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*Title Page

The environmental impact of air pollution on the built Heritage of Historic Cairo (Egypt)

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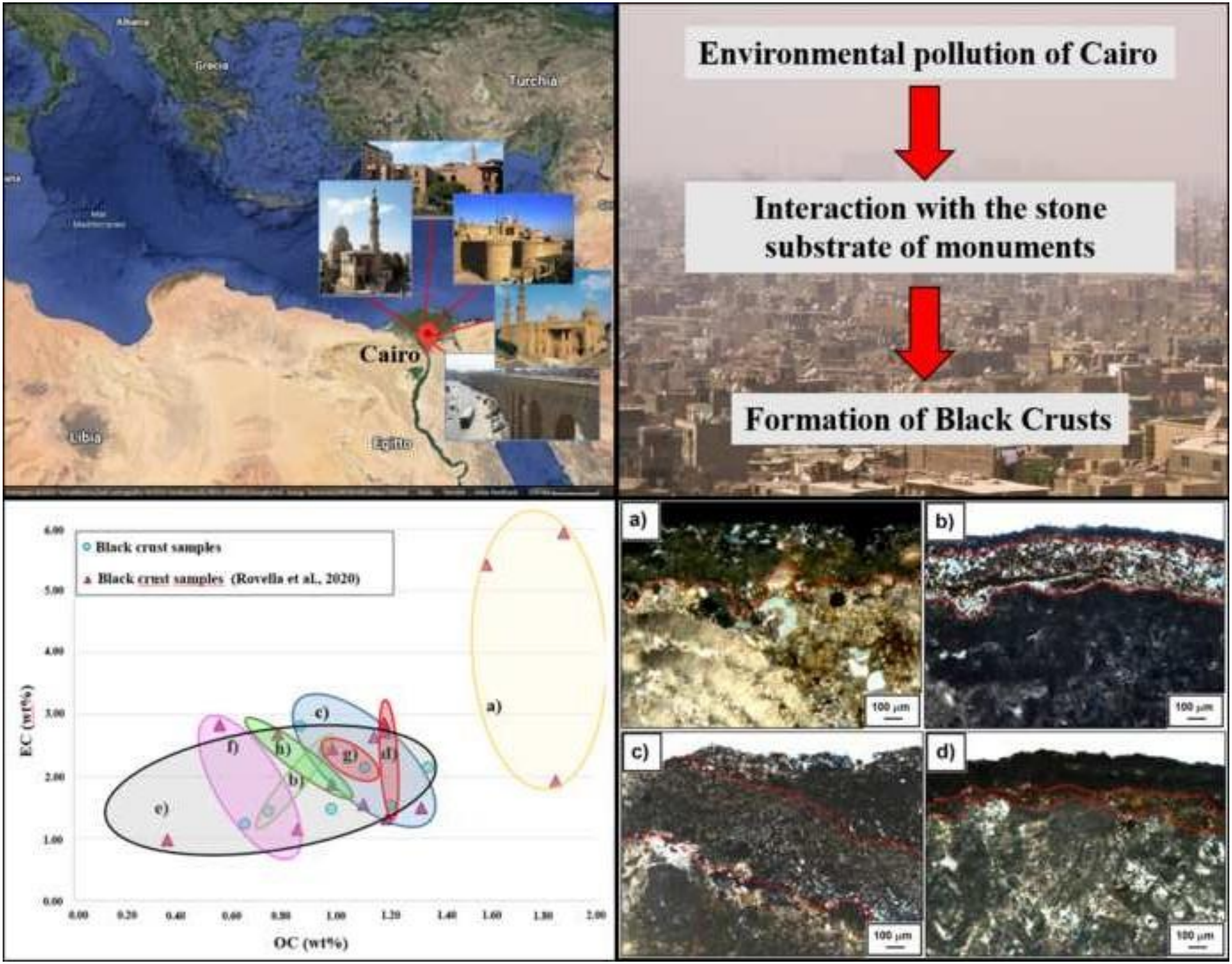
*Graphical Abstract



***Highlights (for review : 3 to 5 bullet points (maximum 85 characters including spaces per bullet point)**

Highlights:

-Black crusts from Cairo have been analyzed by several techniques

-The effect of urban air pollution on the monuments of Cairo have been investigated

- The methodology allowed identification of pollution sources in the black crusts

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Abstract

In the last decades, many researchers investigated the relation between environmental pollution and the degradation phenomena on the built heritage, because of their rapid increase and growing harmfulness. Consequently, the identification of the main pollution sources has become essential to define mitigation actions against degradation and alteration phenomena of the stone materials. In this way, the present paper is focused on the study of the effect of air pollution on archaeological buildings in Historic Cairo.

A multi-methodological approach was used to obtain information about the chemical composition of examined black crusts and to clarify their correlation with the air pollution, specifically the heavy metals and the carbonaceous fraction, their main sources, and their impact on the state of conservation of the studied sites.

All specimens were characterized by polarized optical microscopy (POM), X-Ray Diffraction (XRD), Electron Probe Micro Analyser coupled with energy dispersive X-ray spectrometry (EPMA-EDS), laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and Thermo-gravimetric analysis (TGA).

The results indicate a good correlation between the composition of black crusts and the main pollutant sources in Cairo such as vehicular traffic and industrial activities.

Keyword: air pollution; built cultural heritage; black crust; heavy metals; carbonaceous fraction; degradation.

1. Introduction

Cairo is the largest city in Egypt and in Africa; here, the air pollution produced many environmental problems related to aerosol particulate matter and to the high levels mostly of sulphur dioxide and lead. For this reason, it was listed as one of the most polluted cities in the world (Gurjar et al., 2010). The air pollution sources in the city are different and include burning of rubbish, vehicle emissions (~4.5 million cars on the streets of Cairo) and urban industrial activities. The city has 15–20 million inhabitants and is characterized by high congestion due to a population density of 13107/km^2 (Abbass et al., 2020). Furthermore, the lack of rain helps the accumulation of pollutants. The entire area of Cairo is severely affected by industrial and urban emissions of metals and metalloids (Abdel-Latif and Saleh, 2012). For example, only the cement industry releases around 2.4 million tons per year of cement bypass dust into the atmosphere (Alkhdhairi et al., 2018).

Moreover, it was estimated that the high Particulate Matter (PM) concentrations cause around 10 % of premature deaths in Egypt, where the national cost of air pollution is estimated at $20.9 million (Abbass et al., 2020).

An important factor that contributes to the air pollution increase is represented by the climatic conditions (Lowenthal et al., 2014; Alkhdhairi et al., 2018) and the remarkable seasonal temperature changes; in fact, its climate is classified as hot arid (BWh, according to the Köppen and Geiger (1936) climate classification).

At the same time, Cairo city produces 10,000 Tm of waste daily, often burned illegally. Previous studies on air pollution and atmospheric aerosols emissions from industrial and urban sites in Greater Cairo Area (GCA) highlighted how heavy metals represent a relevant and worrying component (Robaa, 2003; Abu-Allaban et al., 2007, 2009; Zakey et al., 2008; Abdel-Latif and Saleh, 2012; Shaltout 2013a,b, 2014).

Borai and Soliman (2001) demonstrate a direct relationship in Cairo city between the trace metals (e.g. Pb, Cd, Zn, Ni, Mn, Pb, Zn, and Cu) present in the aerosol PM and the anthropogenic activities such as vehicular traffic and industries, specifically, ferrous metallurgical work, foundries, lead smelters, lead batteries, ceramics, glass, bricks, textiles and plastics.

In this regard, many lead and copper smelters that heavily pollute the city air are unregistered. This fact produced a permanent haze over the city with PM reaching over three times the normal levels (Creighton et al., 1990).

In some studies (Khairy et al., 2011; Abdel-Latif and Saleh, 2012), the role of the road dust is clarified: dust deposits and accumulates on ground surfaces, along roadsides that are contaminated by heavy metals and organic matter. It does not remain deposited in place for long but is easily re-suspended back into the atmosphere, where it provides a significant amount of trace elements. The mentioned reference indicates that road dust within Cairo contains higher concentrations of elements (Pb, Zn, Cd, As, Sn and V) mainly reflecting the contribution of vehicular traffic and industrial activities.

Pollutants are deposited on the surface of stone materials constituent of the historical buildings. Indeed, those ones suffer serious deterioration phenomena in Cairo as a result of physical-chemical and biological effects (El-Tawab et al., 2012), favouring black crust formation, alveolization, chemical alterations, disaggregation pitting, cracks, erosion (Davidson et al., 2000).

Black crusts are one of the most dangerous degradation products in building stones and are closely connected with environmental pollution, especially the atmospheric one. They are very common on the carbonate substrates such limestones. This lithotype is widely used for the construction of historical monuments in the whole Mediterranean area thanks to its workability, durability and aesthetic features; nevertheless it is frequently affected by degradation phenomena (Fitzner et al., 2002; La Russa et al., 2013a; Ricca et al., 2019) firstly black crusts.

They are formed through sulphating processes of the stone surface where calcium carbonate ($CaCO_3$), which is the main constituent of limestone, is transformed into gypsum $CaSO_4*2H_2O$

(Whalley et al., 1992; Comite et al., 2012, 2019, 2020a,b; Rovella et al., 2020). Metals and metal oxides, present in the atmosphere, catalyse the sulphating reaction (Fermo et al., 2020). This process affects mainly stone materials having carbonate nature (for example limestone, marble, lime mortar). In addition, during the crust formation, particulate matter, which contains mainly amorphous carbon and several heavy metals, can be embedded into the gypsum, providing its characteristic black colour (La Russa et al., 2018) and altering the aesthetic appearance of the monuments. For instance, the old structures in Cairo, originally of a whitish colour and some even striped with the “ablaq” style (in some instances it is hard to spot the stripes due to the amount of dust covering the surface) are now completely blackened (Orphy and Hamid, 2004). Moreover, black crusts threaten the conservation of the stone surfaces: hard crusts, usually firmly attached to the stone are very hard to remove and can weaken the surface on which they develop.

For all these reasons the attention of the scientific world is steadily increasing on the effect of air pollution on archaeological buildings in Cairo and, consequently on the relative degradation products, (Fitzner et al., 2002; Khallaf, 2011; Kukela and Seglins, 2011; Abdelmegeed et al., 2019).

The present research was conceived in this context and deals with the relation between air pollution and the historical building in Cairo.

The study areas are located in the historic Cairo (Fig. 1S available in *Supplementary material*) and includes the outer walls of Salah El-Din citadel, the Magra El-Oyoun wall, and monuments of the Northern Mamluk cemetery such as the Mosque of the Sultan Faraj ibn Barquq, the Qaitbay Mosque and the tomb of Qansuh Al-Ghuri. They were selected for historical-artistic relevance, location in the urban context characterized by different prevailing pollution sources and building stone materials (i.e., limestone).A complementary analytical approach was applied to gain information on the chemical composition of the collected black crusts and define a correlation between the air pollution, especially the heavy metals contribution and the carbonaceous fraction, and their main sources , as well as to study the conservation state of the investigated sites.

The samples were characterized by polarized optical microscopy (POM), X-Ray Diffraction (XRD), Electron Probe Micro Analyser coupled with energy dispersive X-ray spectrometry (EPMA-EDS), laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and Thermo-gravimetric analysis (TGA).

2. Materials and Methods

The limestones used for the construction of the historical stone monuments in Cairo come from local middle and late Eocene outcrops (47.8- 33.9 million years ago) located in Mokattam, Helwan and Giza areas (El-Nahhas et al., 1990; Ahmed et al., 2006; Park and Shin, 2009; Aly et al., 2015, 2020). These materials are still being used for stone replacement or rebuilding works in monuments preservation practice as well as for modern buildings.

All the monuments underwent various rebuilding interventions over time and there is not very reliable information about them. Regarding restoration in modern epoch, it is known that several interventions were carried out in the 19th century, 1990s and early 2000s.

Samples consist of black crust and stone substrate, were taken from some portions located on vertical surfaces of the selected monuments, seriously affected by degradation phenomena and exposed to high rates of environmental pollution (Table 1).

A complete characterization of stone substrate and black crust associated was carried out, applying different analytical techniques aimed to determining the stationary and mobile combustion sources, major responsible for the blackening and soiling encountered.

POM analyses were performed on polished thin sections by using a Zeiss Axiolab associated with AxioCam MR for digital image acquisition. This technique is aimed to characterize both substrate and black crusts and to investigate the substrate/black crust interface determining minero-petrographic features and evaluating the degradation degree of each sample.

XRD analysis was carried out to identify the mineralogical phases constituting the black crusts sampled. Measurements were performed using a Siemens D5000 diffractometer and spectra were taken in the range 5°–65° 2Θ, using a step-size of 0.02° 2Θ and a step-time of 2 s/step.

Samples were carefully prepared by separating the limestone substrate from the black crust and pulverized them in an agate mortar.

An EPMA - JEOL - JXA 8230 —coupled with an EDS spectrometer - JEOL EX-94310FaL1Q - Silicon drift type— was used in order to observe the micro-morphology and analyse the composition in terms of major chemical elements. The EDS analyses were carried out according to the following operating conditions: 15 keV HV; 10 nA probe current; 11mm working distance; 40° take off; and 30 seconds live time. Before measuring, samples were graphite (ultra-pure graphite) sputtered to facilitate the electron conductivity by generating a ± 5 nm thick film, applied by Sputter - Carbon Coater QUORUM Q150T-ES, 70 A pulse current and 2.5 sec pulse time).

Chemical analyses of the black crusts, as well as of the substrates, in terms of trace elements were performed by LA-ICP-MS. This method can analyse a great number of chemical elements with a spot resolution of approximately 40–50 μm, which also allows the determination of compositional variations at a micrometric scale. Analyses were carried out using an Elan DRCe instrument (Perkin Elmer/SCIEX), connected to a New Wave UP213 solid-state Nd-YAG laser probe (λ=213 nm). Samples were ablated by a laser beam in a cell following the method tested by Gunther and Heinrich (1999). The ablation was performed with spots of 40–50 μm with a constant laser repetition rate of 10 Hz and a fluency of ~ 20 J/cm^2 (Barca et al., 2011). Calibration was performed using the NIST 612-50 ppm glass reference material as external standard (Pearce et al., 1997). Internal standardization to correct instrumental instability and drift was achieved using CaO concentrations from EPMA-EDS analyses. Accuracy was evaluated on BCR 2G glass reference material and on an in-house pressed-powder cylinder of the standard Argillaceous Limestone SRM1d of NIST (Barca et al., 2011). The resulting element concentrations were compared with reference values from the literature (Gao et al., 2002). Accuracy, as the relative difference from reference values, was always better than 12 %, and most elements plotted in the range of ±8 %. Analyses were performed on 100 μm thick cross-sections including both the black crust and the unaltered substrate samples in order to reveal the geochemical variability. TGA was carried out for the quantification of the carbonaceous fraction (TC total carbon= OC organic carbon + EC elemental carbon), Ox oxalate, CC carbonatic carbon and gypsum, present in the black crusts. It was performed by a Mettler Toledo TGA/DSC 3+, which allows simultaneous TG and DSC (Differential Scanning Calorimetry) analyses. The analyses were conducted in the range 30°- 800° C, increasing temperature with a rate of 20° C/minute. The carbonaceous components were estimated in temperature ranges defined by previously studied standards and using two different atmospheres, i.e. the inert and the oxidant one. The complete methodology is described also in previous works La Russa et al. (2017).

3. Results and discussion

3.1. POM Analysis

Sample 2, coming from Salah El-Din citadel, is classified as biomicrite (Folk, 1959) and wackestone (Dunham, 1962). Moreover, quartz, iron oxides and macroforaminifera, i.e. nummulites (Khallaf, 2011) were also identified.

The crust overlapping the substrate is brownish in colour, has a roughly uniform thickness of about 175 μm, it is composed by microcrystalline gypsum, brownish iron oxides and carbonaceous particles (Fig.1a).

The crust-substrate contact is rather clear with a marked separation between them.

The substrate in sample 3 is classified as biomicrite (Folk, 1959) or mudstone (Dunham, 1962). It includes allochems as quartz, rare iron oxides and fossils. The crust is located in small areas of the substrate and has a slightly variable thickness of about 20-30 μm, containing iron oxides inside. It is well adhered to the substrate and appears with irregular and strongly discontinuous edges.

The substrates of samples 12 and 14 are classifiable as biomicrite (Folk, 1959) and mudstone (Dunham, 1962).

In particular, the substrate of sample 12 includes rare quartz and plagioclase crystals. The black crust overlying the substrate is rather compact with an overall thickness varying between 50 and 200 µm. It shows a not so clear stratification but at least two layers are recognizable. The crust is well adhered to the substrate, has irregular morphology, is made up of microcrystalline gypsum and incorporates numerous spherical and sub-spherical carbonaceous particles.

In sample 14, the crust has an average thickness of 400 µm and shows an evident stratification (Fig.1b): an external dark brown layer with an average thickness of 50 µm and a rather regular external profile; an innermost layer, light brown in colour, reaching in some places a thickness of 300 µm and deepening into the substrate for about 100 µm. The contact crust/substrate is mainly sharp.

The crust is made up of microcrystalline gypsum and includes from sub-spherical to spherical carbonaceous particles, particularly numerous, especially in the inner layer (Fig.1b) and averagely 30 µm in size.

Sample 15 is classified as biomicrite (Folk, 1959) and mudstone (Dunham, 1962). The crust is thick from 400 to 1000 µm, and not well adhered to the substrate. It consists of microcrystalline gypsum and is layered in three levels (Fig. 1c): the outermost one shows a dark brown colour and an average thickness of 200 µm; the intermediate and the inner layers show a gradually lighter grey-brown colour and vary in thickness from 200 to 500 µm. Carbonaceous particles are present throughout the thickness of the crust, but are noticeably abundant in the inner layer. They show a spherical-subspherical shape and a variable size from 20 to 50 µm

The substrate of samples B and E is biomicrite (Folk, 1959) and wackestone (Dunham, 1962) with bioclasts of considerable size exceeding 1mm (Fig.1d). The crust overlies regularly the limestone to which is well adhered; however, the morphology and thickness are rather irregular, the last one varying from 50 to 400 µm.

The crust in sample B is constituted by microcrystalline gypsum and contains rare carbonaceous particles and iron oxides. It is possible to identify a darker brown outer layer, with a regular and thin thickness of about 20 μm, and a brownish inner layer that has a greater and irregular thickness, from 50 to 300 μm in the points where it deepens into the substrate.

The crust in sample E is discontinuous, with a variable thickness from 50 to 500 μm, consists of microcrystalline gypsum and, at least, two irregular levels are distinguished (Fig.1d): the outer one is browner and contains numerous carbonaceous particles; the internal layer, where present, is lighter and reddish, about 100 μm thick and the carbonaceous particles are less common. The substrate of sample H is classified as biomicrite (Folk, 1959) and mudstone (Dunham, 1962). The allochem fraction includes quartz and macroforaminifera fragments.

Overall, the crust is fractured, jagged with very irregular edges (Fig. 1e). It also appears divided into two layers: the outermost dark coloured with a thickness of about 500 μm, the innermost light grey with a thickness of 200 μm. Microcrystalline gypsum, iron oxides and numerous carbonaceous particles are visible in both.

3.2 XRD Analysis

The analysis (Table 1S available in Supplementary material) revealed the presence of gypsum, calcite and secondarily quartz as the main mineralogical species in almost all the crusts examined. Quartz and calcite come from the limestone substrate, while gypsum is the main constituent of the crusts (Barca et al., 2011; Belfiore et al., 2013; La Russa et al., 2013b; Ruffolo et al., 2015). Among the other mineralogical phases, plagioclase, K-feldspar, hematite and clay minerals were identified in subordinate amount.

The crusts include halite, the most common sodium chloride salt in the subsurface water of Egypt and in sea spray coming from the Mediterranean Sea (Aly et al., 2015) and consequently also in Egyptian limestones (Gauri and Holdren, 1981; Gauri et al., 1986; Helmi, 1990). The salt is linked to the capillary rise of water from the subsoil and the consequent precipitation of the salt inside the stone (Charola, 2000; Fitzner et al., 2002; Gomez-Heras and Fort, 2007).

3.3 EPMA-EDS Analysis

EPMA-EDS morphological and microchemical analyses were carried out on the black crusts of the five sites.

In the samples 2 and 3 the crusts show an irregular morphology. Compositional analysis revealed CaO as major component, followed by SO_3, SiO_2, Al_2O_3, ClO e FeO, Na_2O, MgO, K_2O.

Black crusts of samples 12-14 are adherent to the substrate, especially sample 12 (Fig. 2S a); they appear rather compact. Gypsum microcrystals and carbonaceous sub-spherical particles were identified.

The crusts are constituted mainly by CaO and SO_3 thanks to gypsum-based composition, secondly by SiO_2, and lastly ClO, Al_2O_3, Na_2O, MgO, K_2O, FeO. In sample 12, gypsum was detected also in substrate, where the crust is thicker and deepens in.

The black crust in sample 15 shows a homogeneous morphology (Fig. 2S b). It does not properly adhere to the underlying substrate, due to the presence of numerous fractures, that in some points cross the entire body of the crust.

The most abundant component is mostly CaO, followed by SiO_2, SO_3, ClO, and lastly Al_2O_3, FeO, K_2O, MgO, Na_2O, TiO_2 and P_2O_5.

The crusts taken from Qaitbay Mosque show slight different morphological features.

Sample E is rather compact, with a regular external profile and a sharp contact with the substrate (Fig. 2S c). The crust in sample B is more porous with a dendritic morphology. It is adherent to the substrate except in some points, where the two portions are separated by fractures. In both crusts, acicular crystal of gypsum and sub-spherical carbonaceous particles were recognized.

The chemical analysis suggested how CaO is the predominant component, followed by SiO_2, SO_3, secondly by, ClO, Al_2O_3, Na_2O, K_2O, FeO and lastly by MgO, P_2O_5 and TiO_2.

The sample H shows in general an irregular morphology, fractures, and jagged edges. However, it was individuated little portions more homogeneous, compact and adherent to substrate, that were analysed by EDS and then by LA-ICP-MS. Gypsum microcrystals and carbonaceous particles were identified in the crust. The chemical composition is characterized by a high amount of CaO, Al_2O_3, SiO_2 and SO_3, followed by Na_2O, P_2O_5, K_2O, and TiO2.

3.4 LA-ICP-MS Analysis

Trace elements concentrations were determined by LA-ICP-MS on the black crusts and underlying substrates of all the examined samples. The results obtained for each spot analysis are listed in Table 2S, where average values and corresponding standard deviations are displayed.

Looking at the concentrations of the most significant trace elements (Table 2S), elements like lead (Pb), barium (Ba), vanadium (V), chromium (Cr), cobalt (Co), zinc (Zn) and arsenic (As) have relatively high concentrations, indicating an accumulation of atmospheric pollutants on the gypsum crusts, regardless of the sampling location. The documented high concentrations of lead suggest that this element is still present in the urban environment of Cairo city many years after the ban of leaded gasoline in Egypt (Fujiwara et al., 2011), as it has been also shown by previous studies in other cities around the world (Sanjurjo Sánchez et al., 2011; Török et al., 2011; Graue et al., 2013).

As well known, all these elements can be introduced in the urban environment by a wide range of different anthropogenic processes, mainly mining, smelting, industrial manufacturing, metal processing, etc. (Johnson et al., 2011) but also by domestic and residential activities (heating, vehicles, transport). However, some elements occur naturally in the same urban environment as a result for example of geologic processes (erosion of outcropping bedrocks). The proportion of natural and anthropogenic components may vary widely depending thus on the geology and the industrial history of the urban centre. Our geochemical approach was addressed to define the relation between pollution sources and degradation state of stone materials; for this purpose, Enrichment Factor was calculated both for heavy metals, metalloids and Rare Earths Elements (hereafter REE). Enrichment factors calculation is a procedure commonly used in geochemical studies for the determination of the anthropogenic origin of chemical elements. For the purpose of our study, the chemical procedure was followed by normalizing the chemical composition of trace elements in black crusts with respect to those of calcareous substrates on which they grew (Table 3S).

The normalization procedure performed here used Scandium (Sc) as 'conservative' element, as it was presumed to have no anthropogenic enrichment or a minor anthropogenic input (Loring, 1991; Gallego et al., 2013). This calculation is carried out by comparing the concentrations of the trace elements with those of the conservative element by following the formula $EF = (M/N)_{sample}/(M/N)_{substrate}$, which is the ratio between the concentrations of the metal (M) and those of the normalizer (N), both for the sample and for substrate samples (Reimann and Caritat, 2000). Figure 2 show EFs for all the examined samples grouped for sampling location criterion. As shown in the Figure 2, samples 2 and 3 are enriched in Zn, As, Pb, REE (L-REE, light and H-REE, heavy) and Sn, Ba, Pb and HREE, respectively. Similarly, samples 12 and 14 show enrichment in all the LREE and in most metals and metalloids elements. The same enrichment trend (Fig. 2) is highlighted by the remaining samples (B, E, 15 and H).

Samples B and E reveal enrichments in Co, Mo, Sn, Sb, Ba, Pb, and Sn, Ba, Pb, respectively with associated null or slight enrichment in REE. As regards sample 15, metals and metalloids are similarly enriched as in the previous samples, while the REE show values close to the background. Conversely, sample H shows only a slight enrichment in Sn, Sb and Ba, with no enrichment in REE.

Finally, some heavy metal and metalloids concentrations (V, Cr, Co, Ni, Zn, As, Cd and Pb, Mn and Cu) in the studied black crusts were compared to the corresponding concentrations in road dust samples (after Abdel-Latif and Saleh, 2012), collected across the Cairo city (Fig. 3).

It is worth to note that Zn, Mn and Cu are, together with Fe (not determined in this study), the metals present in the higher concentrations in PM (Atzei et al., 2014). Road dust includes deposits and accumulates on ground surfaces, along roadsides, which is contaminated by heavy metals. It usually does not remain deposited in place for long, but it is easily re-suspended back into the atmosphere, as it was already mentioned. For the purposes of this work, the concentrations of the above-mentioned metals in the <125 μm fraction were considered for the comparison as these sizes are easily resuspended in atmosphere contributing with a significant amount of trace elements in residential, main traffic roads and industrial areas. Metals concentrations in the dust were higher in main traffic roads and industrial areas compared to those of residential areas. Figure 3 shows the box plot diagram, in which minimum, maximum and average values for the selected elements in black crusts samples are reported together with the values corresponding to the metal concentration in the dust collected in Cairo (Abdel-Latif and Saleh, 2012). As can be seen, most of the heavy metal average values in the black crusts fall within the ranges relevant to the dust of the Cairo city. Exceptions in this trend are the value of arsenic (As) and, at lesser extent, the value of cadmium (Cd). In fact, black crusts samples experienced values of these two elements greater than those of dust samples. Both these metals have been widely used in industrial sector, i.e. man-made emissions from metal smelters (iron, steel, copper, lead and zinc production), mining activities, combustion processes (coal and oil) and refuse incineration (stabilizers and pigments in plastics). Studied black crusts may have accumulated these elements over time being considered as good traps for atmospheric particles, useful for the identification of the particulate matter pollution emission sources in urban areas.

3.5 Carbonaceous fraction

Carbonaceous particles emitted by combustion processes are among the main constituents of aerosol particulate matter (PM) (Bove et al., 2016; Bozzetti et al., 2017) and one of the main factors responsible for the blackening of buildings.

The quantification of the carbonaceous species that form the non-carbonatic fraction, i.e. OC (organic carbon) and EC (elemental carbon) in damage layers, are required particularly in urban areas in order to investigate atmospheric deposition processes on building surfaces, to get information on the possible particulate matter sources and to suggest mitigation measurements to fulfil a better conservation of the stone surfaces (Fermo et al., 2015).

Black carbon (also known as elemental carbon, EC, because of its structure quite similar to that of graphite) is emitted by combustion processes, such as traffic and biomass burning (Piazzalunga et al., 2010, 2011; Belis et al., 2011), and is the main responsible for soiling on monuments surfaces (Ghedini et al., 2000; Tidblad et al., 2012). On the other hand, OC that includes hundreds of organic substances of different nature, is emitted by combustion processes as a primary pollutant but is also of secondary origin and can form starting form gaseous organic precursors (i.e. volatile organic compounds, VOC) (Fuzzi et al., 2006; Robinson et al., 2007; Bernardoni et al., 2011; Gentner et al., 2012; Vassura et al., 2014; Daellenbach et al., 2016). It is also known that the Mediterranean region is characterized by an intense photochemistry during summer which brings to high concentration in the aerosol PM of secondary organic substances (Bozzetti et al., 2017) and this phenomenon in Cairo is particularly favoured.

Table 2 shows the values obtained by thermogravimetric analysis and reported as percentages by weight (wt.%) of TC (Total Carbon), OC (Organic Carbon); EC (Elemental Carbon); OX (Oxalate), Gy (Gypsum); OC/EC and EC/TC ratios are reported as well; TC=OC +EC.

At first sight, by comparing the samples taken from the same monument it is possible to highlight slight differences between them.

It should be noted that the greatest variability in the various samples was found for gypsum (minimum value of 9.7%, maximum value 51.25). In particular, the highest concentrations were obtained for samples 12, 14 and B in accordance with what was observed by XRD analysis.

In general, all the crust samples show higher EC values (wt. %) than OC (Table 2). The EC values are higher than what was generally observed for the samples of atmospheric particulate matter in

Cairo (Favez et al., 2008; Kanakidou et al., 2011; Lowenthal et al., 2014; Cheng et al., 2016). It is also important to stress out that the carbonaceous substances dominate the PM2.5 composition of megacities atmosphere, especially in Cairo (Cheng et al., 2016).

Furthermore, data in the literature show that PM in the city of Cairo has an average annual OC/EC ratio of 2.45 (Lowenthal et al., 2014). This ratio is rather linked to seasonal conditions, with values of 3.45 (autumn season), 2.64 (winter season) and 2.17 for the summer season (Abu-Allaban et al., 2007). The highest levels observed during autumn season have been related to episodes of biomass combustion on the Nile delta. In fact, during this period of the year the residual straw from rice cultivation is commonly burned after the harvests. Carbonaceous particles emitted by this combustion could therefore partially reach the city thanks to the influence of prevailing winds from the North (Favez et al., 2008).

According to Kanakidou et al. (2011) the polluting sources contributing to the OC fraction into the air in Cairo are mainly represented by industry, residential, energy production and incinerators, while

EC is mainly emitted from mobile sources (diesel traffic) and combustion processes (e.g. domestic heating or industrial activities) (Abu-Allaban et al., 2007; Favez et al., 2008).

The obtained OC and EC values of the crust samples were compared with other black crust samples from Cairo taken, in some cases, from the same monuments (Rovella et al., 2020), whose study was focused on the state of conservation of the building materials. These data were obtained with the same TGA methodology and their use was essential to better understand the interaction between the polluted environment of Cairo city and the black crusts.

Figure 4 shows that, in general, as the sampling height of the crusts decreases, the concentration of EC increases. This confirms that the main source of this pollutant could be vehicle traffic which is responsible for the emission of particles which mainly affects surfaces at lower heights in direct contact with the road. The OC value on all the analysed samples varies from a minimum of 0.36 to a maximum of 1.88, while that of EC varies from a minimum of 0.99 to a maximum of 5.95. From the trends shown in the Figure 4, it is also observed that the OC values are more constant than the EC values.

The clustering based on the relationship between the concentrations of EC and OC and showed in Figure 5a, suggest similar trends for most of the samples nevertheless they come from different areas of Cairo. The only exception is represented by site a) (Fig. 5b) where high EC values are observed especially for the relative three samples (samples 8, 9 and 10 of figure 5a which were both taken at low heights).

In order to evaluate potential differences on the accumulation of OC and EC within the crusts analysed in the city of Cairo and other polluted cities, comparisons were made with crusts taken from Italian monuments (Fig. 6) such as: Trevi Fountain in Rome (La Russa et al., 2017); several private buildings in Venice (La Russa et al., 2018), Church of Santa Maria delle Grazie in Milan (Comite and Fermo et al., 2018) and the Monza Cathedral located in the homonymous city (Comite et al., 2020c).

The comparison (Fig. 6a) allowed highlighting the presence of two types of samples for which quite good correlations between OC and EC were observed. Characteristic OC/EC ratios have been identified for the two groups corresponding to the angular coefficients of the trend lines: the first group has an OC/EC ratio = 0.47, while the second shows an OC/EC ratio = 0.42. This allows hypothesizing that for the second group, in which all the Cairo samples fall, the primary sources prevail while for the samples belonging to the first group, and a mixed contribution of the sources (primary + secondary) can be suggested. The high EC contents in the Cairo samples can be explained by a combination of various polluting sources such as mobile emissions or combustion processes (e.g. domestic heating or industrial activities) (Abu-Allaban et al., 2007; Favez et al., 2008).

In fact, the city is characterized by high congestion due to, as mention before, a population density of 13107/km^2 and 2.4 million cars (El-Mansy et al., 2013; CAPMAS, 2017; Moustafa et al., 2018). Urban growth rates are higher than the development rate of public transport services with a consequent increase in the use of private vehicles and taxis (Duquennois and Newman, 2009; El-Dorghamy et al., 2015) which release a lot of black carbon into the air thus dominating the other potential polluting sources (Mahmoud at al., 2008). Vehicle traffic in the past has also been characterized by the presence of vehicles with old generation technical characteristics that have increased the pollution of the city (El Mowafi and Atalla, 2005; Kanakidou et al., 2011). Even in the past, domestic heating or industrial sector introduced significant quantities of black carbon into the air (Abu-Allaban et al., 2007; Favez et al., 2008). For these reasons, the first actions for environmental protection were introduced in the early 1990s and after that, a slight air quality improvement emerged (Kanakidou et al., 2011).

A further confirmation of our statement arises, comparing the OC/EC ratio (Fig. 6b) with that performed on the carbonaceous aerosols (Schauer et al., 1999, 2002; Saarikoski et al., 2008). Generally, relatively low values equal to or less than 1 are attributable to primary emissions and combustion of fossil fuels (Perrino et al., 2008), while ratios greater than 1 usually indicate different polluting emissions. Observing (see Table 2) the ratios (minimum value of 0.23 and maximum 0.75) obtained for these samples, the polluting sources that have likely affected the accumulation of the carbonaceous fraction in the black crusts of Cairo are primary sources including vehicular road traffic.

In fact, it has been highlighted that for urban sites in Europe (Pio et al., 2011), where vehicular emissions are the dominant source of pollution, the values obtained from the OC/EC ratios fall in the range 0.3-0.7, suggesting a low contribution of secondary OC.

Finally, the correlation between the gypsum content, the carbonaceous fraction and the concentrations of heavy metals can provide further information on the sources of pollutants. Figure 3S shows the correlation matrix between all the experimental variables quantified on the examined samples in the present paper. The observation of the matrix shows how gypsum is positively related to different heavy metals, namely Cu, Pb, Sb and Zn, and to, a lesser extent, the remaining metals and metalloids. This could indicate that probably some elements are closely related to the sulphation processes. In fact, heavy metals have long been considered capable of catalysing the sulphation processes (Rodriguez-Navarro and Sebastian, 1996; Cultrone et al., 2004; Simaõ et al., 2006; Wahba and Zaghloul, 2007). A good correlation has been observed between Gy and Cu (0.92). According to Boke et al. (1999), the Cu^{+2} ion increases the absorption of SO_2 in the aqueous film present on a carbonate surface. This ion has also been shown to dissipate any gradient of electrical potential allowing hydrogen ions to spread much faster on surfaces (Chang et al., 1981). As a result, an increase in SO_2 uptake is observed which accelerates the sulphation process. Furthermore, Cu has been shown to be released from the exchangeable carbonate phase making this metal potentially available to catalyse surface reactions (McAlister et al., 2008).

The correlation matrix also allows highlighting the correlation existing between metals. For example, there is a very good correlation between Ni and V indicating the contribution of heavy oil combustions (Bove et al., 2016).

On the contrary, the carbonaceous fraction EC is negatively correlated with gypsum and also with various heavy metals. In fact, the surface of EC particles contains numerous adsorption sites that are capable of enhancing catalytic processes because of their high surface reactivity. As result of its catalytic properties, EC may affect some important chemical reactions involving atmospheric sulphur dioxide (SO_2), nitrogen oxides (NO_x), ozone (O_3) and other gaseous compounds (Gundel et al., 1989) other than could have a catalytic effect on the oxidation of sulphite to sulphate (Böke et al., 1999).

As observed in the figure 3, where the greatest polluting contribution seem to be linked to vehicle traffic along the major road arteries, it is clear that the pollution produced by vehicles could also be the main source of enrichment of black crusts.

4. Conclusion

The results achieved in this work highlighted the strong correlation between the atmosphere composition and the degradation processes affecting stone materials used in the built cultural heritage of Cairo city. The multi-analytical approach demonstrated how black crusts can be considered such as an efficient “natural sample holder” of atmospheric pollutants, capable to provide information about atmospheric composition especially in terms of heavy metals. Precisely, the study revealed that the black crusts analysed are constituted mainly by heavy minerals ascribable to the road dust of Cairo city, with the exception of As and Cd, being widely used in the industrial sector.

The data on the carbonaceous fraction suggested that the formation of black crusts sampled is influenced by a preeminent action of the primary sources. At the same time, the high EC contents confirmed the contribution of various polluting sources, such as mobile emissions or combustion processes (e.g. domestic heating or industrial activities) in the formation of the black crusts. Additionally, EC data affirm the clear predominance of pollution produced by vehicles, becoming the main source of enrichment of the black crusts.

In particular, the sulphation processes in the Cairo city is improved by heavy metals, i.e. Cu, Pb, Sb and Zn that play a catalysing role.

This research demonstrated how the contribution of atmospheric pollution is crucial in the evolution of the degradation phenomena, affecting the built cultural heritage in Historic Cairo. Consequently, the reduction of emissions into the atmosphere, adopting for example more eco-sustainable policies, becomes extremely necessary not only for the conservation of cultural heritage but more in general, for the safeguard of the environment and human health.

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Caption Figures

Fig. 1. Microphotographs obtained by OM observations highlighting the main textural features of the limestones and the overlaying black crusts. The red dashed lines mark the contact substrate/crust. Each image is relative to a different sample at 5X magnification. a) sample 2 (Crossed Polarized Light view - CPL). b) Sample 14 (Plane Polarized Light view – PPL). c) Sample 15 (CPL). d) Sample E (CPL). e) Sample H (CPL).

Fig. 2. EFs of black crusts from Salah El Din Citadel and Magra El-Oyoun sampling sites, Qaitbay Mosque, Sultan Faraj ibn Barquq Mosque and Qansuh Al-Ghuri Mausoleum sampling sites.

Fig. 3. Box plot variations of heavy metal concentrations in black crusts samples.

Fig. 4. Graph of the OC and EC concentrations (wt.%) obtained from the analysis of the black crust samples in relation to the sampling height for each site. The monuments of the entire Cairo data set are: a) Al Manial Palace; b) Magra El-Oyoun wall; c) Salah El Din citadel; d) Tower of Bab Al Azab; e) Qaitbay Mosque; f) Sultan Faraj ibn Barquq Mosque (collection of a new sample 15), g) Quansuh Al-Ghury Mausoleum; h) Al Silahdar Mosque.

* after Rovella et al. (2020).

Fig 5. a) EC vs OC binary diagram of the crust samples analysed by the different monuments in Cairo (this work and after Rovella et al., 2020); b) map of the city of Cairo where the different monuments are located.

Fig. 6. a) Binary diagram OC vs EC of the analysed black crusts. b) Histogram of the average OC/EC ratios of the analyzed black crust from the Cairo city (this work and after Rovella et al., 2020). Literature data used for the comparison refer to the crust samples taken from Cairo after Rovella et al., 2020; from the Trevi Fountain in Rome (La Russa et al., 2017); from several private buildings in Venice (La Russa et al., 2018), from the Church of Santa Maria delle Grazie in Milan (Comite and Fermo, 2018) and from the Cathedral of Monza located in the homonymous city (Comite at al., 2020).

Table 1 Information about samples in terms of position and age of construction (William, 2004). They consist of both black crust and limestone substrate.

Monument	Sample ID	Position	Height of sampling
Salah El Din citadel (1176-1183)	2	Western walls	1 m
	3		1,90 m
Magra El-Oyoun (1193)	12	Western walls	2,5 m
	14		1,3 m
Sultan Faraj ibn Barquq Mosque (1400-1411)	15	Main Facade	2,5 m
Qaitbay Mosque (1472-1474)	B	Main Facade	0,80 m
	E		1,0 m
Qansuh Al-Ghuri Mausoleum (1503-1505)	H	Main Facade	1,8 m

Table 2 TC (Total Carbon), OC (Organic Carbon), EC (Elemental Carbon) OX (Oxalate) CC (Carbonate Carbon) Gy (Gypsum) concentrations (wt%); and OC/EC and EC/TC ratio

Sample	TC	OC	EC	OX	CC	Gy	OC/EC	EC/TC
2	7.4	0.87	2.83	0.28	3.70	8.45	0.31	0.38
3	6.61	1.22	1.53	0.14	3.72	22.63	0.75	0.23
14	6.65	0.96	2.40	0.15	3.14	25.55	0.40	0.36
12	5.43	0.75	1.45	0.22	3.01	51.25	0.52	
15	5.11	0.66	1.23	0.11	3.11	15.01	0.54	0.24
B	7.88	0.99	1.48	1.15	4.26	32.98	0.23	0.19
E	6.41	1.36	2.15	0.15	2.75	9.57	0.49	0.34
H	7.75	1.12	1.99	0.09	4.55	9.57	0.25	0.26

Figure
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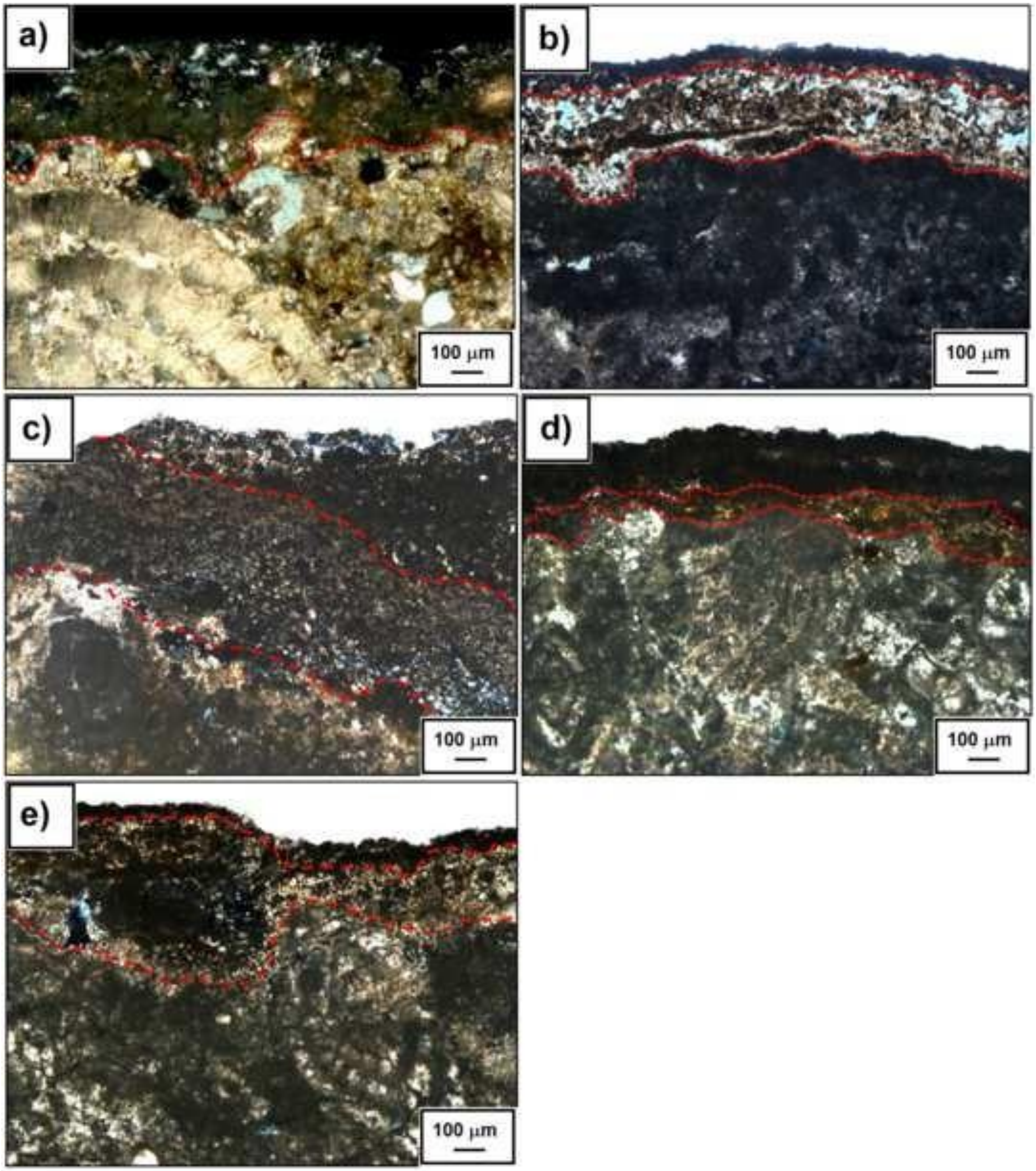

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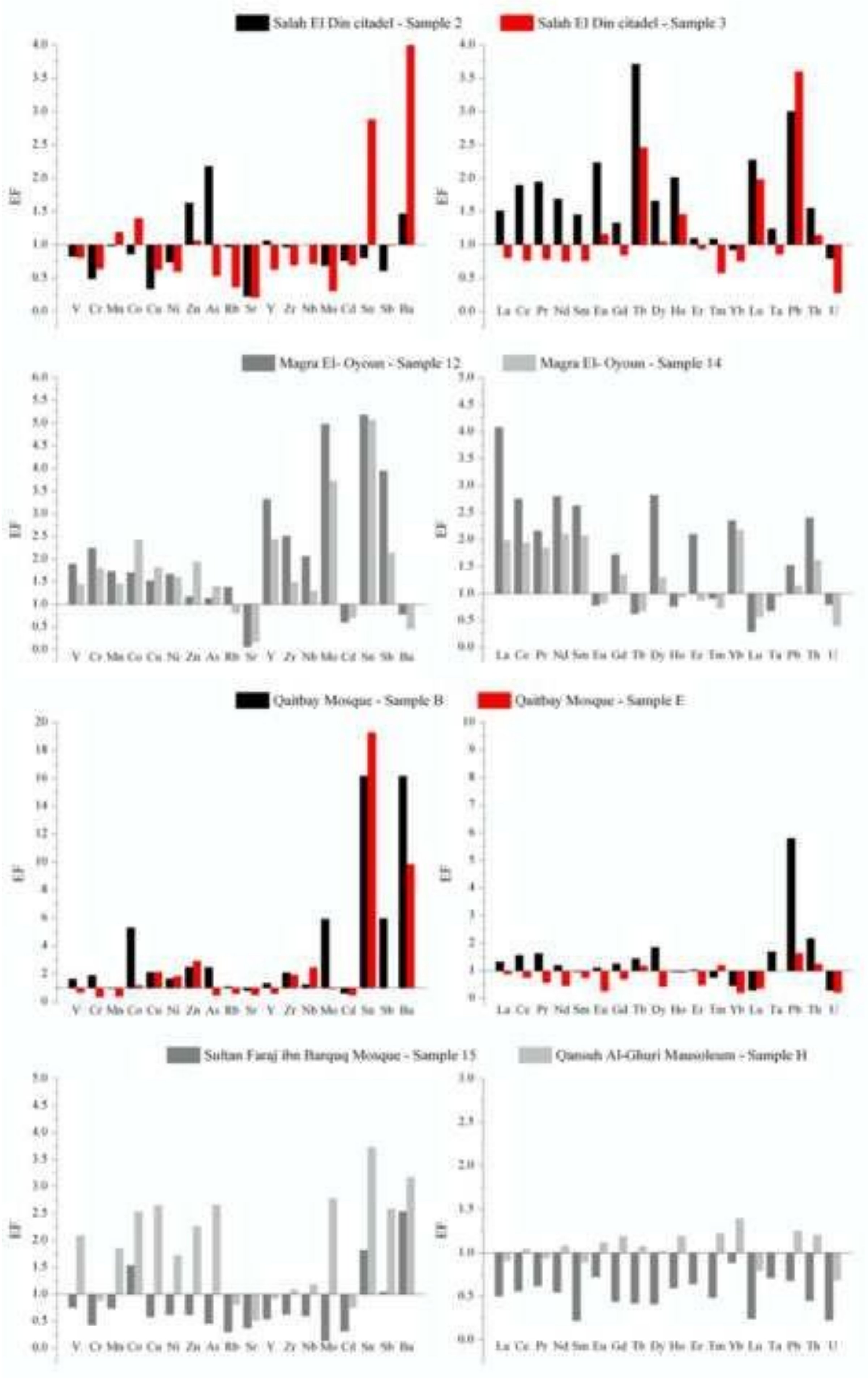

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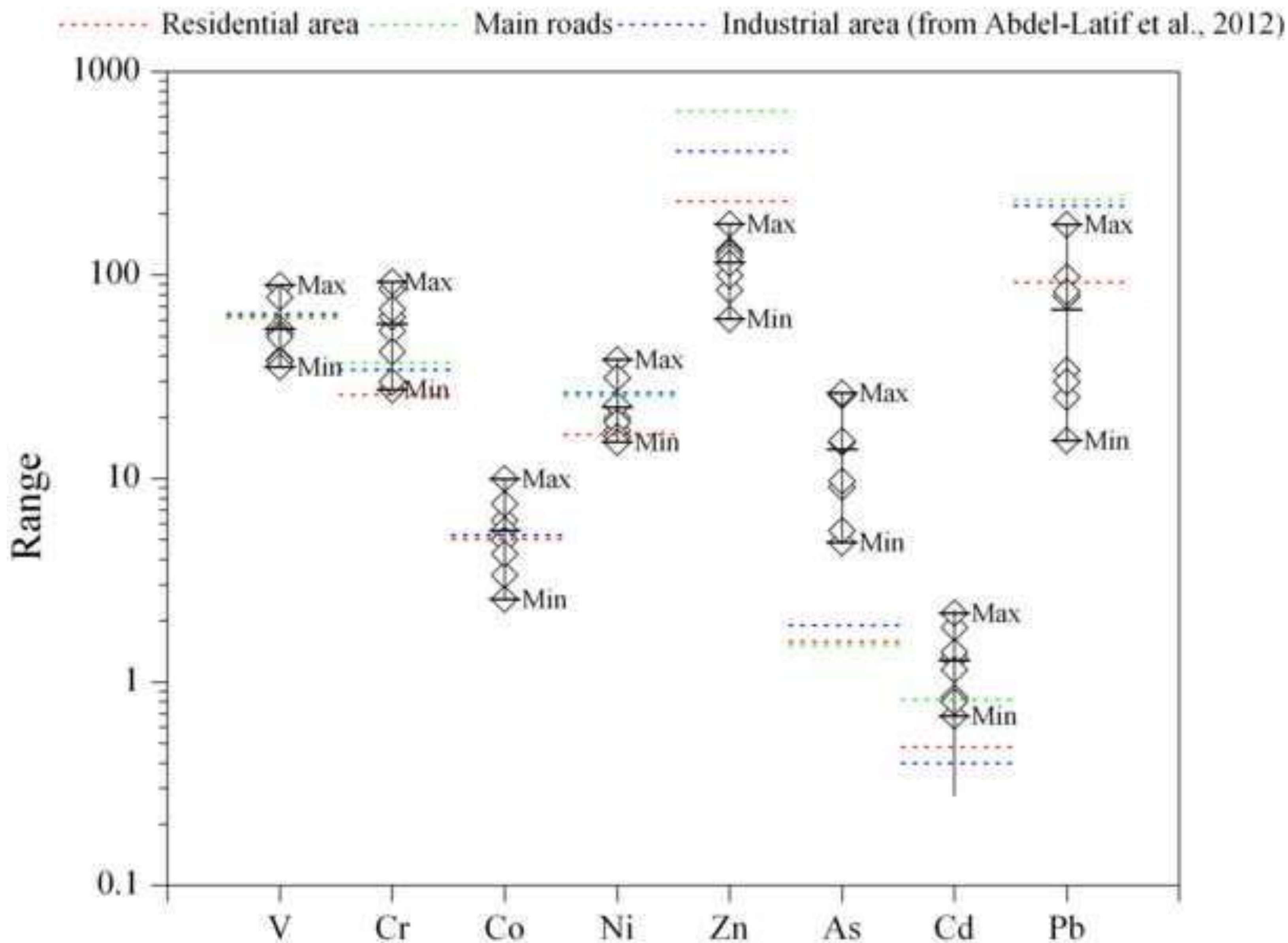

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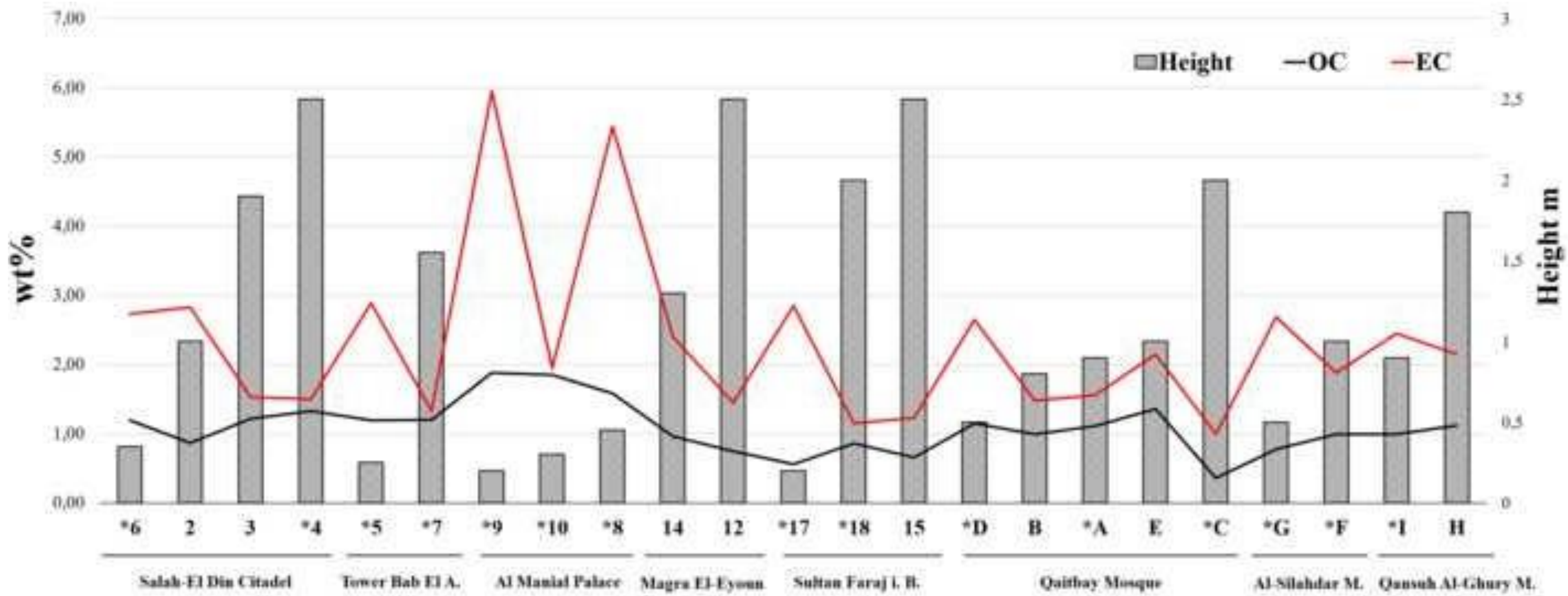

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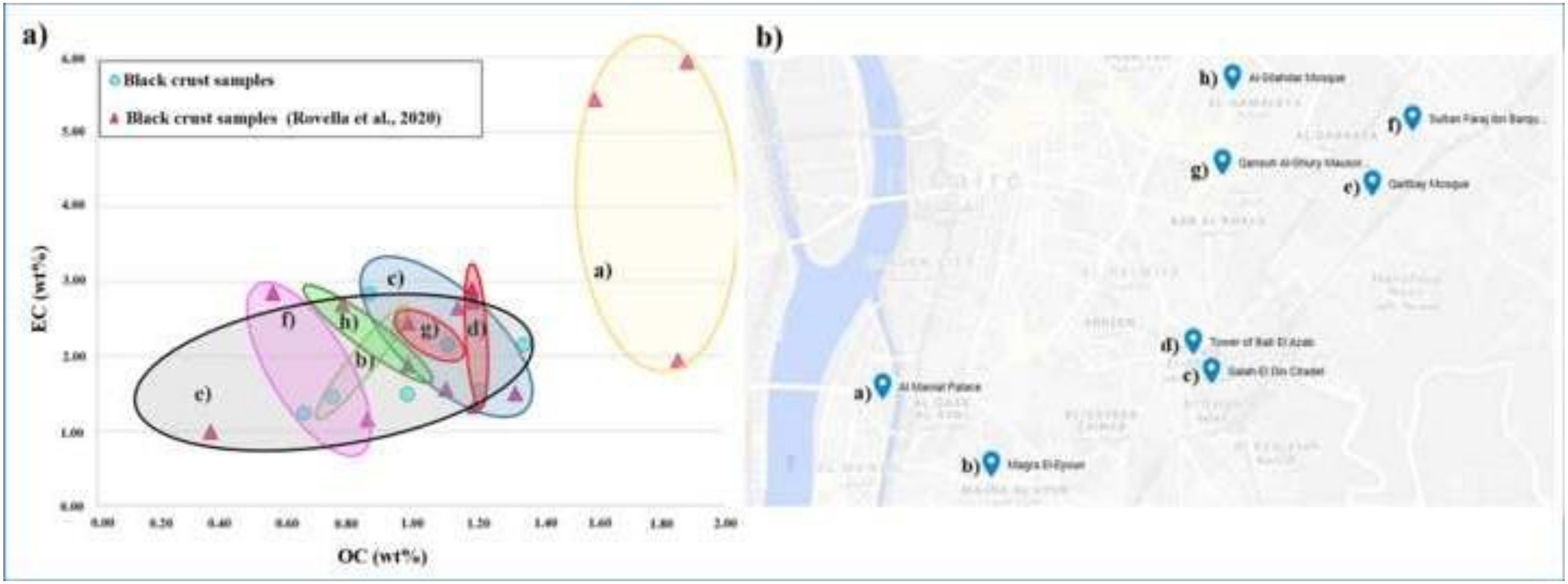

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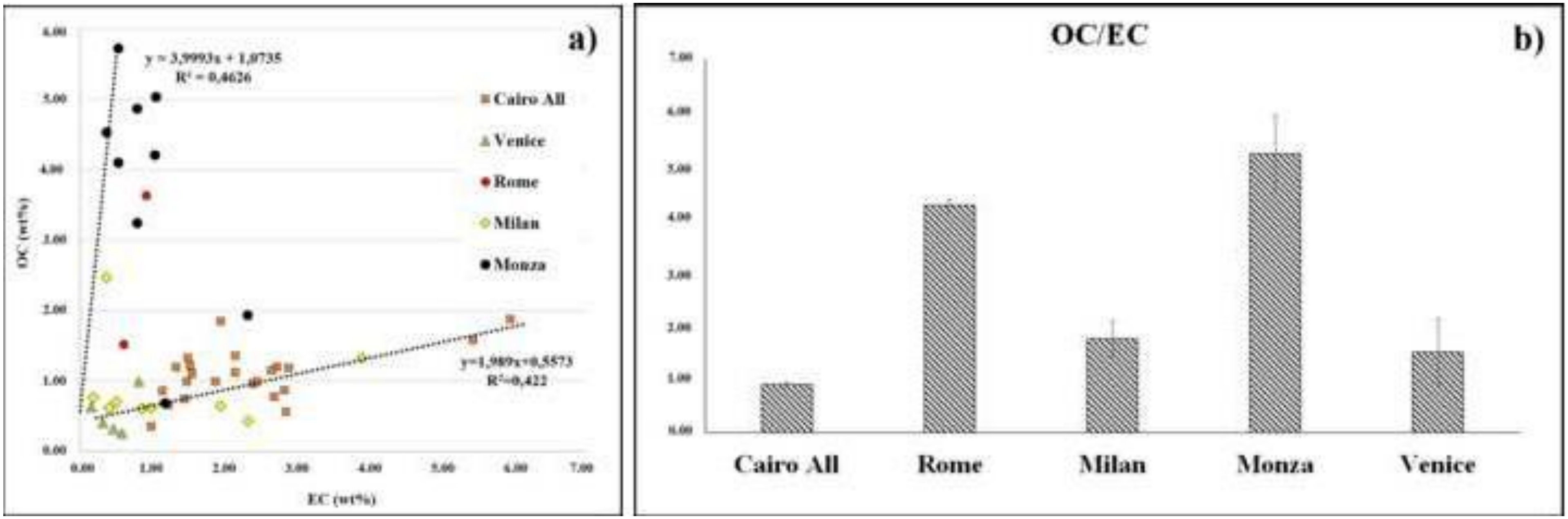

***conflict of Interest Statement**

Declaration of interests

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

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Credit Author Statement

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