Pb, Zn and V in the atmosphere [42, 43], is not to be overlooked, the high concentrations of most heavy metals (As, Sb, Pb, Zn, Cu, Sn, Ni, Cd and Cr) found in the examined crusts of both types (Fig. 7) can be mainly associated with coal combustion [44–46]. Indeed, since the 13th century and until the 1960s [47] the pollution in the city of London has been characterized by an excessive use of this fuel (due to the ease of supply and low cost), which provided the necessary energy for domestic life and industrial production [21, 22].
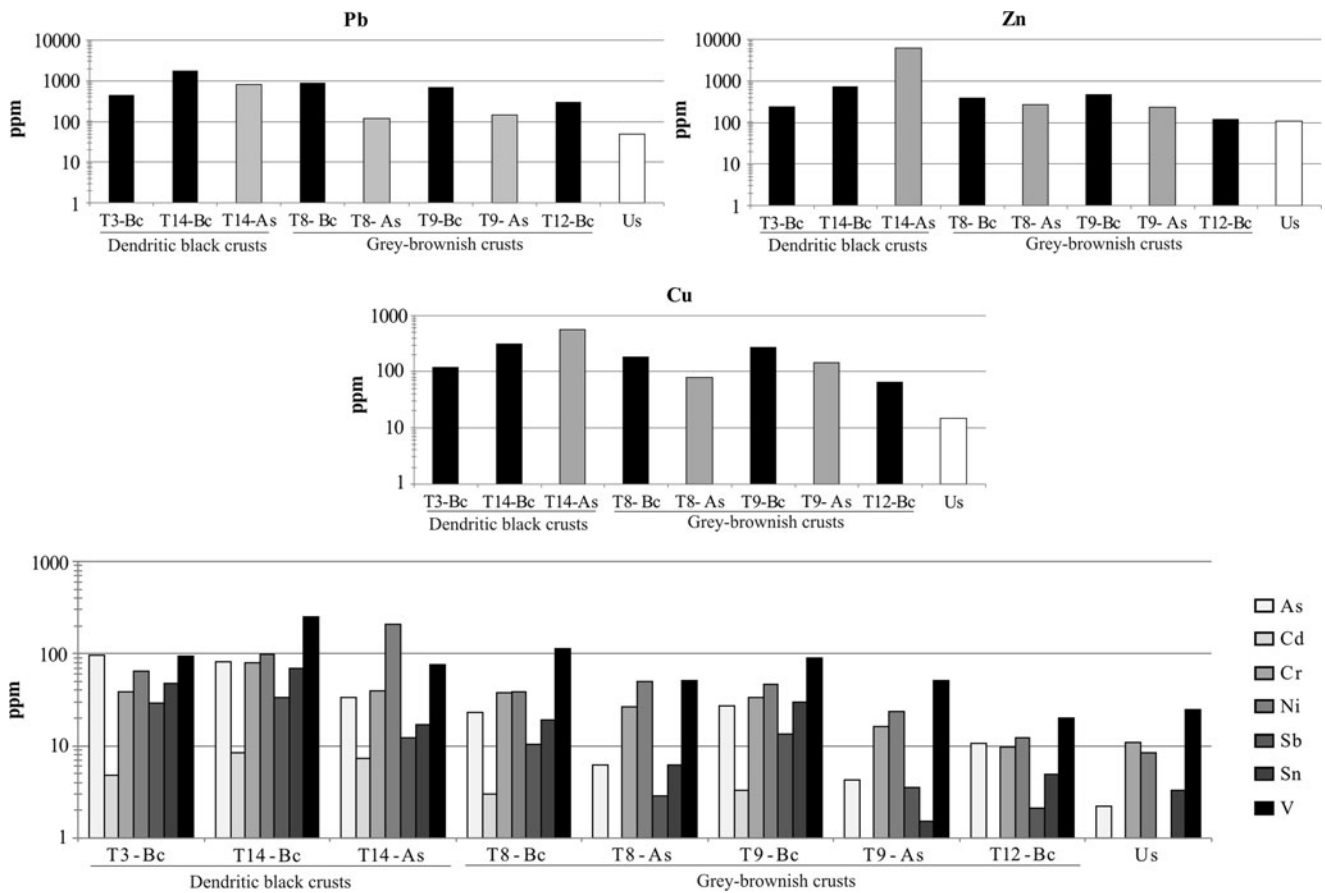
Fig. 7 Histograms showing the average concentrations (in ppm) of heavy metals in all examined samples. The elements are grouped according to their order of abundance. Bc = black crust, As = altered substrate, Us = unaltered substrate

The high concentrations of Pb, Zn, Cu, Cr, Ni, Sb and V found in some examined crusts may also be attributed to the direct exposure of the northern and eastern sides of the Tower to vehicular emissions. Indeed, samples T8, T9 and T12 of the recent crusts and T14 of the oldest ones (Fig. 1) were collected at 1.5–2.5 m of height, in the proximity of roads (Tower Hill and Tower Bridge Approach) with high traffic, thus being subject to direct pollution. Therefore, the above-mentioned heavy metals (Pb, Zn, Cu, Cr, Ni, Sb and V) in these samples can be ascribed to the combustion of fossil fuels, such as gasoline and diesel or fuel oil [48, 49], or the attrition and friction of mechanical parts of vehicles [43] or even the consumption of the asphalt [50]. It is worth noting that concentrations of all the above heavy metals in the sample T12 are lower than those in T8 and T9. This is probably due to the fact that this sample was taken from a more protected area in the Inner Curtain Wall (so being less exposed to the vehicular pollution), which was restored more recently with respect to the areas of T8 and T9 sampling, so representing a shorter period of deposition.

Therefore, on the whole, the different concentrations of heavy metals and EF values in all analyzed samples can be attributed to several factors, such as different exposure to atmospheric agents, different exposure to direct (road or boat traffic) or indirect (industries) sources of pollution and different accumulation time of pollutants on the surfaces. This is particularly evident for crust samples which represent the same period of formation and have similar morphology and thickness but different amounts of heavy metals. Specifically, among the oldest crusts, T3 has lower concentrations of most trace elements with respect to T14, sometimes even lower than the recent samples T8 and T9. This can be explained by considering that sample T3 is less exposed to mobile emission sources since it was collected in the southern area of the monumental complex (facing the River Thames), which, as stated above, is mainly exposed to the prevailing winds and undergoes a more intense washing out by rain.

The last consideration worth mentioning is that in the altered substrate of the T8, T9 and T14 samples, the concentrations of Cu, Zn and Ni resulted to be high and, in the case of T14, even higher than in the crust (Figs. 6–8). Such high amounts can be justified by the geochemical mobility of these elements in certain environmental conditions. In-
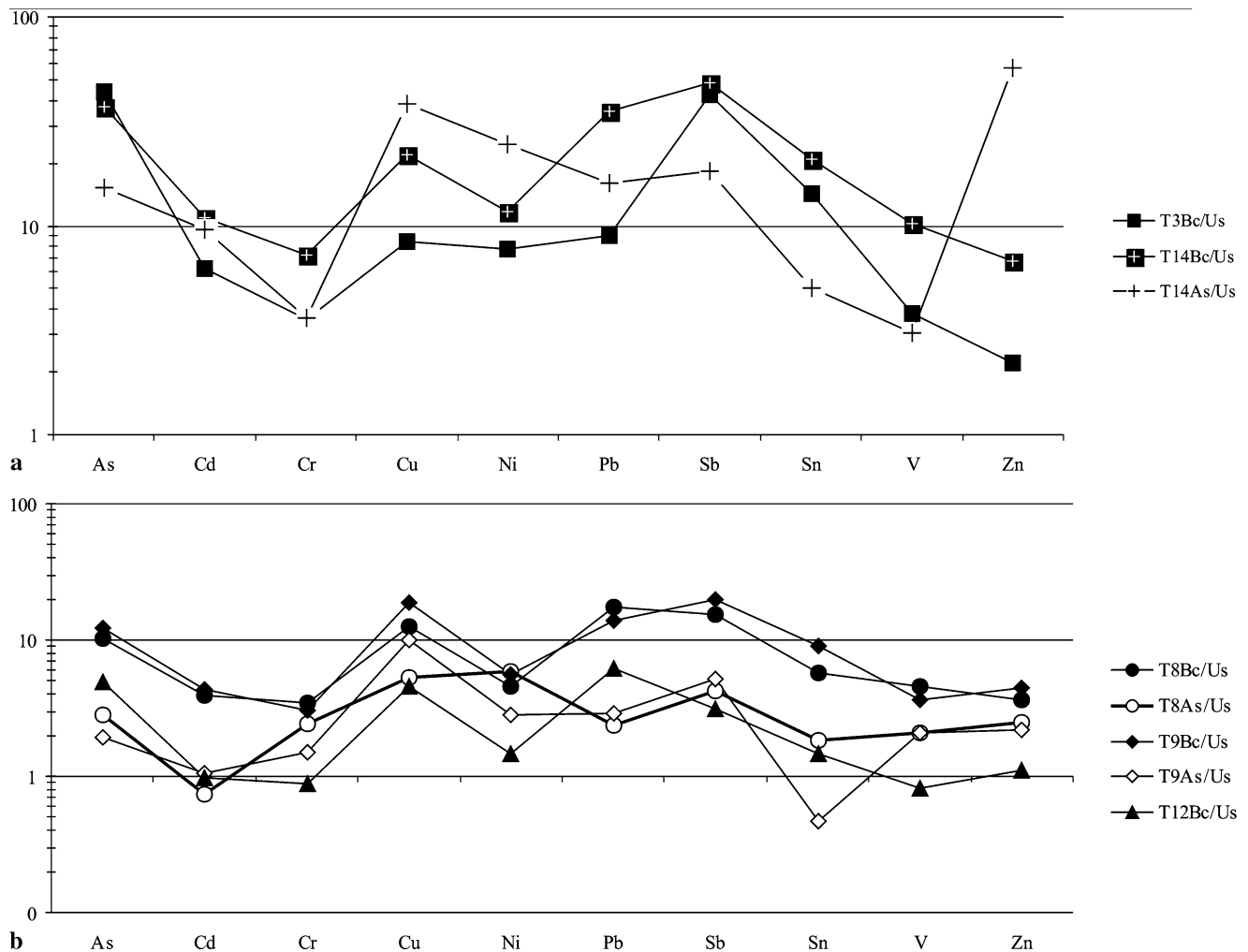
Fig. 8 Spider diagrams (logarithmic scale) of mean values of trace elements in black crusts and altered substrate normalized to the unaltered substrate for: (**a**) samples T3 and T14, (**b**) samples T8, T9 and T12, from the Tower of London

deed, as demonstrated by McAlister et al. [51–53], cations such as Zn^{2+}, Cu^{2+} and Ni^{2+} have higher mobility than others. In addition, these elements also have a strong affinity with calcite, hence increasing their concentrations onto the carbonate substrate and, moreover, acting as continuous catalysts for the oxidation of S(IV) and the formation of new crust [53]. In our case, the high Cu, Zn and Ni contents found in the upper part of the substrate in the three above-mentioned samples allows us to believe that past restorations made in the Tower of London did not take into account, before cleaning, the real contaminating metals which certainly the substrate had absorbed from the crusts and that probably accelerated the process of sulfating.

These considerations highlight the essential role of cleaning interventions of architectural surfaces, since the accumulation of contaminants in the crust and their action over time could cause a progressive deterioration of the stone substrate.

6 Conclusions

In this work, two types of crusts taken from the Inner and Outer Curtain Walls of the Tower of London were studied, specifically dendritic black crusts (the oldest) and thin brownish-grey crusts (of more recent formation).

The importance of this study is mainly due to the opportunity of analyzing crust samples from the same monumental complex but developed on sites with different exposures to the atmospheric agents (prevailing winds and washing out by rain), exposure to sources of pollution (boat or road traffic) and deposition time (documented past restorations were carried out in different historical periods in the diverse areas of the Tower).

Results obtained from the chemical characterization of damage layers in terms of trace elements allow us to make some important considerations:

(a) the oldest crusts collected from areas restored before the 1960s show higher concentrations of some specific heavy metals (As, Sb, Pb, Zn, Cu, Sn, Ni, Cd and Cr), which can be associated with coal combustion, this fuel being widely used in the city of London since the 13th century and until about 1960;

(b) samples taken in the proximity of roads show high amounts of Pb, Zn, Cu and V due to pollution by vehicular emissions;

(c) among the dendritic old crusts, the sample facing south on the River Thames exhibits lower concentrations of almost all heavy metals with respect to the coeval sample facing north-east, this side of the monument being more exposed to wind impact and rain washing out;

(d) a final consideration concerns the poor state of conservation of the substrate, which appeared to be highly altered due to the presence of numerous microfractures and displayed high amounts of Zn, Cu and Ni, sometimes higher than in the crust. Such a result can be explained by the high geochemical mobility of these elements and their high affinity with the calcite so that they can become catalysts for the formation of new crust and are responsible for the progressive deterioration of the stone substrate. As a result, this work wants to emphasize the importance of suitable restoration interventions that should be more frequent in time and carried out not only with the simple removal of the crust but taking into account the real state of conservation of the stone substrate.

References

1. M. Del Monte, C. Sabbioni, O. Vittori, Atmos. Environ. **15**, 645 (1981)
2. G.G. Amoroso, V. Fassina, *Stone Decay and Conservation* (Elsevier, Amsterdam, 1983), p. 453
3. A.V. Turkington, B.J. Smith, W.B. Whalley, in *Proc. 4th Int. Symp. Conservation of Monuments in the Mediterranean Basin*, Technical Chamber of Greece, Rhodes, May (1997), pp. 359–372
4. G. Zappia, C. Sabbioni, C. Riontino, G. Gobbi, O. Favoni, Sci. Total Environ. **224**, 235 (1998)
5. P. Brimblecombe, in *Urban Air Pollution—European Aspects*, ed. by J. Finger, O. Herter, F. Palmer (Kluwer, Dordrecht, 1999), pp. 7–20
6. P. Brimblecombe, J. Archit. Conserv. **6**, 30 (2000)
7. A. Bonazza, C. Sabbioni, N. Ghedini, G. Gobbi, Pollut. Atmos. Numèro Spèc. **7** (2007)
8. N. Ghedini, C. Sabbioni, A. Bonazza, G. Gobbi, Environ. Sci. Technol. **40**, 939 (2006)
9. C. Sabbioni, G. Zappia, Sci. Total Environ. **126**, 35 (1992)
10. C. Saiz-Jimenez, Atmos. Environ. B **27**, 77 (1993)
11. C. Sabbioni, G. Zappia, N. Ghedini, G. Gobbi, in *Proc. 8th Int. Congr. Deterioration and Conservation of Stone*, Berlin, ed. by J. Riederer (1996), pp. 333–337
12. P. Ausset, F. Bannery, M. Del Monte, R.A. Lefevre, Atmos. Environ. **32**, 2859 (1998)
13. C. Saiz-Jimenez, in *Air Pollution Reviews 2*, ed. by P. Brimblecombe, London (2004), p. 225
14. P. Brimblecombe, C.M. Grossi, in *Heritage, Weathering and Conservation*, ed. by Fort (Taylor & Francis, London, 2006), pp. 387–393
15. D. Barca, C.M. Belfiore, G.M. Crisci, M.F. La Russa, A. Pezzino, S.A. Ruffolo, Environ. Sci. Pollut. Res. **17**, 1433 (2010)
16. D. Barca, C.M. Belfiore, G.M. Crisci, M.F. La Russa, A. Pezzino, S.A. Ruffolo, J. Anal. At. Spectrom. **26**, 1000 (2011)
17. V. Comite, D. Barca, C.M. Belfiore, A. Bonazza, G.M. Crisci, M.F. La Russa, A. Pezzino, C. Sabbioni, in *Rendiconti Online della Società Geologica Italiana*, vol. 21, ed. by S. Critelli, F. Muto, F. Perri, F.M. Petti, M. Sonnino, A. Zuccari. 86° Congr. Naz. Società Geologica Italiana, Arcavacata di Rende, Roma, 18–20 September (2012), p. 652
18. C.M. Belfiore, D. Barca, A. Bonazza, V. Comite, M.F. La Russa, A. Pezzino, S.A. Ruffolo, C. Sabbioni, Environ. Sci. Pollut. Res. (2013). doi:10.1007/s11356-013-1810-y
19. P. Maravelaki-Kalaitzaki, V. Zafiropulos, V. Kilikoglou, M. Kalaitzaki, C. Fotakis, Spectrochim. Acta, Part B **52**, 41 (1997)
20. P. Maravelaki-Kalaitzaki, G. Biscontin, Atmos. Environ. **33**, 1699 (1999)
21. P. Brimblecombe, in *The Big Smoke*, ed. by P. Brimblecombe (Methuen, London, 1987), p. 185
22. P. Brimblecombe, in *Stone Cleaning*, ed. by R.G.M. Webster (Donhead, London, 1992), pp. 56–62
23. A. Bonazza, P. Brimblecombe, C.M. Grossi, C. Sabbioni, Environ. Sci. Technol. **41**, 4199 (2007)
24. E. Impey, G. Parnell, *The Tower of London: the Official Illustrated History* (Merrell & Historic Royal Palaces, London, 2000)
25. I. Lapper, G. Parnell, in *The Tower of London: a 2000-Year History* (Osprey, Colchester, 2000)
26. A. Bonazza, C. Sabbioni, N. Ghedini, Atmos. Environ. **39**, 2607 (2005)
27. C.M. Grossi, P. Brimblecombe, A. Bonazza, C. Sabbione, J. Zamagni, in *Heritage, Weather and Conservation*, ed. by Fort, Alvarez de Buergo, Gomez-Heras, Vazquez-Calvo (2006), pp. 441–446
28. F.G. Dimes, J. Ashurst, *Conservation of Building and Decorative Stone* (Routledge, New York, 2011), pp. 86–256
29. D. Gunther, C.A. Heinrich, J. Anal. At. Spectrom. **14**, 1363 (1999)
30. N.J.G. Pearce, W.T. Perkins, J.A. Westgate, M.P. Gorton, S.E. Jackson, C.R. Neal, S.P. Chenery, Geostand. Newsl. **1**(21), 115 (1997)
31. B.J. Fryer, S.E. Jackson, H.P. Longerich, Can. Mineral. **33**, 303 (1995)
32. S. Gao, X. Liu, H. Yuan, B. Hattendorf, D. Gunther, L. Chen, S. Hu, Geostand. Newsl. **26**, 181 (2002)
33. R.L. Folk, Am. Assoc. Pet. Geol. Bull. **43**, 1 (1959)
34. R.J. Dunham, in *Classification of Carbonate Rocks, Memoir 1*, ed. by W.E. Ham (American Association of Petroleum Geologists, Tulsa, 1962), p. 108
35. M. Del Monte, C. Sabbioni, Environ. Sci. Technol. **17**, 518 (1983)
36. C. Sabbioni, G. Zappia, Aerobiologia **7**, 31 (1991)
37. M. Monte, J. Cult. Herit. **4**, 255 (2003)
38. G. Barone, M.F. La Russa, A. Lo Giudice, P. Mazzoleni, A. Pezzino, Environ. Geol. **55**, 449 (2008)
39. A. Lluveras, S. Boularand, J. Roqué, M. Cotte, P. Giràldez, M. Vendrell-Saz, Appl. Phys. A **90**, 23 (2008)
40. C.M. Belfiore, M.F. La Russa, A. Pezzino, E. Campani, A. Casoli, Appl. Phys. A **100**, 835 (2010)
41. D. Gulotta, M. Bertoldi, S. Bertolotto, P. Fermo, A. Piazzalunga, L. Toniolo, Environ. Earth Sci. **69**(4), 1085 (2013)
42. H. Harmens, D.A. Norris, G.R. Koerber, A. Buse, E. Steinnes, A. Rühling, Atmos. Environ. **41**(31), 6673 (2007)
43. H. Harmens, D.A. Norris, The Participants of the Moss Survey, Spatial and Temporal Trends in Heavy Metal Accumulation in Mosses in Europe (1990–2005), ICP Vegetation Programme, Coordination Centre, Centre for Ecology & Hydrology/Natural Environment Research Council (2008)

44. C.J. Dore, T.P. Murrells, N.R. Passant, M.M. Hobson, G. Thistlethwaite, A. Wagner, T. Bush, Y.L.K.R. King, J. Norris, P.J. Coleman, C. Walker, R.A. Stewart, I. Tsagatakis, C. Conolly, N.C.J. Brophy, M.R. Hann, UK Emissions of Air Pollutants 1970 to 2006, UK NETCEN, AEA Technology, Culham, Oxfordshire (October 2008)
45. V. Keith, P. Neil, Assessment of Heavy Metal Concentrations in the United Kingdom. AEA Technology plc, Northern Ireland (April 2006)
46. Department for Environment, Food and Rural Affairs, National Atmospheric Emission Inventory. http://uk-air.defra.gov.uk/reports/empire/naei/annreport/annrep96/sect6_3.htm. Accessed 14 March 2013
47. M. Williams, Sci. Total Environ. **334**, 15 (2004)
48. C. Rodriguez-Navarro, E. Sebastian, Sci. Total Environ. **187**, 79 (1996)
49. M.D. Geller, L. Ntziachristos, A. Athanasios Mamakos, Z. Zissis Samaras, D.A. Schmitz, J.R. Froines, C. Sioutas, Atmos. Environ. **40**, 6988 (2006)
50. M. Winther, E. Slentø, NERI Tech. Rep. No. 780, National Environmental Research Institute, Aarhus University (2010)
51. J.J. McAlister, B.J. Smith, J.B. Neto, J.K. Simpson, Environ. Geochem. Health **27**, 429 (2005)
52. J.J. McAlister, B.J. Smith, A. Tőrők, Atmos. Environ. **40**, 6780 (2006)
53. J.J. McAlister, B.J. Smith, A. Tőrők, Atmos. Environ. **42**, 7657 (2008)