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The environmental impact of air pollution on the built heritage of historic Cairo (Egypt)

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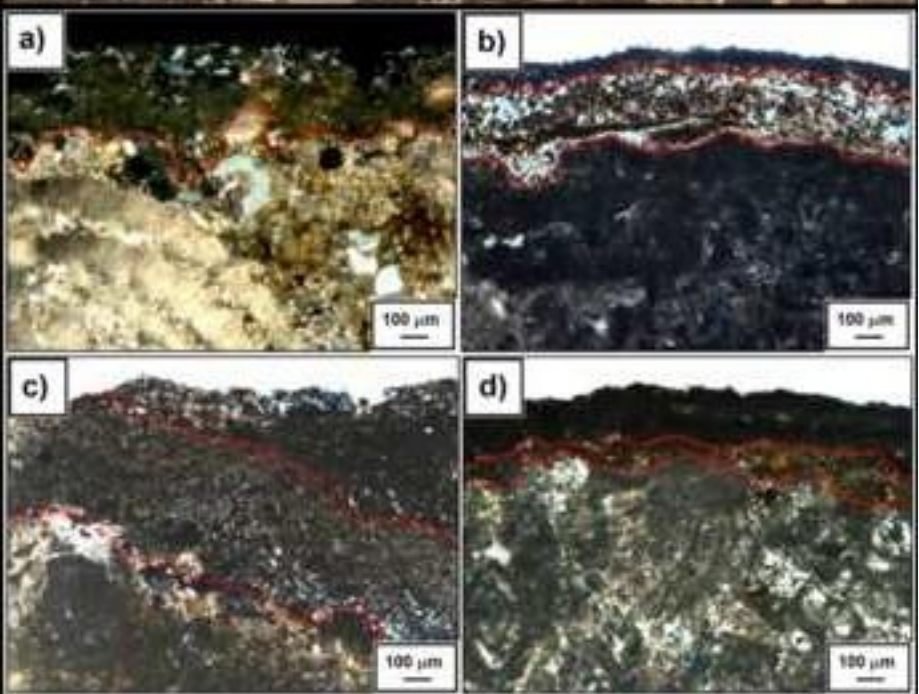
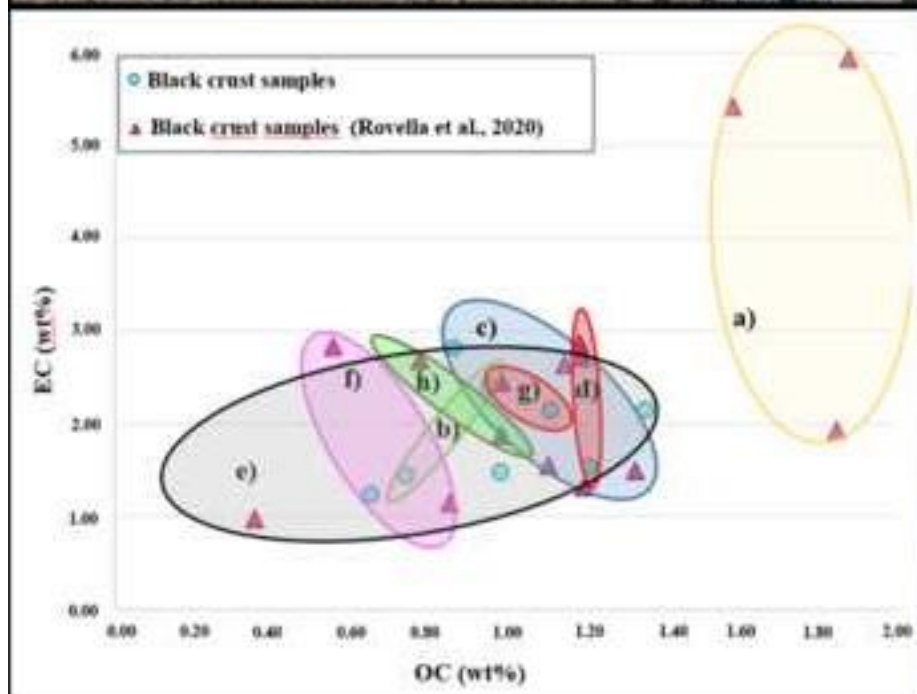
Environmental pollution of Cairo



Interaction with the stone substrate of monuments



Formation of Black Crusts



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

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

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26

27 **Abstract**

28

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

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

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

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

45

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

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1. Introduction

51

52
53 Cairo is the largest city in Egypt and in Africa; here, the air pollution produced many environmental
54 problems related to aerosol particulate matter and to the high levels mostly of sulphur dioxide and
55 lead. For this reason, it was listed as one of the most polluted cities in the world (Gurjar et al.,
56 2010). The air pollution sources in the city are different and include burning of rubbish, vehicle
57 emissions (~4.5 million cars on the streets of Cairo) and urban industrial activities. The city has 15–
58 20 million inhabitants and is characterized by high congestion due to a population density of
59 13107/km² (Abbass et al., 2020). Furthermore, the lack of rain helps the accumulation of pollutants.
60 The entire area of Cairo is severely affected by industrial and urban emissions of metals and
61 metalloids (Abdel-Latif and Saleh, 2012). For example, only the cement industry releases around
62 2.4 million tons per year of cement bypass dust into the atmosphere (Alkhdhairi et al., 2018).
63 Moreover, it was estimated that the high Particulate Matter (PM) concentrations cause around 10 %
64 of premature deaths in Egypt, where the national cost of air pollution is estimated at \$20.9 million
65 (Abbass et al., 2020).

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

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

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

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

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

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

93 Black crusts are one of the most dangerous degradation products in building stones and are closely
94 connected with environmental pollution, especially the atmospheric one. They are very common on
95 the carbonate substrates such limestones. This lithotype is widely used for the construction of
96 historical monuments in the whole Mediterranean area thanks to its workability, durability and
97 aesthetic features; nevertheless it is frequently affected by degradation phenomena (Fitzner et al.,
98 2002; La Russa et al., 2013a; Ricca et al., 2019) firstly black crusts.

99 They are formed through sulphating processes of the stone surface where calcium carbonate
100 (CaCO_3), which is the main constituent of limestone, is transformed into gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

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

112 For all these reasons the attention of the scientific world is steadily increasing on the effect of air
113 pollution on archaeological buildings in Cairo and, consequently on the relative degradation
114 products, (Fitzner et al., 2002; Khallaf, 2011; Kukela and Seglins, 2011; Abdelmegeed et al., 2019).
115 The present research was conceived in this context and deals with the relation between air pollution
116 and the historical building in Cairo.

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

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

130130

131 **2. Materials and Methods**

132 The limestones used for the construction of the historical stone monuments in Cairo come from
133 local middle and late Eocene outcrops (47.8- 33.9 million years ago) located in Mokattam, Helwan
134 and Giza areas (El-Nahhas et al., 1990; Ahmed et al., 2006; Park and Shin, 2009; Aly et al., 2015,
135 2020). These materials are still being used for stone replacement or rebuilding works in monuments
136 preservation practice as well as for modern buildings.

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

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

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

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

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

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

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

162 Chemical analyses of the black crusts, as well as of the substrates, in terms of trace elements were
163 performed by LA-ICP-MS. This method can analyse a great number of chemical elements with a
164 spot resolution of approximately 40–50 μm , which also allows the determination of compositional
165 variations at a micrometric scale. Analyses were carried out using an Elan DRCe instrument (Perkin
166 Elmer/SCIEX), connected to a New Wave UP213 solid-state Nd-YAG laser probe ($\lambda=213$ nm).
167 Samples were ablated by a laser beam in a cell following the method tested by Gunther and
168 Heinrich (1999). The ablation was performed with spots of 40–50 μm with a constant laser
169 repetition rate of 10 Hz and a fluency of ~ 20 J/cm² (Barca et al., 2011). Calibration was performed
170 using the NIST 612-50 ppm glass reference material as external standard (Pearce et al., 1997).
171 Internal standardization to correct instrumental instability and drift was achieved using CaO
172 concentrations from EPMA-EDS analyses. Accuracy was evaluated on BCR 2G glass reference
173 material and on an in-house pressed-powder cylinder of the standard Argillaceous Limestone
174 SRM1d of NIST (Barca et al., 2011). The resulting element concentrations were compared with
175 reference values from the literature (Gao et al., 2002). Accuracy, as the relative difference from

176 reference values, was always better than 12 %, and most elements plotted in the range of ± 8 %.
177 Analyses were performed on 100 μm thick cross-sections including both the black crust and the
178 unaltered substrate samples in order to reveal the geochemical variability. TGA was carried out for
179 the quantification of the carbonaceous fraction (TC total carbon= OC organic carbon + EC
180 elemental carbon), Ox oxalate, CC carbonatic carbon and gypsum, present in the black crusts. It
181 was performed by a Mettler Toledo TGA/DSC 3+, which allows simultaneous TG and DSC
182 (Differential Scanning Calorimetry) analyses. The analyses were conducted in the range 30°- 800°
183 C, increasing temperature with a rate of 20° C/minute. The carbonaceous components were
184 estimated in temperature ranges defined by previously studied standards and using two different
185 atmospheres, i.e. the inert and the oxidant one. The complete methodology is described also in
186 previous works La Russa et al. (2017).

187187

188 **3. Results and discussion**

189 **3.1.POM Analysis**

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

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

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

197 The substrate in sample 3 is classified as biomicrite (Folk, 1959) or mudstone (Dunham, 1962). It
198 includes allochems as quartz, rare iron oxides and fossils. The crust is located in small areas of the
199 substrate and has a slightly variable thickness of about 20-30 μm , containing iron oxides inside. It is

200 well adhered to the substrate and appears with
201 irregular and strongly discontinuous edges.

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

204 In particular, the substrate of sample 12 includes rare quartz and plagioclase crystals. The black
205 crust overlying the substrate is rather compact with an overall thickness varying between 50 and
206 200 μm . It shows a not so clear stratification but at least two layers are recognizable. The crust is
207 well adhered to the substrate, has irregular morphology, is made up of microcrystalline gypsum and
208 incorporates numerous spherical and sub-spherical carbonaceous particles.

209 In sample 14, the crust has an average thickness of 400 μm and shows an evident stratification
210 (Fig.1b): an external dark brown layer with an average thickness of 50 μm and a rather regular
211 external profile; an innermost layer, light brown in colour, reaching in some places a thickness of
212 300 μm and deepening into the substrate for about 100 μm . The contact crust/substrate is mainly
213 sharp.

214 The crust is made up of microcrystalline gypsum and includes from sub-spherical to spherical
215 carbonaceous particles, particularly numerous, especially in the inner layer (Fig.1b) and averagely
216 30 μm in size.

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

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

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

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

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

242242

243 **3.2 XRD Analysis**

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

250 The crusts include halite, the most common sodium chloride salt in the subsurface water of Egypt
251 and in sea spray coming from the Mediterranean Sea (Aly et al., 2015) and consequently also in
252 Egyptian limestones (Gauri and Holdren, 1981; Gauri et al., 1986; Helmi, 1990). The salt is linked

253 to the capillary rise of water from the subsoil and the consequent precipitation of the salt inside the
254 stone (Charola, 2000; Fitzner et al., 2002; Gomez-Heras and Fort, 2007).

255255

256 **3.3 EPMA-EDS Analysis**

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

259 In the samples 2 and 3 the crusts show an irregular morphology. Compositional analysis revealed
260 CaO as major component, followed by SO₃, SiO₂, Al₂O₃, ClO e FeO, Na₂O, MgO, K₂O.

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

264 The crusts are constituted mainly by CaO and SO₃ thanks to gypsum-based composition, secondly
265 by SiO₂, and lastly ClO, Al₂O₃, Na₂O, MgO, K₂O, FeO. In sample 12, gypsum was detected also in
266 substrate, where the crust is thicker and deepens in.

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

270 The most abundant component is mostly CaO, followed by SiO₂, SO₃, ClO, and lastly Al₂O₃, FeO,
271 K₂O, MgO, Na₂O, TiO₂ and P₂O₅.

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

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

277 The chemical analysis suggested how CaO is the predominant component, followed by SiO₂, SO₃,
278 secondly by, ClO, Al₂O₃, Na₂O, K₂O, FeO and lastly by MgO, P₂O₅ and TiO₂.

279 The sample H shows in general an irregular morphology, fractures, and jagged edges. However, it
280 was individuated little portions more homogeneous, compact and adherent to substrate, that were
281 analysed by EDS and then by LA-ICP-MS. Gypsum microcrystals and carbonaceous particles were
282 identified in the crust. The chemical composition is characterized by a high amount of CaO, Al₂O₃,
283 SiO₂ and SO₃, followed by Na₂O, P₂O₅, K₂O, and TiO₂.

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285285

286 3.4 LA-ICP-MS Analysis

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

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

298 As well known, all these elements can be introduced in the urban environment by a wide range of
299 different anthropogenic processes, mainly mining, smelting, industrial manufacturing, metal
300 processing, etc. (Johnson et al., 2011) but also by domestic and residential activities (heating,
301 vehicles, transport). However, some elements occur naturally in the same urban environment as a
302 result for example of geologic processes (erosion of outcropping bedrocks). The proportion of
303 natural and anthropogenic components may vary widely depending thus on the geology and the
304 industrial history of the urban centre. Our geochemical approach was addressed to define the

305 relation between pollution sources and degradation state of stone materials; for this purpose,
306 Enrichment Factor was calculated both for heavy metals, metalloids and Rare Earths Elements
307 (hereafter REE). Enrichment factors calculation is a procedure commonly used in geochemical
308 studies for the determination of the anthropogenic origin of chemical elements. For the purpose of
309 our study, the chemical procedure was followed by normalizing the chemical composition of trace
310 elements in black crusts with respect to those of calcareous substrates on which they grew (Table
311 3S).

312 The normalization procedure performed here used Scandium (Sc) as 'conservative' element, as it
313 was presumed to have no anthropogenic enrichment or a minor anthropogenic input (Loring, 1991;
314 Gallego et al., 2013). This calculation is carried out by comparing the concentrations of the trace
315 elements with those of the conservative element by following the formula $EF =$
316 $(M/N)_{\text{sample}} / (M/N)_{\text{substrate}}$, which is the ratio between the concentrations of the metal (M) and those
317 of the normalizer (N), both for the sample and for substrate samples (Reimann and Caritat, 2000).
318 Figure 2 show EFs for all the examined samples grouped for sampling location criterion. As shown
319 in the Figure 2, samples 2 and 3 are enriched in Zn, As, Pb, REE (L-REE, light and H-REE, heavy)
320 and Sn, Ba, Pb and HREE, respectively. Similarly, samples 12 and 14 show enrichment in all the
321 LREE and in most metals and metalloids elements. The same enrichment trend (Fig. 2) is
322 highlighted by the remaining samples (B, E, 15 and H).

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

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

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

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353 **3.5 Carbonaceous fraction**

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

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

362 Black carbon (also known as elemental carbon, EC, because of its structure quite similar to that of
363 graphite) is emitted by combustion processes, such as traffic and biomass burning (Piazzalunga et
364 al., 2010, 2011; Belis et al., 2011), and is the main responsible for soiling on monuments surfaces
365 (Ghedini et al., 2000; Tidblad et al., 2012). On the other hand, OC that includes hundreds of organic
366 substances of different nature, is emitted by combustion processes as a primary pollutant but is also
367 of secondary origin and can form starting from gaseous organic precursors (i.e. volatile organic
368 compounds, VOC) (Fuzzi et al., 2006; Robinson et al., 2007; Bernardoni et al., 2011; Gentner et al.,
369 2012; Vassura et al., 2014; Daellenbach et al., 2016). It is also known that the Mediterranean region
370 is characterized by an intense photochemistry during summer which brings to high concentration in
371 the aerosol PM of secondary organic substances (Bozzetti et al., 2017) and this phenomenon in
372 Cairo is particularly favoured.

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

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

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

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

383 Cairo (Favez et al., 2008; Kanakidou et al., 2011; Lowenthal et al., 2014; Cheng et al., 2016). It is
384 also important to stress out that the carbonaceous substances dominate the PM_{2.5} composition of
385 megacities atmosphere, especially in Cairo (Cheng et al., 2016).

386 Furthermore, data in the literature show that PM in the city of Cairo has an average annual OC/EC
387 ratio of 2.45 (Lowenthal et al., 2014). This ratio is rather linked to seasonal conditions, with values
388 of 3.45 (autumn season), 2.64 (winter season) and 2.17 for the summer season (Abu-Allaban et al.,
389 2007). The highest levels observed during autumn season have been related to episodes of biomass
390 combustion on the Nile delta. In fact, during this period of the year the residual straw from rice
391 cultivation is commonly burned after the harvests. Carbonaceous particles emitted by this
392 combustion could therefore partially reach the city thanks to the influence of prevailing winds from
393 the North (Favez et al., 2008).

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

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

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

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

409 the trends shown in the Figure 4, it is also observed that the OC values are more constant than the
410 EC values.

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

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

422 The comparison (Fig. 6a) allowed highlighting the presence of two types of samples for which quite
423 good correlations between OC and EC were observed. Characteristic OC/EC ratios have been
424 identified for the two groups corresponding to the angular coefficients of the trend lines: the first
425 group has an OC/EC ratio = 0.47, while the second shows an OC/EC ratio = 0.42. This allows
426 hypothesizing that for the second group, in which all the Cairo samples fall, the primary sources
427 prevail while for the samples belonging to the first group, and a mixed contribution of the sources
428 (primary + secondary) can be suggested. The high EC contents in the Cairo samples can be
429 explained by a combination of various polluting sources such as mobile emissions or combustion
430 processes (e.g. domestic heating or industrial activities) (Abu-Allaban et al., 2007; Favez et al.,
431 2008).

432 In fact, the city is characterized by high congestion due to, as mention before, a population density
433 of 13107/km² and 2.4 million cars (El-Mansy et al., 2013; CAPMAS, 2017; Moustafa et al., 2018).
434 Urban growth rates are higher than the development rate of public transport services with a

435 consequent increase in the use of private vehicles and taxis (Duquennois and Newman, 2009; El-
436 Dorghamy et al., 2015) which release a lot of black carbon into the air thus dominating the other
437 potential polluting sources (Mahmoud et al., 2008). Vehicle traffic in the past has also been
438 characterized by the presence of vehicles with old generation technical characteristics that have
439 increased the pollution of the city (El Mowafi and Atalla, 2005; Kanakidou et al., 2011). Even in
440 the past, domestic heating or industrial sector introduced significant quantities of black carbon into
441 the air (Abu-Allaban et al., 2007; Favez et al., 2008). For these reasons, the first actions for
442 environmental protection were introduced in the early 1990s and after that, a slight air quality
443 improvement emerged (Kanakidou et al., 2011).

444 A further confirmation of our statement arises, comparing the OC/EC ratio (Fig. 6b) with that
445 performed on the carbonaceous aerosols (Schauer et al., 1999, 2002; Saarikoski et al., 2008).
446 Generally, relatively low values equal to or less than 1 are attributable to primary emissions and
447 combustion of fossil fuels (Perrino et al., 2008), while ratios greater than 1 usually indicate different
448 polluting emissions. Observing (see Table 2) the ratios (minimum value of 0.23 and maximum
449 0.75) obtained for these samples, the polluting sources that have likely affected the accumulation of
450 the carbonaceous fraction in the black crusts of Cairo are primary sources including vehicular road
451 traffic.

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

455 Finally, the correlation between the gypsum content, the carbonaceous fraction and the
456 concentrations of heavy metals can provide further information on the sources of pollutants. Figure
457 3S shows the correlation matrix between all the experimental variables quantified on the examined
458 samples in the present paper. The observation of the matrix shows how gypsum is positively related
459 to different heavy metals, namely Cu, Pb, Sb and Zn, and to, a lesser extent, the remaining metals
460 and metalloids. This could indicate that probably some elements are closely related to the

461 sulphation processes. In fact, heavy metals have long been considered capable of catalysing the
462 sulphation processes (Rodriguez-Navarro and Sebastian, 1996; Cultrone et al., 2004; Simaõ et al.,
463 2006; Wahba and Zaghoul, 2007). A good correlation has been observed between Gy and Cu
464 (0.92). According to Boke et al. (1999), the Cu^{+2} ion increases the absorption of SO_2 in the aqueous
465 film present on a carbonate surface. This ion has also been shown to dissipate any gradient of
466 electrical potential allowing hydrogen ions to spread much faster on surfaces (Chang et al., 1981).
467 As a result, an increase in SO_2 uptake is observed which accelerates the sulphation process.
468 Furthermore, Cu has been shown to be released from the exchangeable carbonate phase making this
469 metal potentially available to catalyse surface reactions (McAlister et al., 2008).

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

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

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

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487 **4. Conclusion**

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

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

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

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

509509

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864 **Caption Figures**

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866 Fig. 1. Microphotographs obtained by OM observations highlighting the main textural features of
867 the limestones and the overlaying black crusts. The red dashed lines mark the contact
868 substrate/crust. Each image is relative to a different sample at 5X magnification. a) sample 2
869 (Crossed Polarized Light view - CPL). b) Sample 14 (Plane Polarized Light view – PPL). c) Sample
870 15 (CPL). d) Sample E (CPL). e) Sample H (CPL).

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

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

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

883 * after Rovella et al. (2020).

884884

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

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889 Fig. 6. a) Binary diagram OC vs EC of the analysed black crusts. b) Histogram of the average
890 OC/EC ratios of the analyzed black crust from the Cairo city (this work and after Rovella et al.,
891 2020). Literature data used for the comparison refer to the crust samples taken from Cairo after
892 Rovella et al., 2020; from the Trevi Fountain in Rome (La Russa et al., 2017); from several private
893 buildings in Venice (La Russa et al., 2018), from the Church of Santa Maria delle Grazie in Milan
894 (Comite and Fermo, 2018) and from the Cathedral of Monza located in the homonymous city
895 (Comite at al., 2020).

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Table[Click here to download Table: Table 1.docx](#)

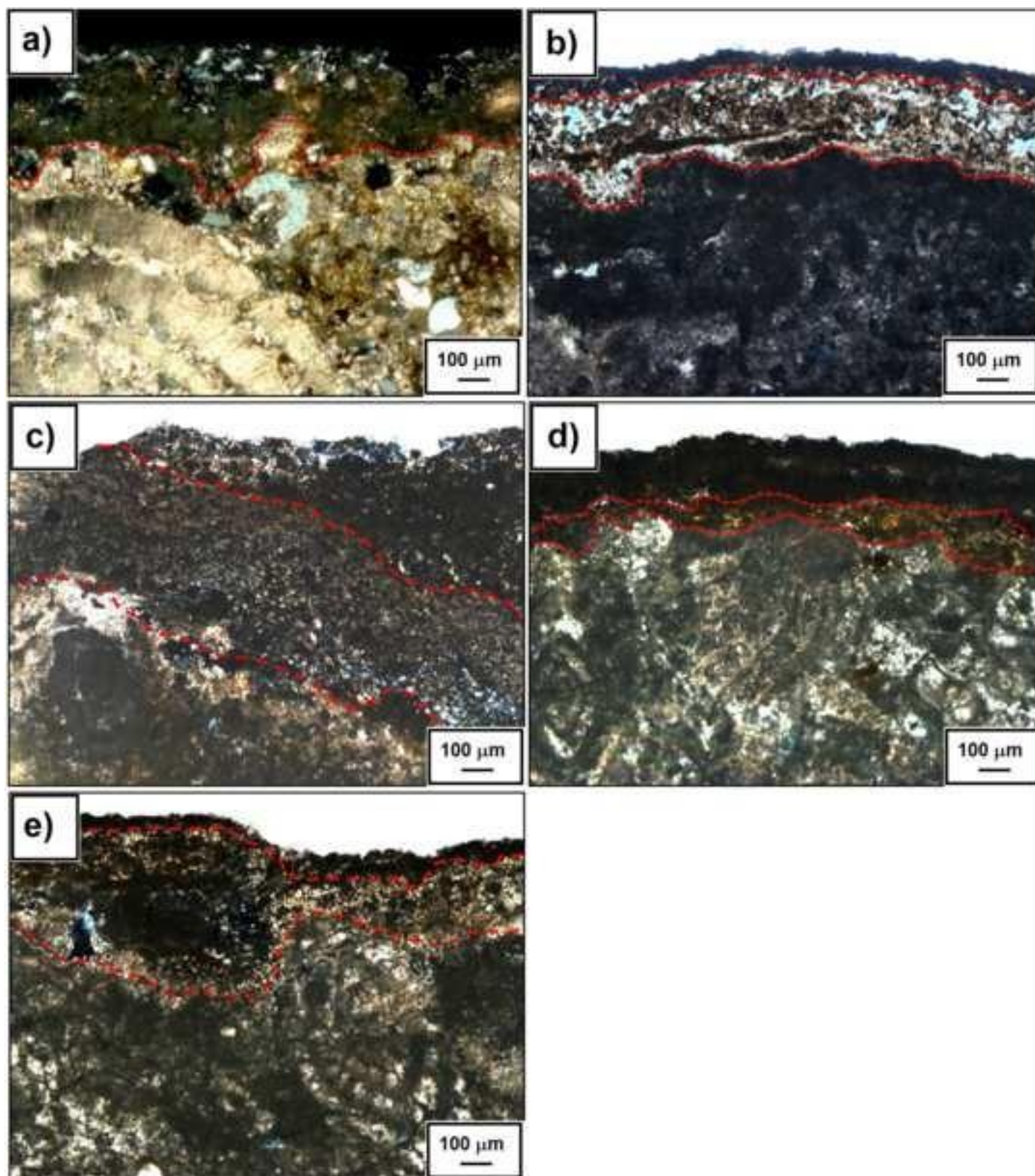
Table 1 Information about samples in terms of position and age of construction (William, 2004). They consist of both black crust and limestone substrate.

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[Click here to download Table: Table 2.docx](#)**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

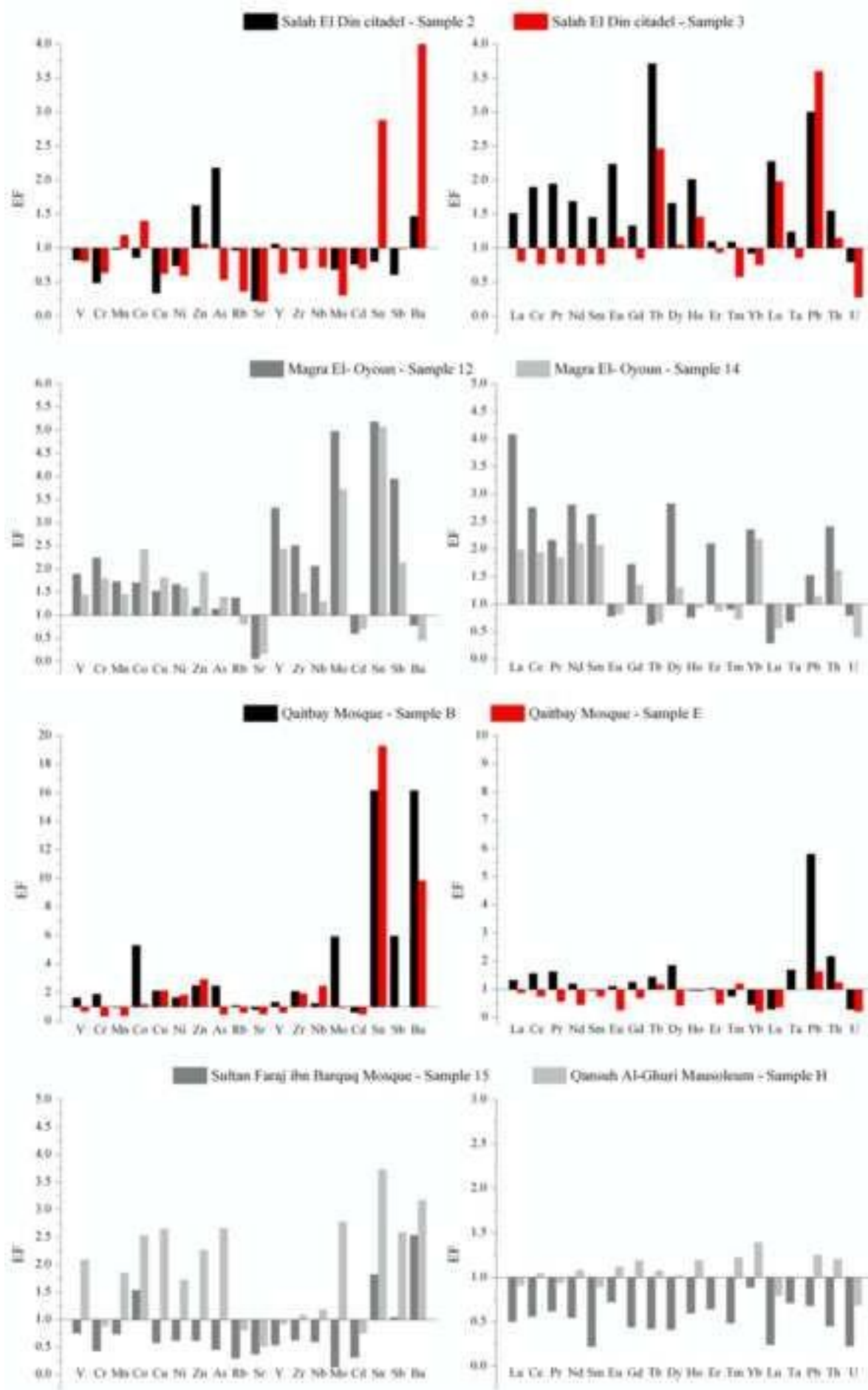
Sample	TC	OC	EC	OX	CC	Gy	OC/EC	EC/TC
2	7.4	0.87	2.83	0.28	3.70	8.45	0.31	0.38
3	6.61	1.22	1.53	0.14	3.72	22.63	0.75	0.23
14	6.65	0.96	2.40	0.15	3.14	25.55	0.40	0.36
12	5.43	0.75	1.45	0.22	3.01	51.25	0.52	
15	5.11	0.66	1.23	0.11	3.11	15.01	0.54	0.24
B	7.88	0.99	1.48	1.15	4.26	32.98	0.23	0.19
E	6.41	1.36	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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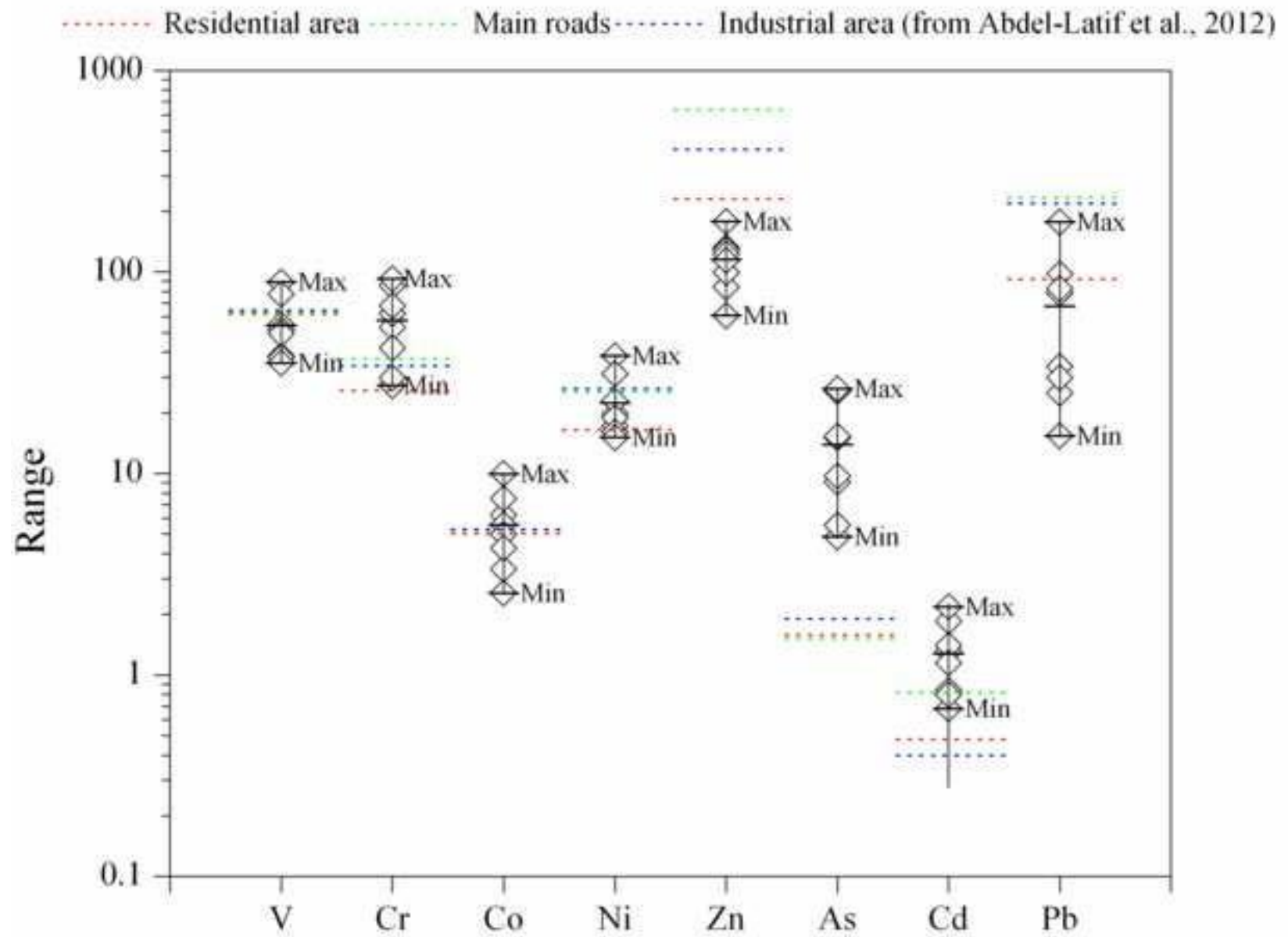
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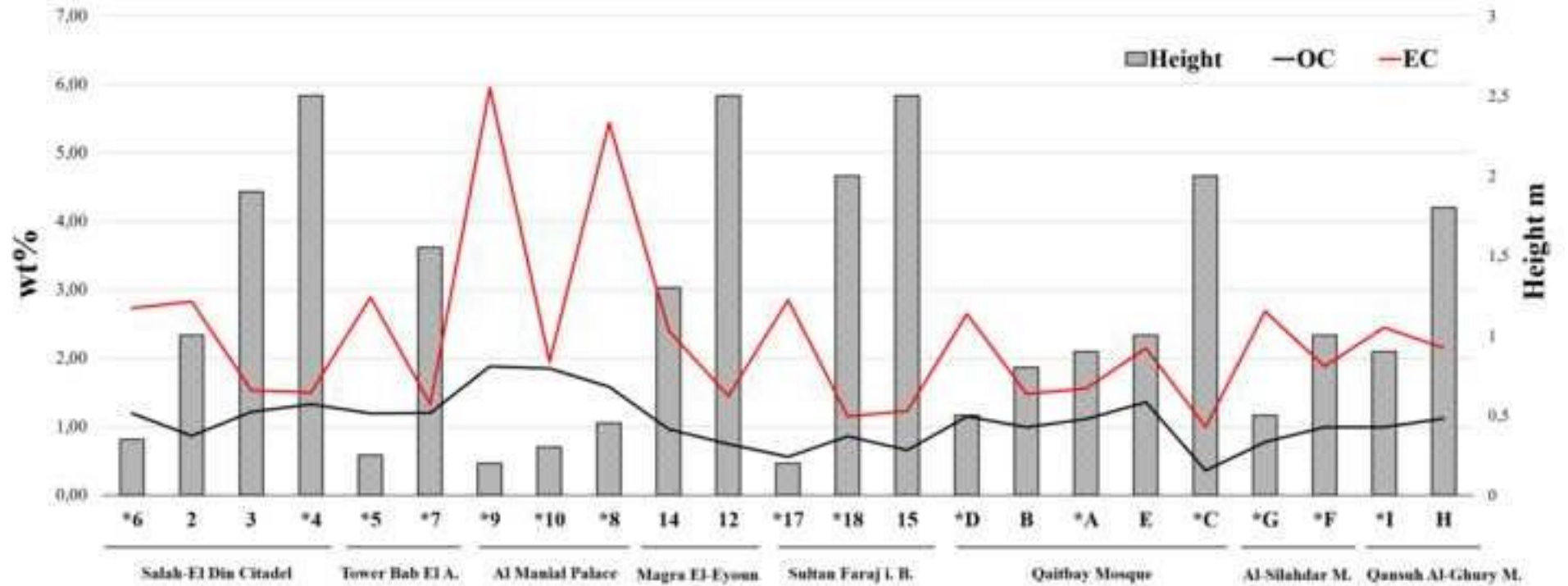
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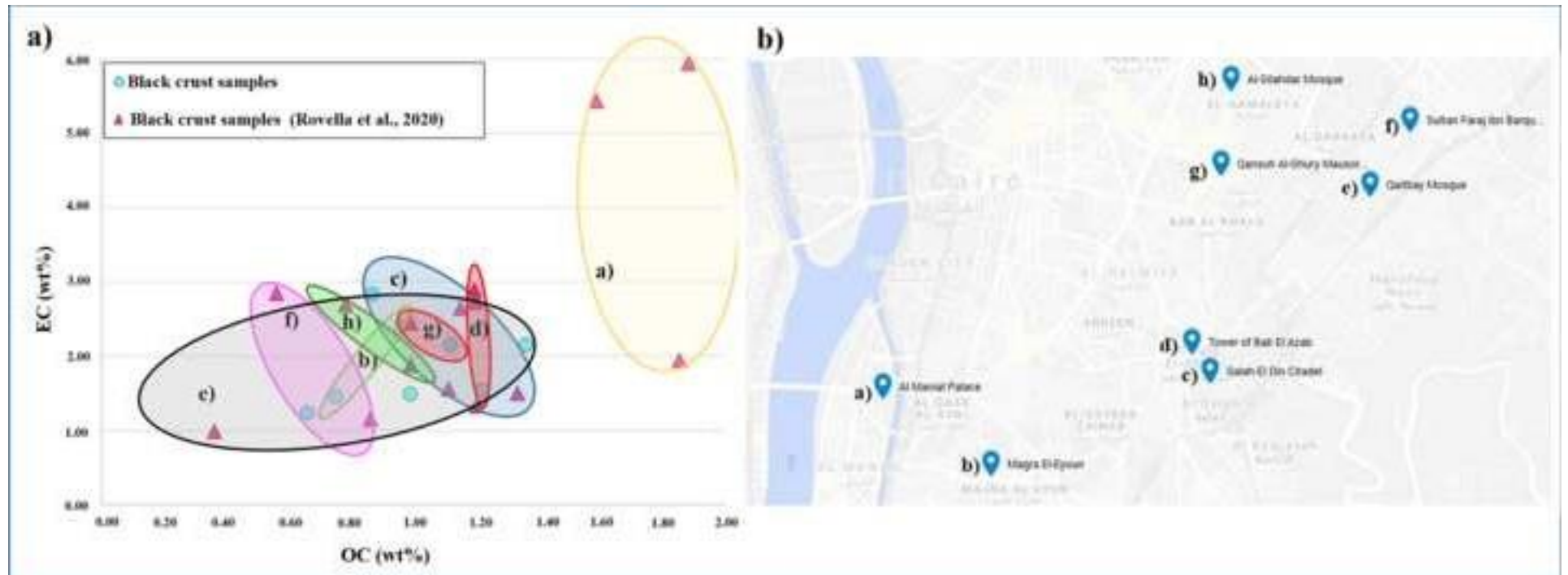
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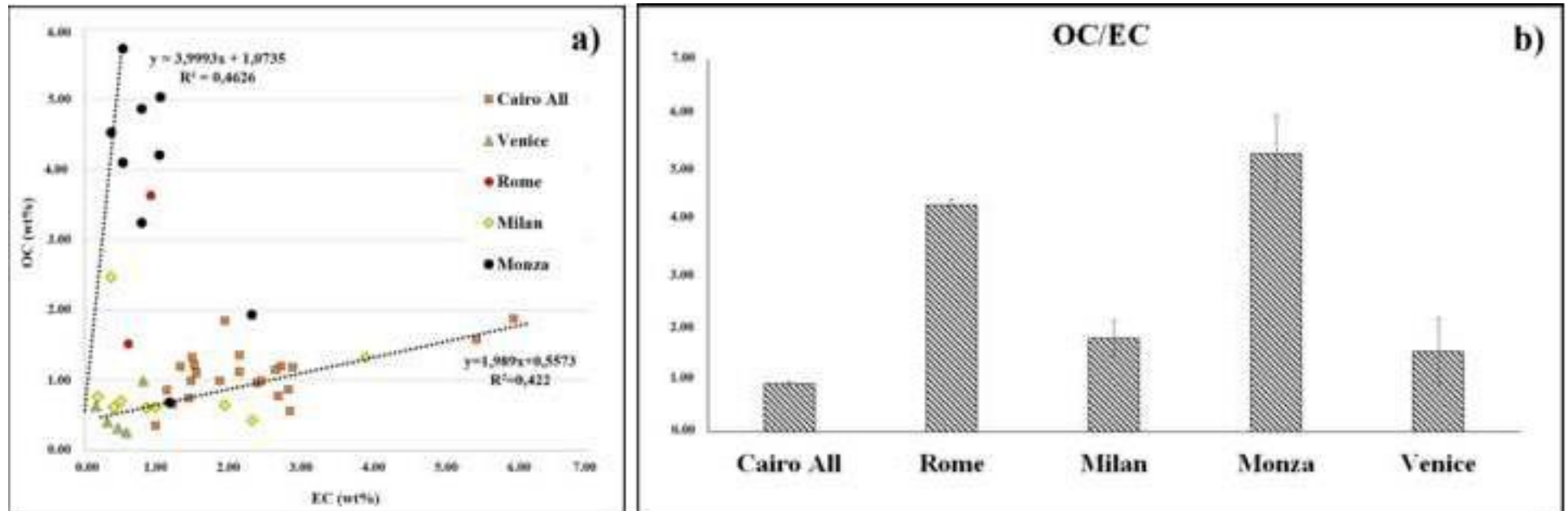
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Declaration of interests

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:

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Valeria Comite, **Formal analysis, Writing - Original Draft, Investigation, Methodology**

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Mauro Francesco La Russa, **Supervision, Writing - Review & Editing, Funding acquisition, Project administration**