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Black layers on historical architecture

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Abstract

Background, aim and scope The external surface of any building in urban polluted environment is unavoidably destined to be covered with layers that assume a grey to black colour and are generally called 'black crusts'. These, according to standard protocols and glossary, are deteriorated surface layers of stone material; they can have variable thickness, are hard and fragile and can detach spontaneously from the substrate, which, in general, is quite decayed. Plain visual examination may lead to consider 'black crusts' all similar, whilst only a careful diagnostic investigation can distinguish 'black crusts' and the consequences of their formation on stone substrates. In this paper, various black layers on marble are studied and compared and the morphological and compositional characteristics discussed according to the related mechanisms of formation. Differences between old (hundred years) and recent crusts (30 years) are investigated and pointed out.

Materials and methods Samples of black crusts collected from the Milan Cathedral façade (Candoglia Marble) have been studied and compared with the careful and synergic employ of traditional techniques: optical (transmission and reflected VIS light) and electron microscopy, X-ray spectrometry and micro-Fourier transform infrared spectroscopy.

Results Visual examination of loose fragments does not allow to point out outstanding differences amongst the various samples; black layers have similar main mineral components, gypsum and airborne particles, with different spatial distribution. The microscopic studies allowed to point out the porosity differences, the gypsum crystallisation habit, different amount of embedded particles, level and progress of marble decay.

Discussion The observations lead to define three main types of black crusts: black crust deriving from marble sulphation, compact deposit and encrustation due to exogenic materials deposition. Black crusts show evidence of sulphation in progress, without a clear continuity solution between crust and marble; the lack of separation is particularly evident in 'recent' crust, where the sulphation process is more active. Black compact deposits show a higher porosity than black crusts because gypsum is not coming from the chemical corrosion of the substrate but from outside; actually, in the former case, the substrate is sound. Encrustations show a highly regular crystal organisation of gypsum (close packed tabular crystals) that cannot be traced back to casual atmospheric deposit or to corrosion of the substrate but rather to the crystallisation of a solution coming from an external source. Also in this case, the marble is sound; evidence of the effect of some protection treatment is pointed out.

Conclusions In spite of the apparent similarity of the examined samples, analytical results have evidenced three

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main types of black crusts: black crust with decayed substrate, compact deposit and black encrustation showing a sound substrate underneath. Experimental evidence of calcite grains sulphation in progress, taking place according to a model recently proposed, has been observed. Sulphation process is prevented where particular conservation treatments had been applied in the past.

Recommendations and perspectives New experimental studies can be focussed to understand the specific conditions (measurements of micro-climatic and thermodynamic parameters) and mechanisms for black crusts formation in situ. The problem of the kinetic of the sulphation process of marble, the assessment of black layers formation in the case of different carbonate stone materials and the study of acid attack in presence of surface protecting layers deserve further investigation.

Keywords Black crust · Heritage conservation · Marble degradation · Soiling · Sulphation

1 Background, aim and scope

Black layers, forming on monuments because of the interaction with the atmosphere, are a serious problem since very old times (Brimblecombe 1992). Great problems arose with the use of coal: England, for example, had to face the darkening of building surfaces since the thirteenth century. In the twentieth century, the use of fossil oils and the atmospheric pollution produced dramatic effects (Saiz-Jimenez and Hermosin 2004) mainly due to the diffusion of factories and vehicular traffic (Rosvall 1988, VVAA 1997; Lèfevre and Ausset 2002).

The most well-known kind of black layer is the so-called black crust (Camuffo et al. 1983; Del Monte and Furlan 1995; Maravelaki and Biscontin 1999; Chapoulie et al. 2008). This, according to standard protocols, glossaries[1] and recent studies (Fitzner and Heinrichs 2002), is a deteriorated surface layer of stone material; it can have variable thickness, is hard and fragile and can detach spontaneously from the substrate, which is, in general, quite decayed or pulverised (Amoroso and Fassina 1983; Johansson et al. 1988; Moropoulou et al. 1998; Charola and Ware 2002). According to ICOMOS (International Council of Monuments and Sites) glossary,[2] the definition of crust is "generally coherent accumulation of materials on the surface, which may include exogenic deposits in combination with materials derived from the stone. A crust is frequently dark coloured ('black crust') but light colours can also be found. Crusts may have an homogeneous thickness and thus replicate the stone surface or have irregular thickness and disturb the reading of the stone surface details. A crust may be weakly or strongly bonded to the substrate. Often, crusts detached from the substrate include stone material". From this, it seems clear that black crusts are essentially formed by a deposition process.

This paper is based on the study of marble samples collected from the façade of the Milan Cathedral. The architectural elements of the façade, built between the seventeenth and nineteenth century with Candoglia marble, are decorated with high and low relieves, pilasters, geometrical and vegetal figures and human sculptures. In the last 70 years, three great restoration campaigns implying a total revision and sometimes the substitution of marble elements have been carried out: the first in 1935–1939, the second in 1972–1974 and the last one, started in 2002, is now ending in 2008. During this conservation work, whilst mapping the weathering forms of marble, it has been remarked that the occurrence of 'blackening' is one of the most serious problems. Dark grey or black surface layers can be found everywhere on the façade, especially on sculpted elements sheltered from direct rainfall, as it could be expected. The morphological and chemical characterisation of samples coming from these deteriorated surfaces has been carried out, evidencing outstanding differences amongst decay patterns.

In this paper, we demonstrate that there are different types of black layers and discuss the implication on the mechanisms of marble degradation. We evidenced deposits, coherent deposits and crusts which imply the transformation of the marble. Actually, we could call them all 'dark coloured crusts' amongst which some are derived only from a deposition mechanism, others are derived from the sulphation of marble and soiling deposition, acting contemporaneously. Black or dark stone surfaces can be rather similar when their examination is limited to the visual inspection in situ, and, therefore, only a careful diagnostic inquiry can distinguish 'black crusts' with degraded substrate and severe consequences for the stone, from others which should cause less concern.

2 Materials and methods

2.1 Sampling

Several samples were collected from the marble surface of the Milan Cathedral showing the aspect of 'black crusts' at a visual examination. The samples were collected with

[1] Website: http://www.lrmh.culture.fr/icomos/Site_Web_Icomos/glossaires/background_glossaries_intro.htm http://www.stone.rwth-aachen.de/atlas.htm.

[2] Website: http://www.lrmh.culture.fr/icomos/Site_Web_Icomos/glossaires/background_glossaries_intro.htm http://www.stone.rwth-aachen.de/atlas.htm.

scalpel or lancet and the small fragments were stored in polyethylene case. Some samples have been collected from ashlars surely dated 1972, as they were substituted during the last restoration of the façade, and have been defined as ‘recent’ or ‘new’ samples, as they are about 30 years old; some others were collected from ashlars dated after the building age, and they have been considered ‘old’ ones. Four different samples have been studied and discussed in this paper as representative of different kind of black layers and ages of laying down. They are described in details in Table 1.

The Milan Cathedral façade is entirely covered and decorated with Candoglia marble, a coarse-grained marble quarried in Val d’Ossola (Candoglia, Verbania, Italy). It is a highly crystalline marble, low porosity metamorphic stone (P=0.5–0.7 vol.%) having poly-disperse pore radius distribution. Calcite is the prevalent mineral; quartz, phlogopite and pyrite mica are accessory minerals (Camisasca 1941; Papageorgakis 1961).

2.2 Analytical techniques

Loose samples and polished cross sections were observed using Leitz Wild M420XRD stereomicroscope and a Leitz Ortholux microscope with Ultropack illuminator in total reflected light, both equipped with video camera and digital image analysis. Thin sections (30 μm) were observed with a Zeiss Standard 25 polarising microscope, equipped with video camera and digital image analysis. Scanning electron microscopic observations were carried out on a JEOL 5910LV microscope equipped with a IXRF System/EDS 2000 energy dispersive X-ray spectrometer. The observations were carried out on polished cross sections following graphitisation. The energy dispersive X-ray (EDX) qualitative spectra of squared areas or spots were registered from 0 to 20 kV and at $1–3\times10^{-7}$ A. Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a Nicolet Nexus spectrophotometer equipped with a DTGS detector working between 4,000–400 cm^{-1}; the spectrophotometer is coupled with a Nicolet Continuum FTIR microscope equipped with a mercury cadmium telluride detector working between 4,000–700 cm^{-1}; micro-samples collected under the microscope were analysed by Graseby-Specac diamond cell in transmission mode whilst polished cross sections were analysed in total reflectance mode. Reflectance spectra have been treated with the Kramers–Kronig algorithm and transformed in transmittance spectra.

3 Results

At a plain visual examination in situ, all these samples present ‘crusts’ with very similar aspect (Fig. 1). Also when observing the surface of loose fragments by stereomicroscopy, they seem similar. They all are very rough because of the deposit of atmospheric particles; the prevalent colour is dark-brown or black: thicker the layer, more intense the colour. On the surface small white crystals are clearly visible. In spite of these similarities, a deeper analysis shows different patterns and characteristics.

As for the aspect of the crust, the observation of polished cross sections (Fig. 2) of ‘old’ samples (11S124, 9V125, 22H128) shows rather thick crusts (ranging from 200 μm to 2 mm) with an irregular top edge. The colour is black because of the accumulation of high amount of fly ashes into the layer, coming from air pollution; other coloured particles, red (iron oxides and hydroxides) or white (quartz and silicates), can be observed. The texture of the layer is rather homogeneous except for the boundary area near the marble surface. The crust of 11S124 sample (Fig. 2a) has a typical dendritic morphology: The gypsum crystals have grown perpendicularly to the marble surface and are associated in radial fibres; the texture is not compact, especially in the outer part, and is crossed by radial microfractures (Garcia-Valles et al. 1996). The crust of 9V125 sample (Fig. 2b) shows a smaller degree of organisation in the crystals. As for the 11S123 sample (Fig. 2d), the ‘recent’ crust collected just below sample 11S124, it is light grey since it contains less carbon particles and particulate matter, like silicates and oxides; the matrix of the layer is less compact and rather transparent and colourless. Sample 22H128 (Fig. 2c) is constituted of two overlaid layers, having a rather homogeneous thickness (80–100 μm). The inner layer is dark, compact, rather similar to that of the other ‘old’ samples (11S124), whilst the outer layer is clearer, transparent, with inclusions of a reduced amount of atmospheric particles, like the ‘recent’ sample 11S123, described above.

Table 1 Examined samples from the façade of Milan Cathedral

Sample	Approximate age	Location
11S124	Nineteenth century ‘old’	Low-relief decoration of a pilaster over the second order level
9V125	Eighteenth century ‘old’	Moulding of a second order window
22H128	1935–1939 ‘old’	Marble decoration of the crowning
11S123	1972–1974 ‘recent’	Low-relief decoration of a pilaster over the second order level

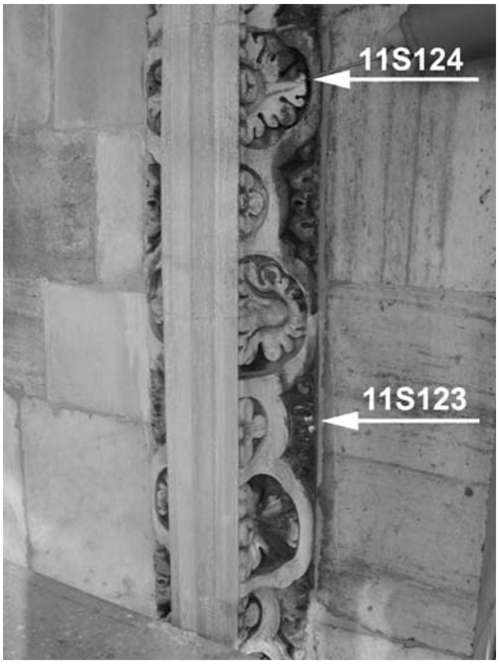
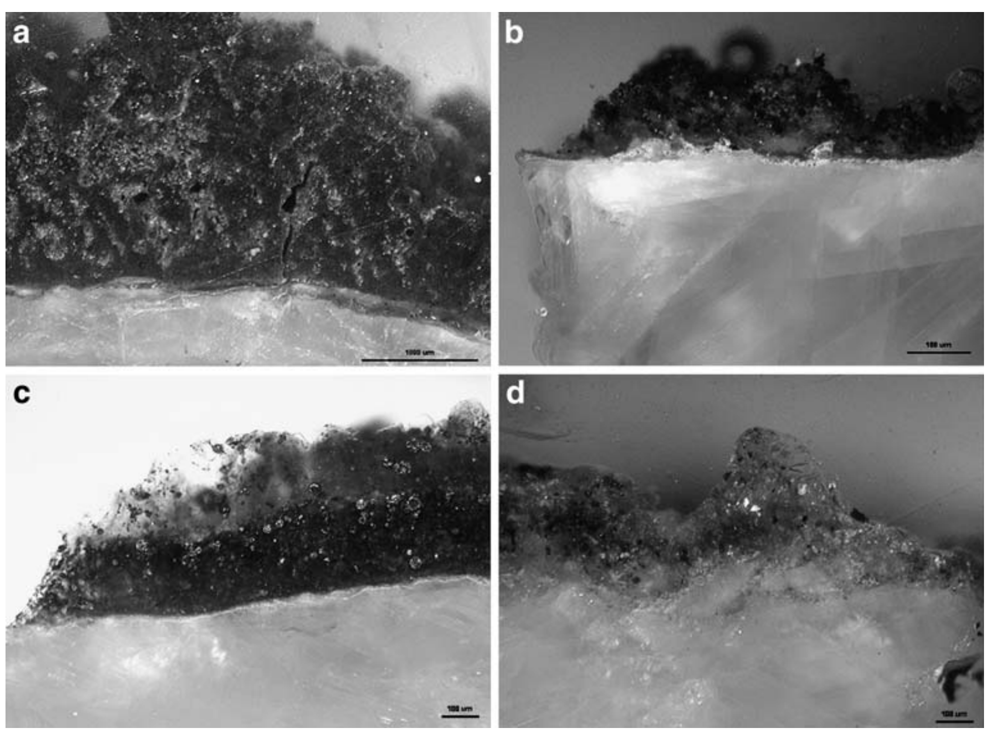


Fig. 1 Sampling area of 11S124 ('old' marble ashlars) and 11S123 samples ('recent' marble ashlars)

It is important to observe the interface area between 'crust' and marble: in the 'recent' sample (11S123), there is not a clear solution of continuity between substrate and grey layer and the new formed gypsum crystals are enclosed amongst surface calcite crystals of the substrate. In the older samples, an intermediate layer can be generally pointed out, between the black gypsum crust and the marble surface; in the case of 11S124 sample, an irregular, pale brown layer with calcite crystals detached from the substrate is clearly visible. Sample 9V125 shows, in the interface area, a thin (thickness 10–40 μm), white-grey layer with several black and red particles included that should be considered a finishing layer, intentionally applied. In 22H128 sample, the crust is perfectly adherent to marble and follows completely the surface trend; no intermediate layer can be observed and the net separation between black layer and substrate recalls a sort of 'painting' layer.

The petrographic examination on thin sections (Fig. 3) shows and confirms important differences amongst the samples. The crust of the 11S124 sample (Fig. 3a) shows gypsum crystals arranged in an irregular way, somewhere forming the well-known 'desert rose' pattern; the high amount of carbon particles prevent from better resolving the crystalline structure. The 'recent' sample 11S123 (Fig. 3b) shows a much more porous and clear gypsum layer than the above mentioned 'old' sample (11S124). The surface layer of 9V125 sample, mainly constituted of gypsum crystals, is full of pores, whilst the finishing layer has not been observed. The 22H128 'crust' (Fig. 3c) shows, when observed in thin section, two sub-parallel layers characterised by close packed tabular gypsum crystals: in the inner layer, the crystals are shaped in lamellae, vertically aligned, with the thinner side at sight; in the outer layer, instead, they are aligned with the widest side at sight. In both the layers, the structure is quite regular. This observation confirms that, at the interface

Fig. 2 Optical microscopic observation of polished cross sections in total reflected VIS light: **a** 11S124 (micrometric bar 1,000 μm), **b** 9V125 (micrometric bar 100 μm), **c** 22H128 (micrometric bar 100 μm) and **d** 11S123 (micrometric bar 100 μm)



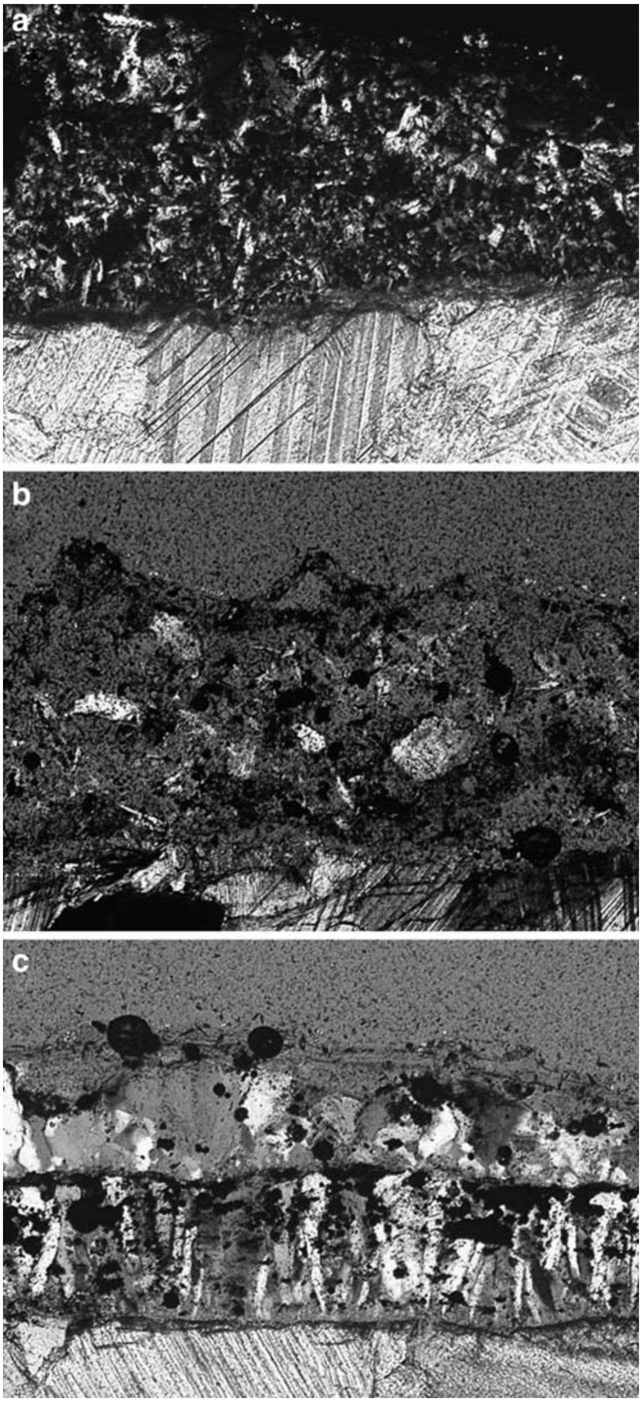


Fig. 3 Petrographic observation on thin sections (PPL, magnification ×125): **a** 11S124, **b** 11S123 and **c** 22H128

between crust and marble, the separation between decay layer and substrate is net.

The micro-FTIR spectra collected on the polished cross sections in total reflectance mode show for all the samples a strong prevalence of gypsum in the crust (3,530, 3,410, 1,684, 1,621, 1,145, 670 cm^{-1}); sometimes, there are also weak bands which prove the presence of organic contaminants deriving from the atmospheric deposition. In 11S124 sample, the micro-FTIR spectrum, registered at the interface with marble (Fig. 4a), shows, beyond the usual intense bands of gypsum, well visible peaks of calcium oxalate (1,648, 1,317, 781 cm^{-1}), whilst the spectrum registered in the outer layer of the black crust (Fig. 4b) shows only the absorption bands of gypsum.

The same polished cross sections have been analysed with scanning electron microscope equipped with EDX spectrometer: In Fig. 5, elemental maps of the examined samples are reported. This analysis confirms that the prevalent compound is gypsum, whilst airborne particles are evidenced by the elemental maps of Si, often correlated to Al and/or K; some Fe containing particles, more abundant in 'old' crusts than in 'recent' ones, are also pointed out.

In 11S124 sample (Fig. 5a), the crust appears to be divided into two sub-layers: an external gypsum layer that is more porous and rich in silicate particles and a thinner internal layer essentially composed of gypsum (Ca, S) having a more compact texture. The two layers are separated by a thin layer containing Si and Al. In some areas, the maps evidence that the crust is detached from the substrate. The S elemental map shows penetration of gypsum into marble, along calcite grains boundaries and micro-fractures.

In 11S123 sample (Fig. 5d), the 'recent' crust from the same area, the prevalent component of the crust is gypsum and the airborne particles are concentrated towards the surface of the crust, as for the 'old' sample; however, the Fe content is lower. The elemental maps show clearly that there is no separation between crust and marble and that the boundary with the substrate is very irregular. The marble shows an appreciable decay. In this sample, it is evident that a corrosion process is in progress, with the transformation of calcite grains into sulphate; Ca and S maps

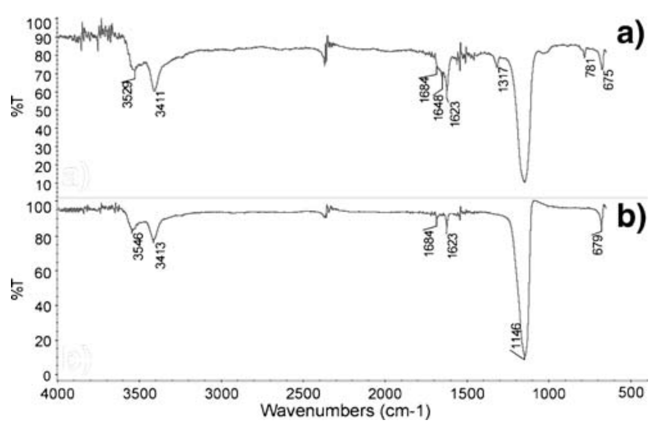


Fig. 4 11S124 sample, micro-FTIR spectra: **a** spectrum registered at the interface crust/marble and **b** spectrum registered near the surface of the black crust

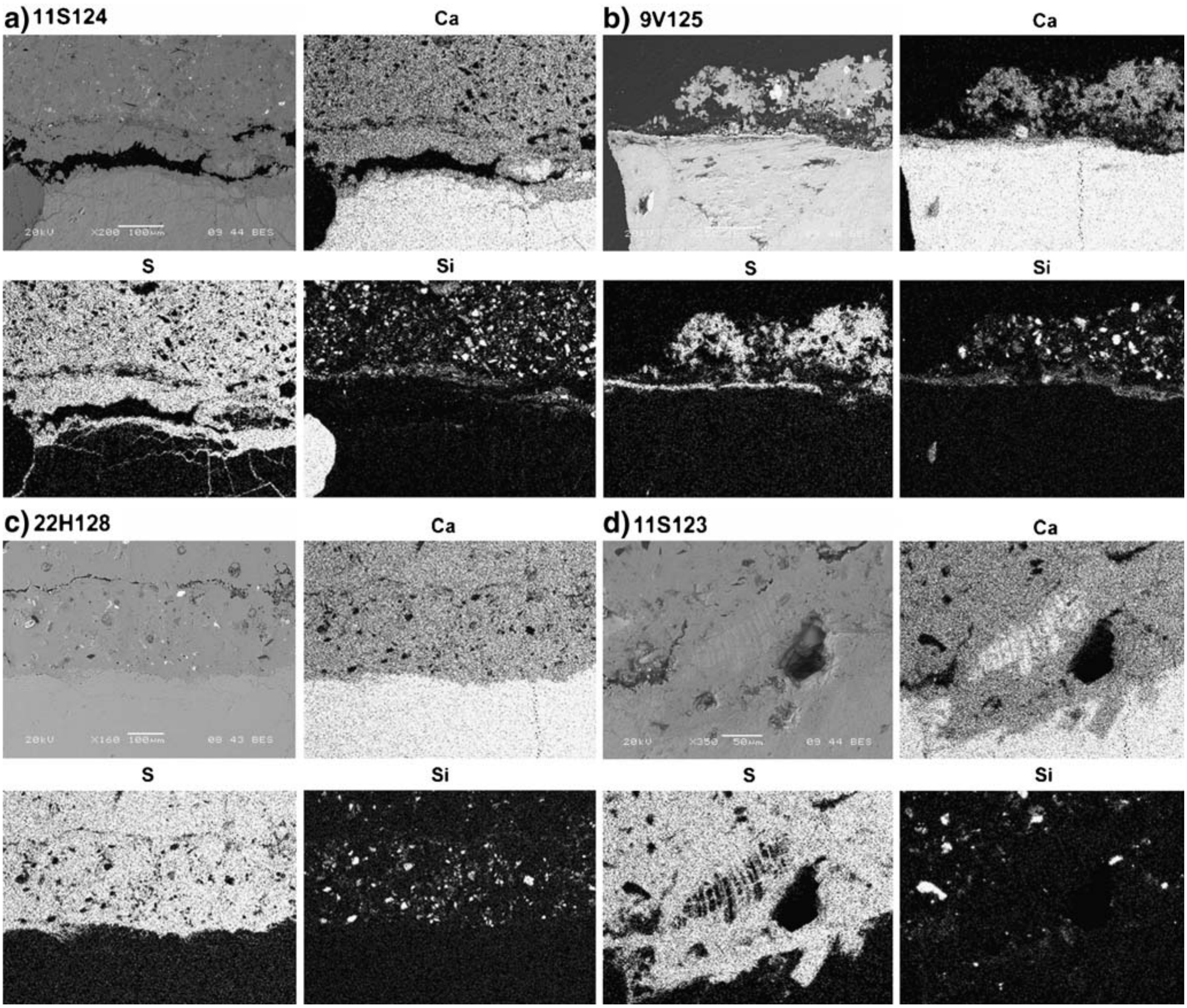


Fig. 5 Backscattered electron images and EDX elemental maps of Ca, S and Si of the polished cross sections of samples: **a** 11S124, **b** 9V125, **c** 22H128 and **d** 11S123

(Fig. 5d) shows a calcite grain, close to the substrate, that is being transformed.

In 9V125 sample (Fig. 5b), the maps of Ca and S confirm the less compact texture of the crust already observed in cross and thin sections. The finishing layer observed in cross section at the interface between crust and marble is well evidenced also in EDX maps and is composed of Ca, S, Si; in some micro-areas, it is covered by a very thin Ti-based layer. The marble does not show any appreciable micro-fracture or penetration of gypsum. As for the 22H128 sample (Fig. 5c), the elemental maps outline the two overlaid layers composed mainly by gypsum, of which the internal one rich in particulate matter; there is no intermediate layer between crust and marble, and the substrate is sound.

4 Discussion

Although the literature report about 'black crusts' as a wide general category of weathering phenomena, the above results demonstrate that we are in the presence of three different types of marble degradation, in spite of the similarity shown by the crusts after visual examination.

Recently, some authors (Siegesmund et al. 2007) examined the presence of white and black crusts on the Parliament façade in Budapest, and, analysing S content, Si/Al ratios and particulates in black crusts, they agree that air pollution (SO_2, dust) contributes to black crust formation. In the case of Milan cathedral, the crust of 11S124 sample is a 'black crust' according to the definition reported above in the "Background, aim and scope". It originates from the well-known process of chemical acid dissolution (sulphation) of marble:

$$CaCO_3 + H_2SO_4 + H_2O \rightarrow CaSO_42H_2O + CO_2$$

which implies the transformation of calcite (calcium carbonate) into gypsum (dihydrated calcium sulphate) under the action of the gaseous pollutant sulphur dioxide (Gauri and Gwinn 1982/1983; Elfving et al. 1994; Ausset et al. 1999; Allen et al. 2004) and to the contemporary deposition of carbonaceous particles from the atmosphere.

The black crust of 11S123 'new' sample is a corrosion layer as well, deriving from acid attack. In this case, the gypsum matrix is much more transparent than that of the 'old' sample, because of the smaller amount of included airborne particles. All the samples collected from recently substituted ashlars show this same characteristic. The gypsum formation kinetic is prevailing over the fly ash deposition. It is well assessed (Amoroso and Fassina 1983; Charola and Ware 2002) that this kind of black crust induces a chemical and mineralogical change in the substrate that is a quite worrying degradation.

The two samples 11S124 and 11S123 provide a nice example of sulphation process in progress. The observations carried out fit to the model recently proposed by other authors (Elfving et al. 1994; Ausset et al. 1999; Ausset et al. 2000; Maravelaki et al. 2002). A sort of pseudomorphism of gypsum after calcite takes place (Vergès-Belmin 1994): the corrosion process starts from the boundaries of calcite grains (Malaga-Starzec et al. 2004) and goes on penetrating through crystal structure and along pre-existent micro-fractures; it may happen that some calcite fragments, still under sulphation, are visible in the crust (Fig. 5d)—the cleavage lines and twinning planes along which the decay agent is corroding calcite and forming gypsum are quite evident. The original level of the artefact is preserved, and the new gypsum crystals are continuously forming at the interface marble/crust. Above the original surface level, the crust thickness increases, thanks to the volume increase of crystallised gypsum and to the atmospheric deposit of new materials (Vergès-Belmin 1994; Hamilton et al. 1995). The effectiveness and kinetic of this corrosion process should not be undervalued (Böke at al. 1999; Bugini at al. 2000): The thickness of the crust is a not completely reliable marker, as it is continuously eaten away by the atmospheric agents (like humidity and wind).

It is worth noting the presence of a Si- and Al-based layer that separates the black crust of 11S124 sample into two parts having different characteristics: the external one, above the Si layer, with high content of mineral clasts and fly ashes, and the inner one in contact with the marble substrate, clear, composed mainly of gypsum with rare inclusions. The Si/Al layer is the residue of an intentional treatment ('silicatization') probably applied in the first half of twentieth century; one can remind the 'silicates' used since the nineteenth century for stone conservation (Cattanei 1993). It is evident that the silica layer does not prevent the substrate sulphation, as far as a gypsum layer (about 70 µm thick) has formed under the treatment.

The black layer (crust) of 9V125 sample should be considered a 'compact deposit': the fact that the substrate is sound indicates clearly that the gypsum in the crust does not come from the chemical transformation of the underneath marble but from the outside environment (Garcia-Valles et al. 1996; Alessandrini et al. 2002). We call this kind of decay 'compact deposit' to distinguish it from the commonly known 'superficial deposit': the latter one is made of airborne particles, gypsum included, with poor coherence and low adherence to the substrate, whilst the former decay is much more thick, compact and shows a good adhesion to the substrate. The 'superficial deposit' becomes a 'compact deposit' through solution and re-crystallisation of gypsum, which can act as binder of the different contaminants and particulate matter (Hutchinson et al. 1992; Hamilton et al. 1995; Esbert et al. 2001; Grossi et al. 2003). Most probably, no corrosive interaction between the substrate and the deposit is taking place because of the presence of the finishing layer that is able to prevent the penetration of SO_2 or other pollutants into the substrate. It is worth noting that this sample is the oldest one and that the protective intervention has been crucially important for its conservation. The application of the finishing layer (20 µm thick) should be ascribed to the restoration of the 1970s, owing to the presence of a Ti rich coating in some areas, and we can assess that the corrosion of the marble did not proceed significantly during the last 30 years.

As for the 22H128 sample, the black layer should be considered an 'encrustation' that is a rather homogeneous deposit, originated by solidification/crystallisation of solution

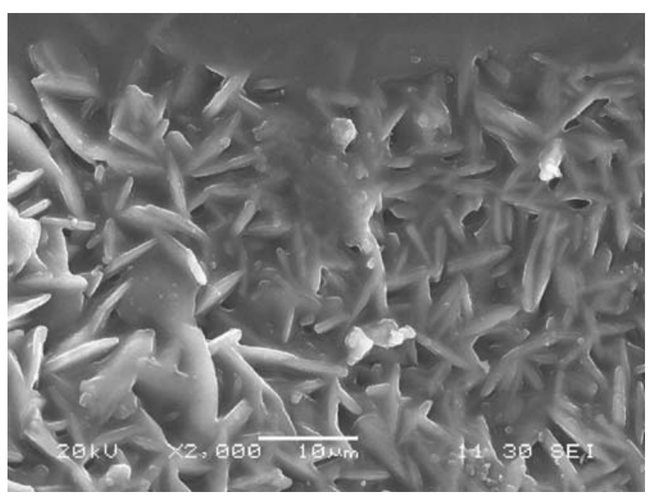


Fig. 6 SEM/SEI: gypsum crystals springing off acrylic resin film

and/or suspension of various components (cations, anions, minerals), coming from a source other from the substrate. In the present case, it could be the result of the slow crystallisation of gypsum from a flowing solution that runs along a surface protected from direct rainfall. The process is slow and allows a regular growth of the gypsum crystals (see the vertical aligned lamellar crystals); the inclusion of airborne particles and fly ashes gives origin to the final aspect of a 'black crust'. Apparently, no decay of the substrate was observed, but further investigations should be carried out to evaluate the possible erosion of the marble surface under the black layer.

In all the observed samples, some residue of the acrylic resin (poly-isobutylmethacrylate) applied in the restoration of the 1970s has been recovered after solvent extraction. At the same time, no acrylic layers were pointed out in the cross-section examination. The crystallisation of the gypsum, both in black crusts and encrustations or deposit, is able to pierce the resin and to fracture the coating film (Fig. 6) which looses its protective role; actually, in large areas, the acrylic treatment has been applied over the black layer. For instance, in the case of 22H128 sample, it can be hypothesised that the two gypsum layers are separated by the application of the acrylic treatment over the first layer and that the external layer would be the encrustation grown up in the last 30 years.

5 Conclusions and recommendations

Three different patterns of decay have been pointed out for marble samples coming from rain sheltered surfaces of the façade of Milan Cathedral, which could all be reported as 'black crusts'. They seem very similar (rough and dark) when observed in situ or by stereomicroscopy, but the analyses evidence decisive differences in their origin, meaning and in the state of conservation of the substrate. Amongst these black layers, 'black crusts' presenting a highly decayed substrate, 'black crusts' originating as compact deposits or slow gypsum encrustations with a rather sound substrate, can be perceived. The present study has shown that gypsum in black layers does not always comes from chemical corrosion (acid attack) of the calcite but may also come from environmental deposition. In particular, gypsum of compact deposits and encrustations comes entirely from the surrounding since there is no evidence of sulphation mechanism in progress. The sulphation attack of calcite may be absent when the surface has been conveniently protected.

Many directions, to fully understand the possible mechanisms of black layers formation, are still deserving attention: the problem of the kinetic of the sulphation process of marble, the assessment of black layers formation in the case of different carbonate stone materials and the study of acid attack in presence of surface protecting layers. As for enhancing the practice of restoration, it is of critical importance to build up a new shared glossary of the deterioration pattern of stone materials.

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