

Characterization of particulate matter in attic and settled dusts collected from two buildings in Budapest, Hungary

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Abstract: We have investigated two buildings covered with Zsolnay glazed architectural ceramics in Budapest (Hungary), one located in the densely built-up area of the city centre with a high traffic rate and one in a city quarter with moderate traffic and more open space. A black crust layer, containing a large amount of artificial particulate matter with different size and chemical composition, was observed on the ceramic material of both buildings, whereas weathered glaze was detected only on the ceramics of the building situated in the city centre. In this paper, our goal is to reveal the role of the particulate matter in the degradation of architectural ceramics. For this reason the attic dust and settled dust from the roofs of the studied buildings were collected. In the attic dust, besides the natural particles of geological origin, three types of artificial particles typically with spherical shape (spherules) were also distinguished: aluminosilicate (two subtypes), carbonaceous, and iron-rich fly-ash. The appearance of gypsum crystallites around the particulate matter in association with all spherule types suggests that the particulate matter greatly contributes to the degradation process.

The degradation of cultural heritage (e.g. presence of black crust and sulphated layers on architectural material) is a challenging question all over Europe because not only the natural building materials, but also the man-made silicate-based materials (i.e. ceramic, glaze) suffer from the consequences of the polluted environment. Numerous studies, associated with this problem, dealt with the high level of particulate matter (PM) in the air (Del Monte & Vittori 1985; Camuffo 1986; Hutchinson *et al.* 1992; Bonazza *et al.* 2005). The deterioration of built heritage has been known for decades, especially in polluted urban environments. Previous studies mainly aimed to determine the comprehensive processes which lead to the degradation of building materials. Most of these papers deal with the deterioration of natural building materials, for instance, carbonate rocks (limestone, marble), sandstones or volcanic rocks (García-Vallés *et al.* 1998; Ausset *et al.* 1999; Maravelaki-Kalaitzaki 2005; Török *et al.* 2011). In contrast with these earlier publications focusing on natural materials, fewer studies engage in the deterioration processes of man-made silicate-based building materials such as architectural ceramic or glaze (Pérez-Rodríguez *et al.* 1994; Pérez-Arantegui *et al.* 1997; Schwarz

et al. 2003; Kopar & Dücman 2007; Zhao *et al.* 2010; Madkour & Khallaf 2012; Ronchetti *et al.* 2013).

The appearance of the so-called black crust is one of the major degradation features affecting natural and artificial building materials alike. The first observations about the black crust layer were reported in the early nineteenth century in London, UK (Schaffer 1930). This author pointed out that the most important factor in connection with the decay of a building material is the action of acid sulphur gases derived from the combustion of coal. Since then, an increasing number of papers started dealing with the processes which initiate the degradation, and many authors revealed the dominant contribution of PM in the decay process. The suggestion had already been highlighted in the 1980s (Del Monte *et al.* 1984a, b), when damaged buildings with the black crust layer were examined in northern Italy (in Venice or Reggio Emilia). The first observations about the damaged building material clarified the connection between the black crust, the PM (e.g. soot, fly-ash), and sulphate minerals, especially gypsum. Del Monte & Vittori (1985) found a direct relationship between the thickness of the black crust and the contained

particles, which are mainly associated with gypsum, and in some cases the sulphate minerals that appear to have been nucleated on them. Camuffo (1986) characterized this black crust as a network of gypsum crystals and black carbonaceous particles.

Initially, Cheng *et al.* (1971) categorized the fly-ash and soot particles physically and chemically, and later the sources of these particles were studied by many authors (Rodríguez-Navarro & Sebastian 1996; Ausset *et al.* 1999; Lefèvre & Ausset 2002; Sabbioni 2003; Grossi & Brimblecombe 2007). In general, the PM is mostly emitted by combustion processes (e.g. public transport, heating, biomass burning) in the urban environment. Due to its origin from high-temperature processes, it often appears with a smooth spherical or sponge-like texture. Chemically, the fly-ash from fuel oil can contain large amounts of S and also some other elements, such as Si, V, Mg, Fe, Ca, Na, Ti, Cr and Al, in lower quantities. Coal fly-ash particles can have a higher Al and Si content compared to having lower amounts of S and Ca; they can also possess a more varied additional element content than the oil fly-ash, typically including K, Fe, Ti and Cl (Hutchinson *et al.* 1992). The carbonaceous or soot particles contain large amounts of C (c. >60 wt%) and low amounts of S and Fe (c. 6 wt% and 4 wt% respectively), and other metals like V, Ni, Fe, Cr, Ni or Pb (Ausset *et al.* 1999). Hutchinson *et al.* (1992) defined the main points of how the PM influences building material: firstly, it affects the sulphation as a nucleation site; secondly, it provides a source of Ca and/or S; and thirdly, it increases the sulphation potential by providing metals (such as V, Ni, Fe, Cr, Ni and Pb), which can catalyse the oxidation process from SO₂ to SO₄²⁻.

Our study aims to provide a better understanding of the complex degradation processes of man-made silicate building materials, which are different in some respects from decay processes in natural rocks. Based on their different structure and high melting points, ceramics and glaze are more resistant to the potentially corroding environmental factors such as precipitation and its acidity, as well as gaseous pollutants like SO_x, NO_x and CO₂ (Tournié *et al.* 2008). In this paper, our major goal is to reveal the role of PM in the degradation of architectural ceramics; therefore, attic dust and settled dust from the roofs of two buildings in Budapest (Hungary) were collected.

Study areas, sampling and methods

We have examined the Zsolnay architectural ceramics (glazed roof tiles) from two buildings in Budapest, Hungary. The Museum of Applied Arts is located in a densely built-up area of the city

centre with a high traffic rate, whereas the Geological and Geophysical Institute of Hungary is situated in a city quarter with moderate traffic and more open space (Fig. 1). Black crust was observed on the ceramic materials of both buildings, whereas weathered glaze was detected only on a few ceramics of the Museum of Applied Arts (Fig. 2). The black crust layer with a thickness between 10 and 50 µm firmly adheres to the surface of both the glazed front and the unglazed back sides of the ceramics and occurs in greater amount on the objects of the Museum. During previous examinations, it was determined that the black crust consists of variable amount of minerals like quartz, talc, dolomite, chlorite, kaolinite, weddellite-whewellite, graphite, hematite (and FeOOH), gypsum, thenardite, glauconite, artificial Fe (ferrite) phase and spherules with various chemical compositions (aluminosilicate, carbonaceous, Fe-rich). A comprehensive study of the black crust and other degradation phenomena of the Zsolnay architectural ceramics is in progress (Baricza *et al.* 2012, 2013, 2014).

We have collected 11 samples of attic dust and 16 samples of settled dust from both buildings altogether. Each side of the buildings was sampled to observe the differences in exposure (Fig. 1). The attic dust sampling was carried out in the autumn of 2013 following international methods and experiences during sampling (Cizdziel *et al.* 1998; Davis & Gulson 2005; Sajn 2006; Völgyesi *et al.* 2014). On average, more than 10–15 g attic dust was collected at each sampling site. The settled dust was gathered during a 5-month period, from June to November in 2013, in order to capture the additional maximum in the mass of dust (Sipos *et al.* 2014). We used uncovered buckets (capacity: 500 ml) to collect bulk deposition of the PM. After sampling, the content of the buckets was filtered in the laboratory of the Institute for Geological and Geochemical Research, Research Centre for Astronomy and Earth Sciences in the Hungarian Academy of Science to remove undesired parts (e.g. bugs, plant fragments). On average, less than 2 g of settled dust was sampled at each sampling site; thus, they were analysed only by X-ray diffraction analysis (XRD). All technical information about the samples and the applied techniques is shown in Table 1.

The phase composition of the powdered dust samples was determined by XRD with a Philips PW 1730 diffractometer at the Institute for Geological and Geochemical Research (RCAES HAS). Analytical parameters were: Cu Kα beam, 45 kV, 35 mA, 0.05°–0.01° 2θ step, 1 s time constant, PW-1050/25 type goniometer, graphite monochromator, proportional counter detector.

The attic dust samples were also studied by Raman microspectroscopy using a HORIBA Jobin–Yvon LabRAM HR confocal Raman

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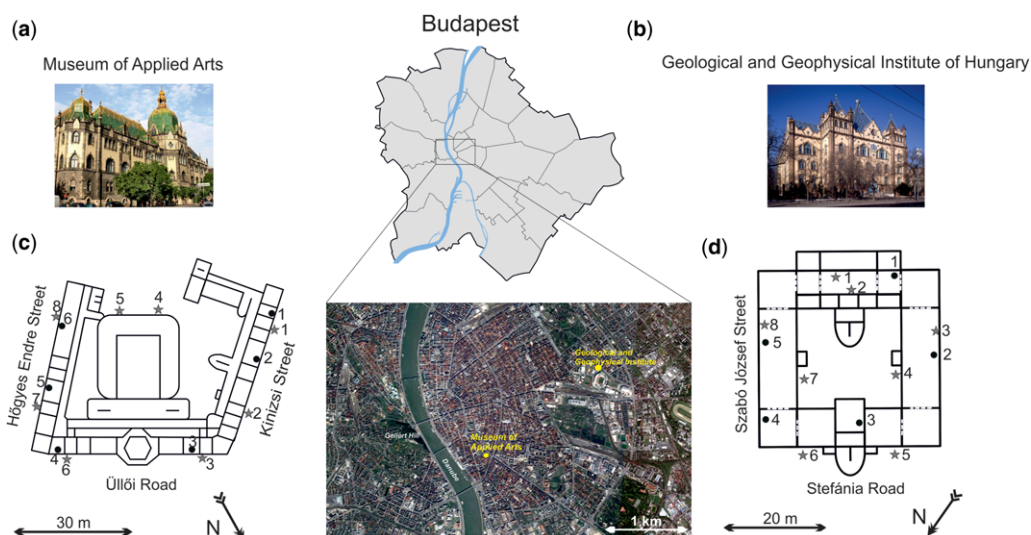


Fig. 1. (a) The Museum of Applied Arts and (b) the Geological and Geophysical Institute of Hungary. (c, d) Schematic drafts of the second floor of the buildings, where numbered dots indicate the sampling sites of the attic dust and numbered stars indicate the sampling sites of the settled dust.

microspectrometer at the Faculty of Science Research and Instrument Core Facility of Eötvös University (ELTE FS-RICF). These samples were not powdered before the analysis in order to

preserve their natural state. For the Raman measurements, we applied the 532 nm emission of a frequency-doubled Nd:YAG laser with a grating of 1800 grooves mm^{-1} . The maximum laser power

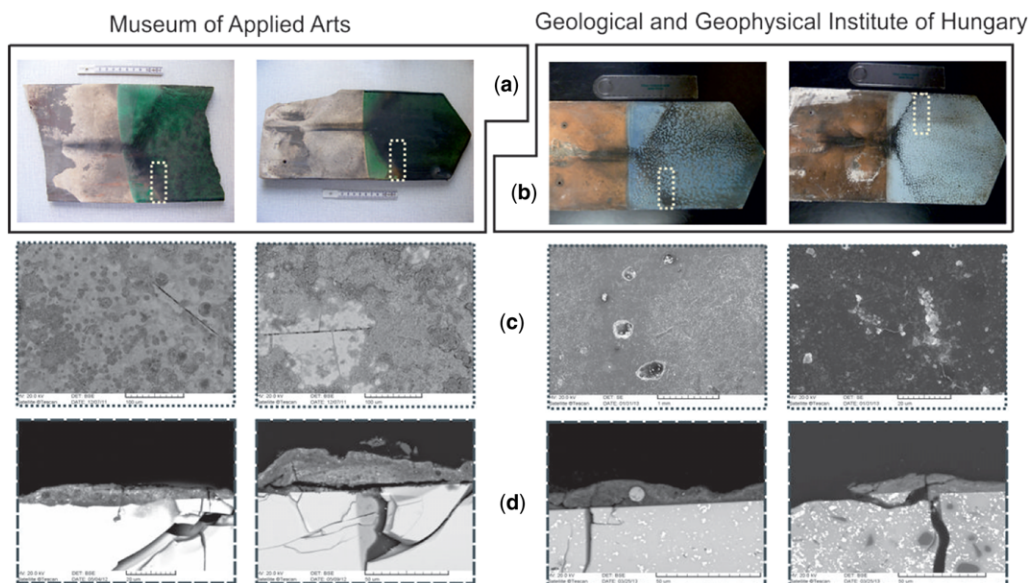


Fig. 2. Degraded architectural ceramics from (a) the Museum of Applied Arts and (b) the Geological and Geophysical Institute of Hungary. Dashed lines show the examined parts where the sections were cut. Black crust and weathered glaze were observed on the ceramics. (c) Dotted-framed images show the surface view of the glazed side of the ceramics and (d) dashed line-framed images show cross-section view of the glazed ceramics (SEM-BSE (back-scattered electron) images).

Table 1. Schematic draft about the technical information of the attic and settled dust samples and the applied preparations

Buildings	Museum of Applied Arts		Geological and Geochemical Institute of Hungary		
Sample types	Attic dust	Settled dust	Attic dust	Settled dust	
Number of samples	6	8	5	8	
Quantities	Mus./d1-6	Mus./s.d1-8	Inst./d1-5	Inst./s.d1-8	
Preparations	>10–15 g	1–2 g	>10–15 g	1–2 g	
Techniques	<div>XRD crystalline phase identification</div>	<div>Raman-spectr. particle identification</div> <div>SEM-EDX particle identification, surface microstructure</div> <div>Microprobe particle quantification</div>	<div>XRD crystalline phase identification</div>	<div>Raman-spectr. particle identification</div> <div>SEM-EDX particle identification, surface microstructure</div> <div>Microprobe particle quantification</div>	<div>XRD crystalline phase identification</div>

The bottom flowchart shows the applied techniques on the dust samples.

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incident on the sample was *c.* 40 mW. Iron oxide particles (e.g. hematite) were analysed by reduced laser power (*c.* 4 mW) to avoid sample degradation. The detected phases were identified by their characteristic Raman peaks.

The morphology and chemical characteristics of attic dust samples were studied with an Amray 1830 I/T6 scanning electron microscope (SEM) with energy dispersive spectrometer (EDS) at the Department of Petrology and Geochemistry of Eötvös University. Analytical conditions were: 20 kV accelerating potential, 1 nA beam current, focused electron beam, diameter *c.* 50 nm.

The quantitative analysis of the two selected attic dusts from each building (point analysis) were done by a JEOL Superprobe-733 type microprobe equipped with an Oxford Instruments INCA Energy 200 EDS at the Institute for Geological and Geochemical Research. Analytical conditions were: 20 kV, 6 nA, 50 s count time. Natural and artificial phases provided by the Taylor Co. (USA) were used as standards. For the measurements, the attic dust samples were fixed with two-sided glue tape on the sample holder.

Results

The XRD analysis indicates that the powdered settled dust samples from both buildings consist mostly of quartz, plagioclase, K-feldspar, dolomite, chlorite, talc, calcite, 10 Å phyllosilicate and minor

amounts of gypsum (Fig. 3). No significant differences were detected among the dust samples; however, the settled dust of the Museum of Applied Arts contains higher amounts of plagioclase, K-feldspar, calcite and gypsum compared to that of the Geological and Geochemical Institute of Hungary. Some settled dust samples (e.g. Inst./s.d_3 sample) may contain organic compounds indicated by a low hump (elevated background) at *c.* 18–20 °2 Theta in the XRD profile (Fig. 3).

The attic dust samples contain quartz, chlorite, kaolinite, plagioclase, 10 Å phyllosilicate, talcum, dolomite, calcite, glauberite, thenardite and gypsum based on their XRD profiles (Fig. 4). Only a minor amount of gypsum as sulphate mineral was detected in the settled dust. In contrast sulphates (primarily gypsum) are present in a significant amount in the attic dust, especially in the attic dust collected at the Museum of Applied Arts.

The attic dust samples from both buildings were also analysed in their natural state with Raman microspectroscopy, and the same phases were detected (e.g. quartz, plagioclase, K-feldspar) with the exception of sulphate minerals, which were found especially as gypsum in the samples from the Museum of Applied Arts. Furthermore, a large amount of spherical, 10–50 µm-sized Fe-rich particles, mainly hematite were observed (Fig. 5). However, the peak position of this mineral was shifted to 216, 282, 397, 488 and 597 cm⁻¹ (Fig. 5). This phenomenon can be explained by the microcrystalline nature of the studied hematite in which

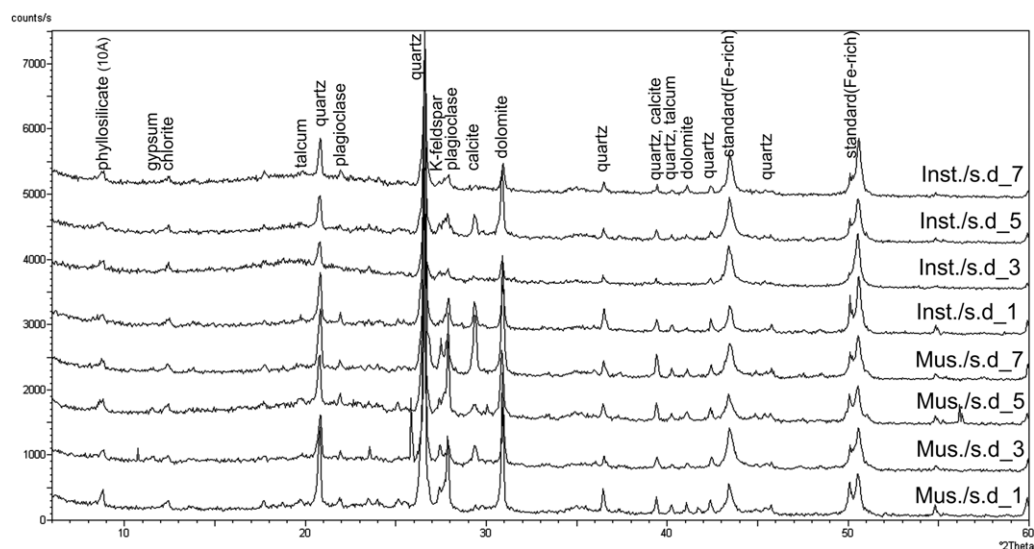


Fig. 3. The XRD profiles of the settled dust collected from June to November 2013 from the studied buildings. The sample names are on the right of the figure. Mus., Museum of Applied Arts; Inst., Geological and Geophysical Institute of Hungary; s.d., settled dust.

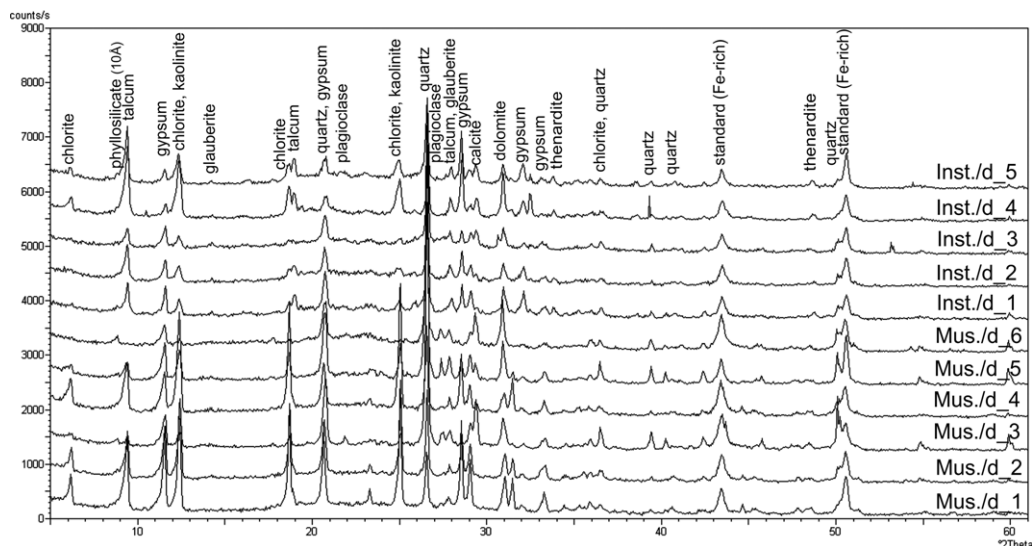


Fig. 4. The XRD profiles of the attic dust from the studied buildings. The sample names are on the right of the figure. Mus., Museum of Applied Arts; Inst., Geological and Geophysical Institute of Hungary; d., dust).

decreased particle size resulted in the shifting of Raman lines to lower wave numbers (Chernyshova *et al.* 2007). The observed shift of Raman lines was also reported by Wang *et al.* (1999) on hematite in highly weathered basaltic rocks.

A large amount of 5–15 μm -sized C-rich particles were identified in all of the attic dust samples from both buildings. The characteristic broad peaks of this C-rich phase were observed around 1344 and 1594 cm^{-1} (Fig. 5), which indicated their disordered structure (Rosen & Novakov 1977).

Three types of spherical artificial particles, so-called spherules, were observed by SEM-EDX in the attic dust (Fig. 6). The studied spherule types occur in similar chemical composition in both buildings:

- (1) Type-1 spherules are 30–50 μm -sized particles with a smooth surface. They mostly consist of Fe and variable amounts of other elements like Si, Al, S, Na, K, Ca and Mg.
- (2) Type-2 spherules are of two subtypes. Type-2a are 5–25 μm in size and have a smooth surface. They principally contain Si, Al, K and/or Ca and also consist of variable amounts of Fe, S, Ti, Na, Cl and P. Type-2b spherules are similar to the Type-2a in their morphology and chemical composition, with the exception that these particles contain mainly Si and Al. Other components such as Fe, S, Ti, Na, K, Ca and Mg occur only in minor amounts.

- (3) Type-3 spherules are 50–70 μm in size and have a sponge-like texture. They mainly consist of C, which is indicated by the elevated background of the EDS spectra. Elements such as S, Si, Al, Fe, Cl, Na, K, Ca, and Mg were also detected.

We selected two attic dust samples from both buildings to get more precise data about their chemical composition by electron microprobe analysis (Table 2). However, only the spherule Types-1, 2a and 2b have been analysed in detail since the instrument that was used is not able to analyse C quantitatively. The spherule Type-1 contains 40–90 wt% of Fe_2O_3 and other elements (SiO_2 , Na_2O , K_2O , CaO and MgO) in various amounts, but <20 wt% quantity (Table 1). In the spherule Type-2a, the SiO_2 content ranges between 22 and 50 wt%. The Al_2O_3 content varies from 1 to 31 wt%, whereas the total alkali and alkaline earth ($\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{CaO} + \text{MgO}$) content is between 15 and 36 wt%. In the spherule type-2b, the SiO_2 content is highly variable, between 42 and 81 wt%, and the Al_2O_3 concentration ranges from 13 up to 41 wt%. The total ($\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{CaO} + \text{MgO}$) content is c. 6–13 wt%, and the Fe_2O_3 content is c. 2–12 wt%. The particles in the spherule type-3 are composed of 2–3 wt% total alkali content, 5–10 wt% SO_3 and SiO_2 in variable quantity (3–18 wt%). The low total is in agreement with the suspected high C content.

We have frequently observed, especially in the attic dust from the Museum of Applied Arts, gypsum crystallites appearing on the surface of the

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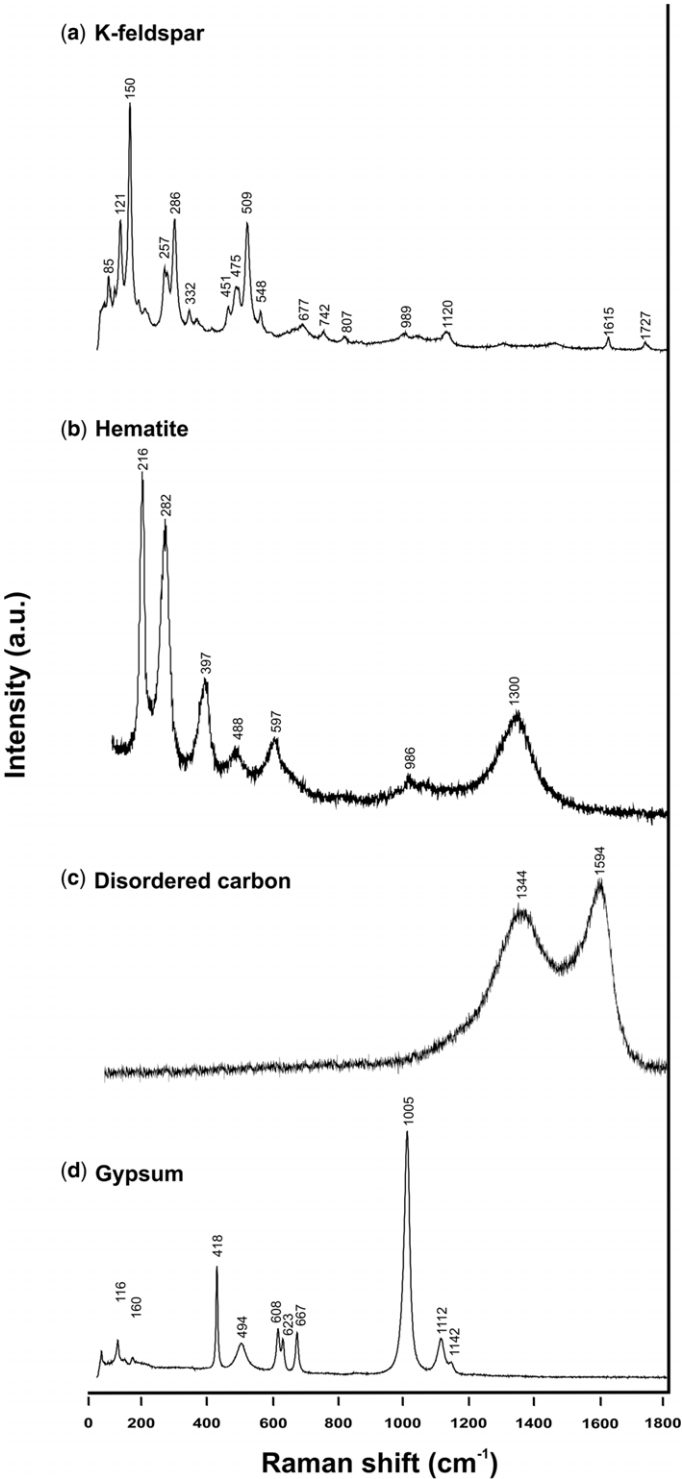


Fig. 5. Raman spectra of the identified phases with their characteristic peak positions in the attic dust from the studied buildings. (a) K-feldspar, (b) hematite, (c) disordered C and (d) gypsum.

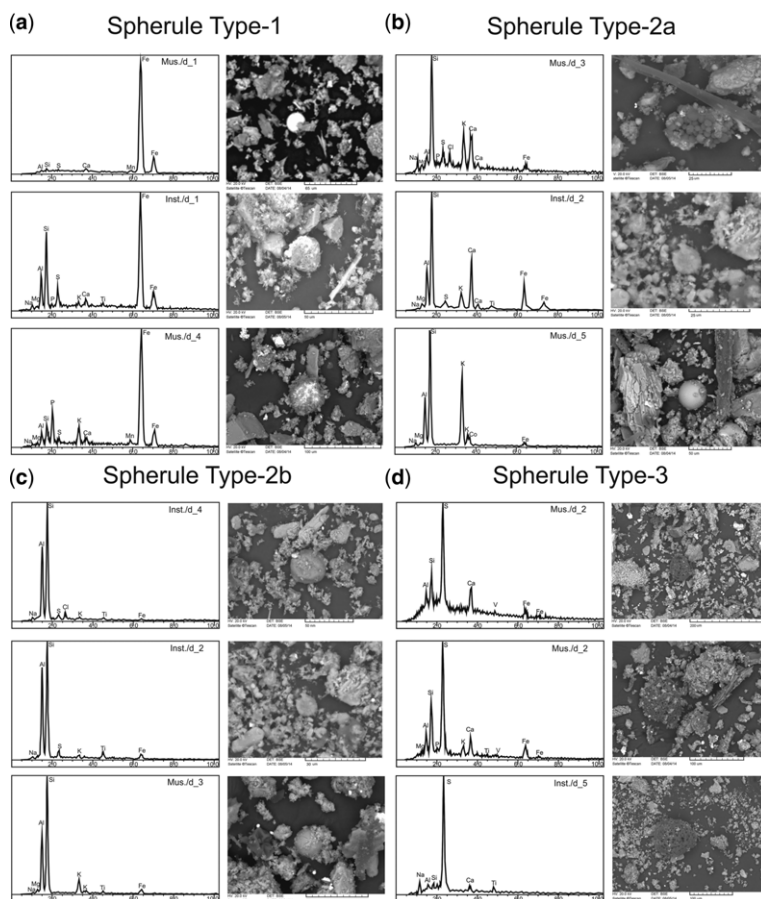


Fig. 6. The three spherule types detected in the attic dust from the studied buildings. (a) Type-1, Fe-rich 30–50 µm-sized particles with smooth surface; (b) Type-2a, Si-Al-rich and alkali/alkaline earth metal-bearing with smooth surface and 5–25 µm in size; (c) Type-2b, mostly Al-Si-rich with similar morphology to Type-2a; (d) Type-3, carbonaceous spherules of 50–70 µm in size with sponge-like texture. Three typical spherules were selected from each group. SEM-BSE images are on the right, and X-ray spectra on the left. The sample numbers are shown on the upper right corner of the spectra.

spherules or precipitating in their surroundings (Fig. 7). This phenomenon was observed for all types of spherules (Fig. 6).

Discussion

Impact of natural environment on the settled dust

Based on the XRD results (Fig. 3), more than half of the settled dust samples collected from the studied buildings consist of particles (e.g. quartz, feldspar, dolomite, mica, chlorite, kaolinite), which originate from the natural (geological) background of the location (Ódor *et al.* 1997). Settled dust shows

differences in the phase composition between the studied buildings. Lower amounts of dolomite, plagioclase and calcite have been determined in the settled dust from the Geological and Geophysical Institute of Hungary than from the Museum of Applied Arts. The differences in phase composition are most probably due to the location of the buildings. The Museum of Applied Arts is located in the city centre and is closer to Gellért Hill (Fig. 1) – a part of the Buda Mountains, which consist mostly of limestone and dolomite – on the right side of the Danube, 600 m away from the Museum (Fig. 1). Moreover, in Budapest the most frequent wind direction is from the NW, which also supports the delivery of these particles (Radics *et al.* 2002).

Table 2. Chemical composition of the spherule types in four attic dust samples measured by electron microprobe analysis

Samples	Spherule types	Chemical composition (wt%)																	
		Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	K ₂ O	CaO	TiO ₂	Cr ₂ O ₃	MnO ₂	Fe ₂ O ₃	NiO	CuO	SnO ₂	Total alkali and alkaline earth metals (Na ₂ O + K ₂ O + CaO + MgO)	Total	
Mus./d_1	1				0.93								88.6				0.00	89.54	
	1				1.36		1.02		0.85				75.6				0.85	78.88	
	1	1.57		1.35	3.67	1.41	1.99		1.56				74.5				3.13	86.02	
	1	2.33	1.44		2.02	2.64	4.78	0.79		2.86			60.5				4.56	77.31	
	1						0.00						90.0				0.00	89.96	
	1	2.17	2.13	2.23	2.59	7.40	2.01	0.62	1.13	2.83			59.1				6.05	82.17	
	2/a	4.01	1.69	3.96	25.8		17.4	0.81	19.6				1.31				26.15	74.60	
	2/a	8.88	3.27	15.3	24.0		14.9	0.45	13.4				3.21				26.0	83.38	
	2/a	4.98	0.79	31.5	36.5			0.90	15.7	2.05			3.67				23.53	96.11	
	2/a	1.93	1.47	17.4	25.8		15.3	4.55	11.7				3.03				19.61	81.21	
	2/a	2.17	15.89	10.7	22.0		4.73	1.53	17.1				5.96				36.68	80.02	
	2/b	7.22	1.20	12.8	81.6		2.04	2.46	2.17	0.77			2.01				112.22	112.05	
	2/b	2.16	2.69	32.3	51.1		3.93	2.88	2.52	0.54			4.32				10.25	102.42	
	2/b	2.11	1.80	25.9	42.8		6.33	2.25	4.06				4.80				10.22	90.07	
	2/b	1.04	1.63	26.4	42.2		3.68	1.27	2.08	4.06			4.35				6.02	86.63	
Mus./d_2	1			1.14	2.02	1.00	1.46		1.04				81.4				1.04	88.10	
	1	0.98	3.54	9.88	14.9	1.39	2.86		4.50	0.68			44.9				9.02	83.58	
	2/a		3.29	3.60	49.8	3.87	6.57		18.7				18.6				22.01	104.42	
	2/a			0.97	24.4	1.95	28.8		21.2				1.81				21.19	79.08	
	2/b	2.09	2.21	38.1	56.3	1.23		1.36	1.08				12.3				6.74	114.76	
	2/b	1.60	0.84	17.0	65.3		1.32	3.86		1.15			5.17				6.30	96.20	
	2/b	1.45	1.63	31.3	58.5	0.77	0.75	2.36	0.84	0.59			4.53				6.28	102.72	
Inst./d_1	1	7.43	3.00	1.91	6.15	0.79	5.68		3.47	2.48	2.80	6.52	40.4				13.9	78.15	
	2/b	4.00	2.22	17.2	69.9		4.00	0.55	1.15	0.82			2.49				7.92	101.47	
	2/b	4.04	1.61	24.1	58.2		4.15	1.10	1.54				2.83				8.29	97.61	
	3	2.34		0.92	3.43		10.5		1.07								3.41	18.22	
Inst./d_2	1	2.84		0.91	5.10		2.16						98.8		2.77	1.49	2.84	114.08	
	1			13.0	0.69								48.3	6.96			0.00	84.50	
	2/a	7.24	2.31	16.1	38.2		2.06	0.42	4.61	2.07	5.47		17.4	1.92			14.58	97.91	
	2/a	8.16	1.67	19.7	42.2		2.53	16.0	2.74				2.99				28.57	95.96	
	2/b	1.98	2.20	29.7	59.0			3.18	2.67	1.00			6.48				10.03	106.25	
	2/b	3.95	1.45	41.4	55.0		2.27	0.93	1.38	0.84			4.08				7.71	111.26	
	3	1.74		0.48	18.6		5.06	0.33									2.07	27.01	

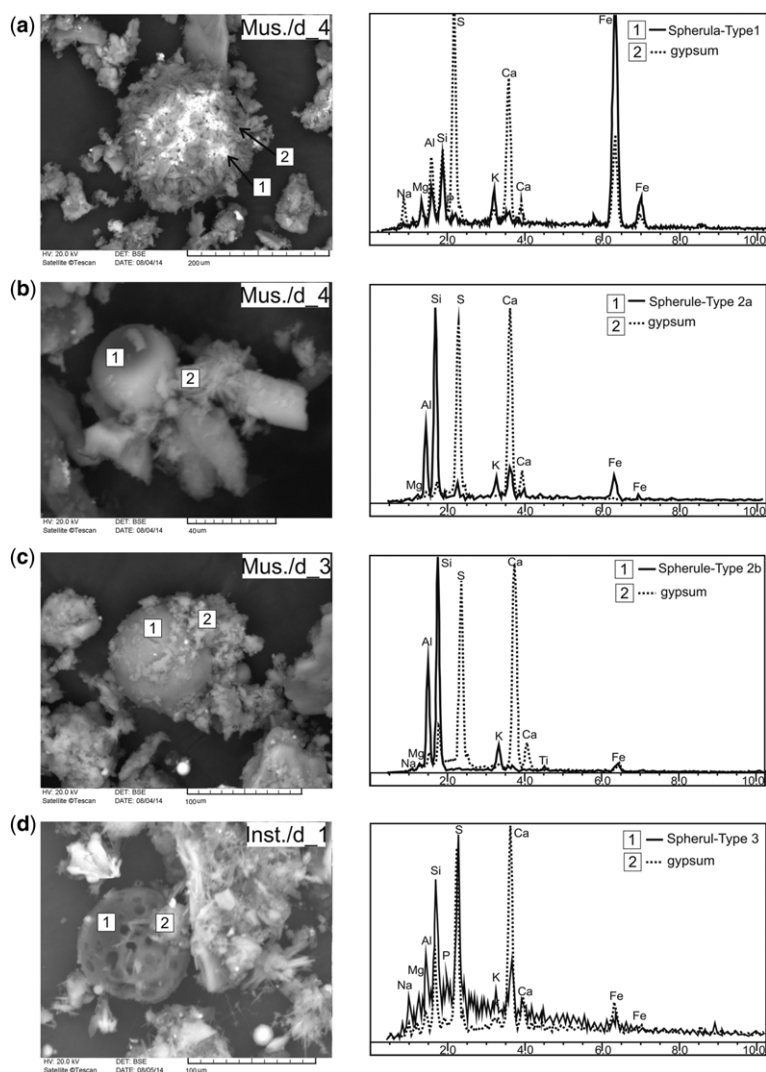


Fig. 7. Representative particles of the three spherule types and gypsum crystallites in association with the particles in the attic dust (SEM-BSE images on the left). X-ray spectra show the chemical composition of the spherules and the gypsum crystals (on the right). (a) Type-1, Fe-rich spherules with dense, needle-shaped gypsum; (b, c) Types-2a and 2b, aluminosilicate fly-ash spherules with needle-shaped (b) and smaller unoriented (c) gypsum particles; (d) Type-3, carbonaceous spherules with needle-shaped gypsum crystals. The sample numbers are shown on the upper right corner of the SEM-BSE images.

Presence of sulphates

In the attic dust, in addition to the minerals of natural origin, we have identified sulphate minerals, especially gypsum and other minor sulphates such as glauberite ($\text{Na}_2\text{Ca}(\text{SO}_4)_2$) and thenardite (Na_2SO_4), which are common in normal terrestrial conditions and frequently appear in various environments (Matović *et al.* 2014). A proportionally higher amount of sulphate minerals was

determined in the attic dust of the Museum of Applied Arts than in that of the Geological and Geophysical Institute of Hungary (Fig. 4). The source of the sulphates could be the reaction of SO_2 – which originates as a gaseous pollutant mainly from anthropogenic sources, especially combustion processes from power plants, industry, or traffic (Fassina 1988; Vestreng *et al.* 2007) – and Ca- and Na-bearing particles (e.g. calcite, feldspar), which easily starts forming gypsum or other

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sulphate minerals (Rodríguez-Navarro & Sebastian 1996; Příkryl *et al.* 2004). Considering that sulphates have not been identified in the studied settled dust samples it is suggested that these minerals were most probably formed *in situ* in the attic of the buildings. Due to an insufficient amount of settled dust, we could only examine this material by XRD technique (Table 1), which does not permit the detection of phases below 5 wt%. Small fragments of gypsum crystallites were detected in the settled dusts (e.g. samples Mus/s.d_3, Mus/s.d_5); thus, gypsum is presumably present in greater amounts than the identified small peaks (Fig. 3) in our settled dust samples. A possible explanation of the absence of gypsum in the settled dust could be the lack of time for mineralization or possibly inadequate conditions. The uncovered buckets, into which the settled dusts were collected, could have been in wet conditions, which are essential for gypsum formation but they were not protected from run-off which prevents the mineralization (Camuffo 1986). Otherwise, the dissolution of gypsum in the buckets with water could be another explanation. Solubility of gypsum reaches a maximum level at *c.* 40 °C (Blount & Dickson 1973), a temperature which is easily reachable in summer on the surface of glazed ceramics in the study area. However, a smaller amount of gypsum was detected in the settled dust than in other studies dealing with the deterioration of limestone in Budapest (Smith *et al.* 2003; McAlister *et al.* 2006; McAlister *et al.* 2008; Török *et al.* 2011). These researchers suggested that the formation of gypsum is a rapid process, and the appearance of gypsum is detectable within 12 months (Ausset *et al.* 1999). In addition, in these papers, the studied dust samples originated from buildings built with limestone, which facilitates gypsum mineralization easy being that Ca a major component of limestone.

Based on the SEM images, mainly acicular (needle-shaped) gypsum crystals were found on the spherules, but in a few cases there was not enough time for the total development of the acicular morphology (Fig. 7, on Mus./d_3). No relationship was found between the gypsum morphology and the nucleation site on the different spherule types because a spherule with certain chemical composition can be the nucleation site of different crystal types (Ausset *et al.* 1999). Needle-shaped gypsum, the typical form of calcium sulphate dihydrate, was developed on the studied spherules. This indicates that a lower concentration of substrate was available in the surroundings of the spherules at the time of the crystallization since at higher concentration of substrates the morphology of gypsum can be changed and spontaneous precipitation can occur (Alimini & Gadri 2004).

Influence of fuel combustion

Raman peaks of disordered carbonaceous particles were observed in the attic dust from the Museum of Applied Arts at *c.* 1344 and 1594 cm^{-1} (Fig. 5). Similar Raman spectra were published by Rosen & Novakov (1977) for automobile and diesel exhaust particles and ambient air samples. Sadezky *et al.* (2005) carried out measurements using a similar technique on eight different industrial soot particles which were available as powder samples. These researchers have verified that different soot particles have characteristically broad Raman peaks at *c.* 1350 and 1585 cm^{-1} , similar to our observation (Fig. 5).

Significance of the spherules

Based on the morphology and the chemical composition, three types of artificial spherules were distinguished in the attic dust: Type-1 (Fe-rich); Type-2 divided into subtype-2a (Si-Al-rich and alkali/alkaline earth metal-bearing) and subtype-2b (mostly Al-Si-rich); and Type-3 (carbonaceous spherules). Several studies have documented the presence of similar atmospheric fly-ash particles (i.e. porous carbonaceous, smooth aluminosilicate, and metal particles mainly composed of Fe) in the damage layers of building materials (e.g. Del Monte *et al.* 1981; Sabbioni & Zappia 1992; Sabbioni 1995; Tanosaki *et al.* 2009). The source and influence of these particles are different according to their physical and chemical characteristics.

Type 1 (Fe-rich spherules). Type-1 spherules, based on well-known chemical and physical properties (Sabbioni & Zappia 1992; Laursen & Frandsen 1999; Tanosaki *et al.* 2009), can be considered as common particles originating from mostly diesel- or to a lesser extent gasoline-engine emissions (Rodríguez-Navarro & Sebastian 1996). In addition to these, Sabbioni (1995) also assumed coal combustion as a potential source. The most important influence of these spherules is their catalytic effects on ambient SO_2 molecules due to their high Fe content. This metal, with other elements like Ni, V or Cr, is able to accelerate SO_2 oxidation into sulphate with the use of other locally originated elements such as Ca or Na (Sabbioni 1995). Moreover, during microprobe analysis not only Fe-rich, but also Fe- and S-rich spherules were identified in a few dust samples (e.g. in Inst./d1 sample) (Table 2). Therefore, it is not surprising that gypsum crystallites appear on the surface of these spherules in some cases.

Types-2a and 2b (aluminosilicate fly-ash spherules). Types-2a and 2b spherules, according to their

physical and chemical features, could have been emitted mostly by coal combustion (Hutchinson *et al.* 1992; Ausset *et al.* 1999). These spherule types also contain Fe (Table 2), which can be a catalyser element in sulphation (Sabbioni 1995), in the process mentioned above. Moreover, in some samples these particles also contain S and Ca, which can locally form gypsum crystals. Del Monte *et al.* (1984b) have analysed coal fly-ash particles from an oil-fired power plant and indicated that they contain both Ca and S, which can generally support gypsum crystal growth. Few spherules of Type-2a in the collected attic dust contain more than 10 wt% SO₃ as well as Ca (11–19 wt% CaO) (Fig. 6; Table 2), which is enough for nucleation of gypsum (Camuffo 1986).

Type 3 (carbonaceous particles). The Type-3 particles in our attic dust samples have a sponge-like texture (Fig. 6), which is the most frequently found texture type among carbonaceous particles (Bonazza *et al.* 2005). Spongy spherules mainly originate from traffic and combustion of fuels, which are responsible for the emission of 0.68 Tg a⁻¹ of black carbon particles in Europe (Kupiainen & Klimont 2007). The importance of this spherule type is twofold: the carbonaceous particles are responsible for the blackening of the deposition layer, and it also supports the sulphation processes based on its higher S content compared to the other types of spherules (Ausset *et al.* 1999). Their influence in the degradation processes is more significant compared to the other spherule types, and they play an active role in the damage processes that affect the surfaces of building materials. Their texture is suitable for capturing other particles; thus, they become nucleation cores (Bonazza *et al.* 2005). Furthermore, they contain a greater amount of components and catalysing metals (such as Ca, S and Fe, V) to launch sulphate crystallization on their surface, as was seen in our dust samples.

Conclusion

The major goal of this paper was to detect the factors which are responsible for initiating the degradation processes on the glazed architectural Zsolnay ceramics on two buildings in Budapest. The Geological and Geophysical Institute of Hungary is in a city quarter with a moderate traffic rate, and the Museum of Applied Arts is in the city centre with a high traffic rate.

Attic and settled dust samples were collected from both buildings. Natural particles and artificial spherules were identified, and the latter were classified into three types: Type-1 (Fe-rich); Type-2 with subtype-2a (Si-Al-rich and K, Ca, Na, Mg bearing) and subtype-2b (Si-Al-rich); and Type-3

(carbonaceous). We have found a difference in the mineral composition of the attic dust between the buildings which was in accordance with the surrounding geology and the direction of the wind. Sulphate minerals (gypsum, glauberite, thenardite) were observed in large amounts in the attic dust of the Museum of Applied Arts, where these minerals were most probably formed *in situ* in the attic of the building.

All of the observed artificial spherules can act as nucleation cores in the sulphation process, since initial gypsum mineralization was detected on the surface of the spherules. Most of the spherules contain the chemical components needed for the precipitation of sulphate minerals; however, only a few spherules contain them in sufficient amount (>10 wt% in the case of S). We have found sulphation-catalysing components (such as Fe) in almost all of the measured spherules.

The results of the present work confirm the influences of artificial particles in launching sulphation, and consequently the degradation processes. The paper emphasizes how artificial particles influence the premature ageing of the built environment if it is made of a special man-made material like glazed ceramics, and the importance of the location of a building, which can increase the extent of deterioration, especially in a city environment.

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