Original Paper

Origin of sulphated grey crusts on glass in polluted urban atmosphere: stained glass windows of Tours Cathedral (France)

Roger-Alexandre Lefèvre, Mélanie Grégoire, Mickaël Derbez and Patrick Ausset

Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA, UMR CNRS 7583), Faculté des Sciences, Université de Paris XII Val-de-Marne, Créteil (France)

The grey crusts covering some places of the weathered stained glass windows of Tours Cathedral were studied by Analytical Scanning Electron Microscopy. These crusts are constituted by a gypsum cement embedding many particles: microspherules (fly ash generated by combustion processes, rounded particles of leached glass, hypersiliceous spherules from tuffeau stone); angular fragments of leached glass; organic objects; siliceous and sulphated aggregates. The particles contained in the sulphated black crusts covering the stone, in the air and in the rain in Tours were studied simultaneously and compared with those of the stained glass windows' grey crusts. In all cases, similar kinds of fly ash are present demonstrating the action of atmospheric microparticulate pollution both on the stained glass windows and on the stone. Furthermore, the presence of hypersiliceous particles in crusts on glass and in the rain suggests transfers from stone to glass by rainwater run-off and possibly directly from the atmosphere. The presence of leached glass in the sulphated crusts on glass leads also to conclude on the modifying of the glass surface by the action of the rainwater run-off. Moreover, calcium and sulphur needed to form superficial gypsum crusts come both from the nearby calcareous stone, from the atmospheric gases and particles, and probably partially from calcium contained in unweathered glass.

Ursprung grauer sulfathaltiger Verwitterungskrusten auf den Glasfenstern der Kathedrale in Tours (Frankreich)

Die grauen Krusten, die Teile der korrodierten mittelalterlichen Gläser der Kathedrale zu Tours überziehen, wurden rasterelektronenmikroskopisch untersucht. Die Krusten bestehen aus einer gipshaltigen Matrix, in die zahlreiche Partikel eingeschlossen sind. Es handelt sich dabei um Mikrokügelchen (Flugascheteilchen, die bei Verbrennungsvorgängen entstehen; runde Partikel von ausgelaugtem Glas; silicatreiche Mikrokügelchen aus dem Tuffeau-Naturstein), eckige Fragmente von ausgelaugtem Glas, organische Teile sowie silicat- und sulfathaltige Aggregate. Gleichzeitig wurden die in den schwarzen sulfathaltigen Krusten auf den Bausteinen, in der Luft und im Regenwasser in der Umgebung der Kathedrale enthaltenen Partikel analysiert. Anschließend wurden diese Partikel mit denjenigen verglichen, die sich in den Verwitterungskrusten der Gläser befinden, und dieselben Ascheteilchen gefunden. Daraus läßt sich schließen, daß sowohl die Gläser als auch die Bausteine einer Umweltbelastung durch die Ablagerung von Mikropartikeln ausgesetzt sind. Ferner legt das Vorhandensein von silicathaltigen Mikropartikeln, die sowohl in den Krusten auf dem Glas als auch im Regenwasser enthalten sind, die Vermutung nahe, daß mit dem Ablaufwasser und wahrscheinlich direkt aus der Luft Bestandteile der Tuffeau-Steine auf die Gläser gelangen. Das Auftreten von ausgelaugtem Glas in den gipshaltigen Krusten auf den Gläsern läßt die Schlußfolgerung zu, daß sich die Glasoberfläche unter Einwirkung des Ablaufwassers verändert. Die für die Bildung von Gips erforderlichen Elemente Calcium und Schwefel stammen aus den Bausteinen der Kirche, aus den Luftschadstoffen, aus den Flugaschen und Calcium wahrscheinlich auch aus den nichtkorrodierten Gläsern.

1. Introduction

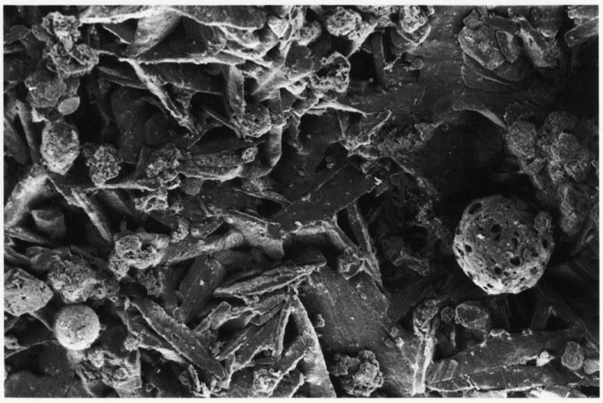
There are usually two main kinds of weathering of ancient stained glass windows. The first one, which is localized and limited, consists of small conical depressions (craters). The second one, covering large surface areas, is organized in layers having different compositions and textures: the deeper part of the glass is generally still sound, whereas its surface is formed of a greatly devitrified, leached and fractured layer. However, in some places a third kind of weathering appears in the form of a crust superposed on the devitrified layer if such a film exists. The colour and the chemico-mineralogical composition of this crust are very different from the compositions of the sound glass and the weathered glass. This discontinuous crust is in immediate contact with the atmosphere.

Received November 11, 1996, revised manuscript July 14, 1997.

This kind of deposit on the stained glass windows has been rarely studied [1 and 2] and therefore, is the subject of this work performed within the framework of the Franco-German Program of Research for the Conservation of Historical Monuments. Samples were removed from the surface of ancient stained glass windows (13th century) at Saint-Gatien Cathedral in Tours (Loire Valley).

2. Current knowledge of the weathering of the ancient stained glass windows of Tours Cathedral

The axial unaffected part of these windows is made from a lime potash glass with the composition (in wt%): 51 to 55 SiO_2, 14 to 19 K_2O, 12 to 14 CaO, 6 to 8 MgO, 4 to 5 P_2O_5, 1 to 3 Na_2O, 0.5 to 2 Al_2O_3, 0.5 to 2.5 MnO, $\leq$1 FeO [3 to 5].



10 μm

Figure 1. Scanning electron micrograph of the external side of a crust sampled from the surface of a blue glass (window no. 125) of Saint-Gatien Cathedral, Tours, constituted of gypsum microcrystals and many different microparticles described in the following figures 2 to 6.

The devitrified and leached layer, 100 to 300 μm thick, is very fractured in the parallel and perpendicular directions to the stained glass window surface. Its percentage in silicon, aluminium and iron increases a lot, specially that in silicon (85% SiO_2), to the detriment of other elements such as potassium, sodium, calcium, magnesium, manganese, phosphorus whose percentages decrease considerably [3]. The fractures parallel to the surface of the stained glass window are the centre of strong accumulations of gypsum ($CaSO_4 \cdot 2H_2O$), and calcite ($CaCO_3$) [3 to 6], of traces of syngenite ($K_2Ca(SO_4)_2 \cdot H_2O$) [3, 4 and 7], and even of quartz [4 and 5] or amorphous silica [4]. The fractures perpendicular to the surface of the stained glass window contain a few deposits. The devitrified and leached layer, which is regarded as a gel is characterized by its high percentage of water [3 to 5].

The outermost superficial crust of the stained glass window, subject of the present work, has been briefly described by previous authors as an abundance of gypsum associated with calcite and hydrated calcium oxalates [6 and 7]. According to these authors, water from run-off or condensation, carbon dioxide and sulphur dioxide contained in the atmosphere [3], or even microorganisms [7], play an important role in the formation of this crust. But the results obtained from previous works [8 to 11] allow to suggest that other factors of weathering also occur.

3. Location of samples collection and analytical procedures

The crust samples were removed from the external part of four different medieval stained glass windows [12] situated at the triforium level (about 15 m high), in the high choir windows (nos 103 and 104) and in the nave (nos 125 and 133). These samples are in flake form peeling off spontaneously. They have a dark colour (grey or brown) and are thin (0.1 to 0.2 mm thick). In areas where the glass is not completely obscured, it is possible to see the colours: blue, red or green.

After photon microscopical examination of the samples in the rough, the preparation was carried out by three different methods. In the first method, the samples were stuck directly onto metallic stubs in order to study their surface using an Analytical Scanning Electron Microscope (ASEM), (Jeol JSM 840 A (Japan)), fitted with a TN 5400 EDX system (Tracor (USA)). In the second method, the samples were embedded in a polyester resin and polished in order to study the cross-section. In the third method, the samples were treated with hydrochloric acid (6 mol/l) in order to remove the sulphates and carbonates. By this way, the particles which were not soluble in the acid were concentrated.

Two samples have been specially studied: the white powder filling and the back cap covering a crater on the blue glass from window no. 133. The white powder was studied by ASEM and X-Ray Diffraction (XRD, Miniflex, Rigaku (Japan)). The cap of lenticular shape, 2 mm in diameter and 0.2 mm in maximum thickness, was studied directly by ASEM.

To gain a better understanding of the origin of the particles in the stained glass window crusts, particles present in the atmosphere around the cathedral have been collected. The filtration of this air was carried out through Nuclepore® calibrated membranes of 0.4 μm porosity and under an extraction rate of 1 m^3/h. The air filtration lasted for several days under a wind of variable speeds and directions. There were two episodes of rain where the water was also collected. It was immediately filtered using the same porous membranes. The membranes with the particles were mounted directly on the ASEM stub.

Finally, the content of the grey crusts developing on the surface of the cathedral stone (Turonian sandy chalk, so-called "tuffeau") was analyzed in the same way to make comparisons with the deposits from the glass surface. Before entering in the analytical microscope, all the samples were covered by a thin carbon film under vacuum in order to make them conducting.

4. Results: microparticulate content of crusts from stained glass windows

Analytical microscopy and X-ray studies show that the crusts are composed mainly of gypsum with either monocrystals (figure 1) or alternated epitaxial strips. The cap covering the crater of the blue glass from the window no. 133 has the same composition and morphology. X-ray diffraction on the white powder filling the crater reveals simultaneous presence of gypsum and of traces of calcite. These two mineral species occur by ASEM as small stocky crystals.

The ASEM reveals the presence of microparticles spread continuously throughout the crystals of the crusts, of the cap and of the white powder. There are four kinds of microparticles,

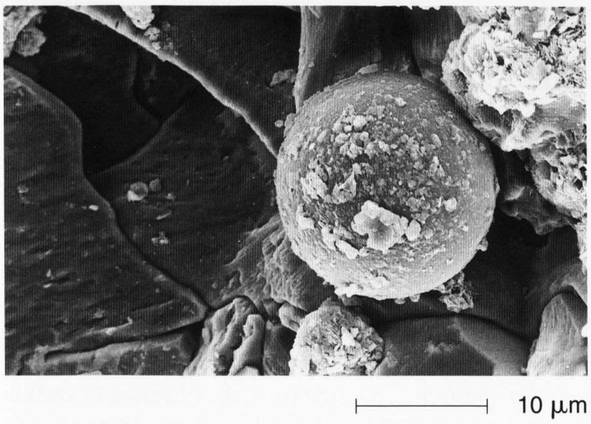


Figure 2. Scanning electron micrograph of a blow-up of a smooth surface microspherule (fly ash) with an aluminosilicate composition (in wt%) of: 50 SiO_2, 34 Al_2O_3, 6 Fe_2O_3, 4 K_2O, 1 Na_2O, 1 MgO, 1 P_2O_5, 1 SO_3, 1 CaO, 1 TiO_2, associated with gypsum crystals inside the grey crust sampled from the surface of a blue glass (window no. 125), Saint-Gatien Cathedral, Tours.

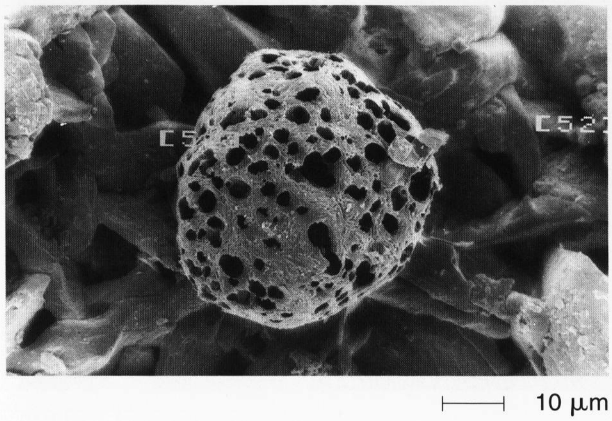


Figure 3. Scanning electron micrograph of a porous microspherule (fly ash), sulphured and carbonaceous in composition (amount of elemental carbon: 60 wt%, composition (in wt%) of the non-carbonaceous part: 5 SiO_2, 2 Al_2O_3, 1 Fe_2O_3, 1 K_2O, 3 Na_2O, 1 MgO, 5 P_2O_5, 75 SO_3, 5 CaO, 2 V_2O_5) inside the gypseous grey crust sampled from the surface of a blue glass (window no. 125), Saint-Gatien Cathedral, Tours.

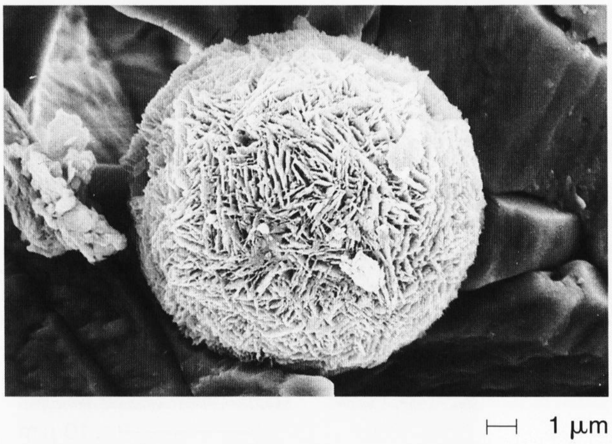


Figure 4. Scanning electron micrograph of a hypersiliceous (opal cristobalite tridymite) lamellar microspherule (composition in wt%: 99 SiO_2, 1 Al_2O_3) originating from the tuffeau stone, associated with gypsum inside the grey crust sampled from the surface of a blue glass (window no. 125), Saint-Gatien Cathedral, Tours.

a) microspherules,

b) siliceous and sulphated aggregates,

c) angular fragments of glass,

d) organic objects.

a) There are four types of microspherules which are different in their morphology and chemistry.

- The first type concerns aluminosilicate microspherules with smooth surface (figure 2). However, there are some which are enriched in other elements e.g. iron, titanium, sulphur, calcium. The diameter of these spherules is in a range of 1 to 35 μm. But the size of the majority is below 10 μm. Some small outgrowths of crystallized gypsum are sometimes observed on the surface. These microspherules are obviously fly ash which are known to be emitted mainly by the combustion of coal, and secondarily by heavy fuel oil combustion in power plants [11 and 13 to 15].
- The microspherules of the second type have a porous aspect (pores separated by walls thicker than their diameter) (figure 3) or a sponge-like aspect (pores separated by walls thinner than their diameter). They have a carbon matrix. The presence of sulphur in greater percentage than in the smooth microspherules can be detected together with silicon, aluminium, calcium and also some transition metals (nickel, vanadium, iron). Some small outgrowths of gypsum can also be observed on them. The diameters of the porous and sponge-like microspherules are in the range of 10 to 120 μm. These microspherules are also in this case fly ash essentially emitted by the combustion of heavy fuel oil and secondarily by coal combustion in power plants [11 and 13 to 15].
- The microspherules of the third type are made up of material with lamellar morphology (figure 4). Their diameter is about 10 μm and they are highly siliceous (83 to 99 wt% SiO_2). The other minor elements (magnesium, aluminium, phosphorus, sulphur, calcium, titanium, nickel) probably come from impurities attached to the surface (gypsum, sheet silicates etc). These microspherules are synsedimentary or diagenetic microconcentrations of opal cristobalite tridymite common in the Turonian sandy chalk of the Loire Valley.
- The fourth type of microspherules have, like the first type, a smooth surface but associated with a high SiO_2 content (60 to 95 wt%) and a low content of Al_2O_3 (up to 3 wt%) that characterize leached glass [3].

b) The siliceous and sulphated aggregates (in wt%: 75 SiO_2, 4 Al_2O_3, 8 SO_3, 4 CaO) having a sponge-like appearance seem to be composed of a mixture of very small

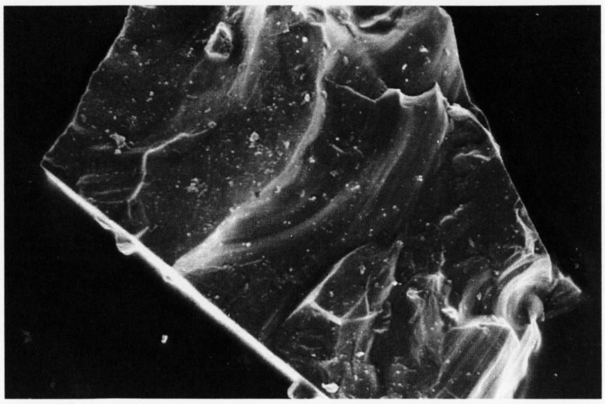


Figure 5. Scanning electron micrograph of an angular and conchoïdal fragment of leached glass (composition in wt%: 87 SiO_2, 1 Al_2O_3, 3 Fe_2O_3, 0 K_2O, 0 Na_2O, 1 MgO, 1 P_2O_5, 3 SO_3, 2 CaO, 2 MnO) present in the powder after acidic attack of the crust sampled from the surface of a green glass (window no. 104), Saint-Gatien Cathedral, Tours.

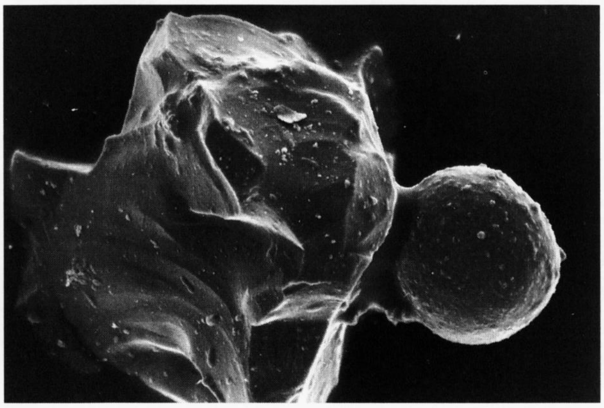


Figure 6. Scanning electron micrograph of an angular and rounded fragment of leached glass (composition in wt%: 86 SiO_2, 2 Al_2O_3, 3 Fe_2O_3, 0 K_2O, 0 Na_2O, 2 MgO, 4 P_2O_5, 3 SO_3, 1 CaO, 1 MnO) present in the powder after acidic attack of the crust sampled from the surface of an opacified glass (window no. 103), Saint-Gatien Cathedral, Tours.

elements with agglomeration of glass, of gypsum, even of opal cristobalite tridymite. The presence of thin sheet silicates and soot particles (in the range of tens of nanometer) cannot be excluded since they are present in the Tours atmosphere.

c) The angular fragments of glass whose sizes can reach several tens of microns have the composition of leached glass (figure 5). They are easily observed in the remains of the acidic treatments as well as the other kinds of micro-objects described previously. Many fragments have a rounded conchoïdal appearance (figure 6). It may indicate that the microspherules of the fourth type having the composition of leached glass could come from the breaking up of the glass during the weathering process.

d) The organic objects consist of spores as previously described by other authors [7 and 16] and of unburnt wood debris.

The chemico-mineralogical composition of the crusts the authors have studied is homogeneous on all the sampled stained glass windows and is not affected by the chemical composition of the underlying glass.

5. Comparison of the microparticles in the air, in the rain and inside the crusts covering the stone of the Cathedral

The microparticles collected from the filtration of the air around the Cathedral have been studied using ASEM [10]. Their morphology, granulometry and chemical composition show that they are similar to microparticles found in the study of the outermost crusts of the stained glass windows: microspherules of the first (smooth), second (porous) and third (lamellar) types and siliceous sulphated aggregates. Moreover, crystals of sodium or magnesium chloride and of calcium sulphate can be observed at the surface of some filters. The study of the air mass trajetories has shown that the air in these cases had passed over the sea.

Finally, there are some soot particles distributed among small aggregates similar to the siliceous and sulphated ones on the stained glass windows. The existence of these soot particles confirms the results of a previous study [8] on particles collected from the air filtration on porous membranes using an Analytical Transmission Electron Microscope (ATEM). In that study, the soot particles have a granulometry of 0.05 μm and have a carbonaceous composition with small amounts of silicon, sulphur and calcium. They are known to be emitted from the combustion of light fuel oil in diesel engines, from domestic heating or even from the biomass combustion (bush, forest or domestic wood fire, papermaking industries etc.).

The microparticles collected from the filtration of rain water, studied using ASEM [10] are similar to the two first kinds of microspherules described in section 4., i.e. the smooth, porous and sponge-like ones. Another sample of rain studied using ATEM [8], contains some soots, some sheet silicates and some smooth and sponge-like microspherules.

The black crusts covering some areas of the tuffeau stone of the cathedral are mainly formed of a cement of gypsum which incorporates the smooth, porous or sponge-like microspherules besides the lamellar microspherules.

The individual chemical compositions of smooth, porous and sponge-like fly ash collected in the air, in the rain and inside the black crusts on tuffeau and on stained glass windows of Tours Cathedral have been plotted on the triangular diagram of the pseudoternary system $SiO_2-Al_2O_3-$other oxides (figures 7a to c) [11 and 15]. In all cases, the two morphological types of fly ash constitute two different chemical groups: the first one is rich in silicon and aluminium (smooth particles), the second one is rich in other oxides (porous and sponge-like particles). It appears clearly that the populations of fly ash are similar in air, in rain, in crusts on stones and in crusts on stained glass windows.

6. Discussion and interpretation

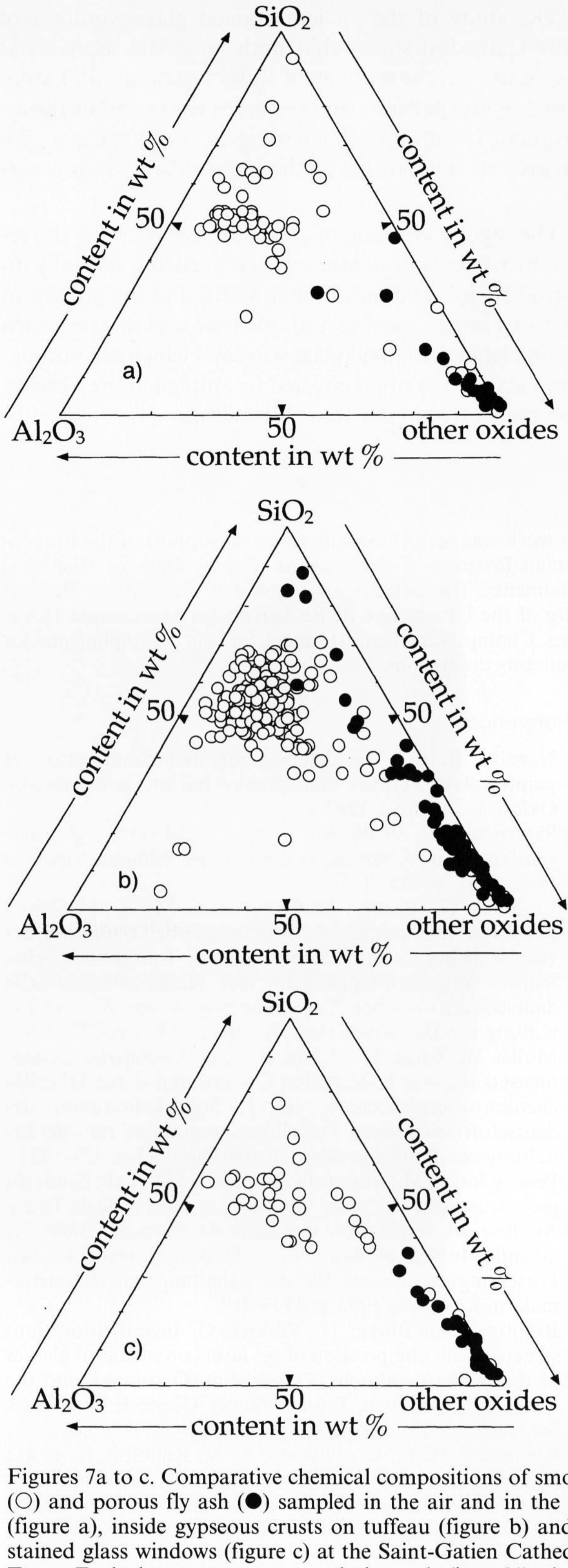
There are two striking results in this work. Firstly, smooth, porous, sponge-like and lamellar microspherules are spread out over the gypsum, and secondly, the gypsum is developed over the whole of the weathered but sheltered surface of the materials (stone, stained glass) of Tours Cathedral exposed to a polluted urban atmosphere.

The smooth, porous and sponge-like microspherules are without any doubt fly ash particles which are dragged by the atmosphere. This work demonstrates their presence in the air and in the rain in Tours. Their association with soot particles confirms the importance of the atmospheric pollution around the cathedral.

The presence of lamellar microspherules of opal cristobalite tridymite originating from the tuffeau both in the crusts covering the stained glass windows and the stone demonstrates the transfer of material from the stone to the glass. This probably happens through the rainwater run-off. However, the presence of these microspherules in the air does not exclude the fact that they may have another indirect trajectory, passing into the atmosphere first before being integrated into the gypsum of the crusts.

The existence of angular fragments of leached glass only in the crusts on the stained glass windows (i.e. they are not found in the crusts on the tuffeau, in the air and in the rain) and their mixture with the fly ash and the lamellar microspherules indicate also that the surface of the weathered stained glass has been modified by the action of the run-off. This feature concerns only the glass. Indeed, the black sulphated crusts grow only on the areas of the stone [14] and metals [17] which are protected from the beating by the rain and from the run-off. The relationship between the leaching of the glass, which requires an important contribution of water, and the existence of the sulphated crusts containing fly ash, which requires the condition of humidity with no run-off, has still to be established: it seems that the porous gypsum crusts maintain a local wetness at the glass surface and thus, do not really protect this surface from leaching, as suggested by other authors [6].

All these facts need to be included in the explanation of the weathering mechanism of the stained glass windows of Saint-Gatien Cathedral and are also complementary to the hypotheses suggested by the most recent authors [3]. According to them, calcium extracted from the glass reacts with carbon dioxide and sulphur dioxide dissolved in the rain to form the carbonates and sulphates present in the glass fractures. Because of the large thickness of the crust, it is thought that calcium contained in the gypsum crust may have another complementary origin. Indeed, the run-off could drag some calcium from the tuffeau. Moreover, the existence of industrial fly ash confirms the atmospheric contribution to the formation of gypsum crust on stained glass windows, stone surfaces [10] or even on bronze surfaces [17]; the role of fly ash is also demonstrated by simulation in an atmospheric chamber [18].



Figures 7a to c. Comparative chemical compositions of smooth (○) and porous fly ash (●) sampled in the air and in the rain (figure a), inside gypseous crusts on tuffeau (figure b) and on stained glass windows (figure c) at the Saint-Gatien Cathedral, Tours. Each dot represents an analysis result (in wt%) plotted in the triangular diagram of the pseudoternary system: $SiO_2-Al_2O_3-$other oxides (Na_2O, MgO, P_2O_5, SO_3, K_2O, CaO, TiO_2, V_2O_5, Fe_2O_3).

The study of the ancient stained glass windows of Tours Cathedral shows that both materials, stones and glasses, used in the monument suffer a general sulphation caused by the particles and the gases contained in the atmosphere. It is also the first description of fly ash in a gypsum grey crust deposited on the stained glass window surface.

The regular cleaning of glass surfaces prevents the remaining of deposits of atmospheric particles, specially industrial fly ash and automobile soots, and the growth of sulphated crusts, as observed on stone and metals which are not cleaned. Stained glass windows which are not regulary cleaned are often covered by sulphated grey crusts, as demonstrated in the Tours Cathedral.

*

This work was performed with financial support of the Franco-German Program of Research for Conservation of Historical Monuments. The authors are grateful to Jean-Marie Bettembourg of the Laboratoire de Recherche des Monuments Historiques, Champs-sur-Marne (France), for help in sampling and for stimulating discussions.

7. References

[1] Newton, R. G.: The deterioration and conservation of painted glass: a critical bibliography. 2nd ed. Oxford (et al.): Oxford Univ. Press, 1982.

[2] Santopadre, P.; Verità, M.: Il degrado del vetro e gli interventi di restauro. Vetrate, arte, e restauro. Milano: Amilcare Pizzi, 1991. p. 105–121.

[3] Libourel, G.; Barbey, P.; Chaussidon, M. et al.: Caractérisation microstructurale et chimique de l'altération des vitraux de la cathédrale Saint-Gatien de Tours et de l'église Sainte-Catherine d'Oppenheim. In: 1. Statuskolloquium des deutsch-französischen Forschungsprogramms für die Erhaltung von Baudenkmälern, Karlsruhe 1993. p. 227–236.

[4] Müller, W.; Torge, M.; Adam, K. et al.: Chemische Zusammensetzung von historischen Gläsern und deren Oberflächenkorrosionsschichten. In: 1. Statuskolloquium des deutsch-französischen Forschungsprogramms für die Erhaltung von Baudenkmälern, Karlsruhe 1993. p. 221–225.

[5] Perez y Jorba, M.; Mazerolles, L.; Michel D. et al.: Etude du processus d'altération des vitraux de la cathédrale de Tours. Analyse des verres. Rôle des éléments mineurs. Etude des grisailles. In: 1. Statuskolloquium des deutsch-französischen Forschungsprogramms für die Erhaltung von Baudenkmälern, Karlsruhe 1993. p. 213–219.

[6] Bräutigam, U.; Bürger, H.; Völksch, G.: Investigations into structure and composition of gel layers on medieval glasses of the Katharinenkirche, Oppenheim (Germany), and the Cathedral St. Gatien, Tours (France). Glastech. Ber. Glass Sci. Technol. **68** (1995) no. 1, p. 29–33.

[7] Krumbein, W. E.; Gorbushina, A. A.; Rudolph, K. et al.: Untersuchungen zur Frage der Korrosion und biogenen Krustenbildung an spätmittelalterlichen Kirchenfenstern der Kathedrale von Tours und der Kirche St. Katharina in Oppenheim unter dem Einfluß von organischer und anorganischer Eutrophierung der Atmosphäre. In: 1. Statuskolloquium des deutsch-französischen Forschungsprogramms für die Erhaltung von Baudenkmälern, Karlsruhe 1993. p. 269–275.

[8] Pertuisot, M. H.: Caractérisation des particules minérales insolubles dans des pluies à la Cathédrale de Tours par microscopie électronique analytique. Mém. Diplôme d'Etudes Approfondies de Chimie de la Pollution Atmosphérique et Physique de l'Environnement. Univ. Paris XII-Val de Marne 1993. (Unpubl.)

[9] Grégoire, M.: La surface des vitraux de la cathédrale Saint-Gatien de Tours: caractérisation et altération atmosphérique. Mém. Diplôme d'Etudes Approfondies de Physicochimie des Surfaces et Interfaces. Univ. Paris XII-Val de Marne 1994. (Unpubl.)

[10] Derbez, M.; Lefèvre, R. A.: Le contenu microparticulaire des croûtes gypseuses de la Cathédrale Saint-Gatien de Tours. Comparaison avec l'air et la pluie. In: 8th International Congress on Deterioration Conservation of Stone, Berlin 1996. p. 359–370.

[11] Lefèvre, R. A.; Derbez, M.; Grégoire, M. et al.: La sulfatation de la pierre et du verre dans l'environement: la cathédrale de Tours. In: 2. Statuskolloquium des deutsch-französischen Forschungsprogramms für die Erhaltung von Baudenkmälern, Bonn 1996. p. 345–355.

[12] Lautier, C.; Frachon-Gielarek, N.; Mahnes-Deremble, C. et al.: Les vitraux du haut-choeur de la cathédrale de Tours: histoire des restaurations, étude iconographique et technique, critique d'authenticité, état sanitaire. In: 1. Statuskolloquium des deutsch-französischen Forschungsprogramms für die Erhaltung von Baudenkmälern, Karlsruhe 1993. p. 205–210.

[13] Fischer, G. L.; Prentice, B. A.; Silberman, D. et al.: Physical and morphological studies of size-classified coal fly-ash. Environ. Sci. Technol. **12** (1978) no. 4, p. 447–451.

[14] Camuffo, D.; Del Monte, M.; Sabbioni, C.: Origin and growth mechanisms of the sulfated crusts on urban limestone. Water Air Pollut. **19** (1983) p. 351–359.

[15] Ramsden, A. R.; Shibaoka, M.: Characterization and analysis of individual fly-ash particles from coal-fired stations by a combination of optical microscopy, electron microscopy and quantitative electron microprobe analysis. Atmos. Environ. **16** (1982) no. 9, p. 2191–2206.

[16] Krawczik-Bärsch, E.; Krumbein, W. E.; Blaschke, R.: Mikroskopische und chemische Untersuchungen zur Korrosion von mittelalterlichen Glasmalereien der Katharinenkirche von Oppenheim und der Kathedrale Saint-Gatien in Tours. In: 1. Statuskolloquium des deutsch-französischen Forschungsprogramms für die Erhaltung von Baudenkmälern, Karlsruhe 1993. p. 259–262.

[17] Ausset, P.; Lefèvre. R.; Philippon, J.: Interactions entre les microsphérules silicatées atmosphériques et les surfaces des monuments en calcaire et en bronze. J. Eur. Group. Phys., Chem., Math., Biol. Appl. Archaeol. **33** (1991) no. II-3, p. 135–147.

[18] Ausset, P.; Crovisier, J. L.; Del Monte, M. et al.: Experimental study of limestone and sandstone sulphation in polluted realistic conditions: the Lausanne Atmospheric Simulation Chamber (LASC). Atmos. Environ. **30** (1996) no. 18, p. 3197–3207.

■ 0398P004

Address of the authors:

R. A. Lefèvre, M. Grégoire, M. Derbez, P. Ausset
LISA Universités Paris 7 et Paris 12
Unité Mixte de Recherche CNRS 7583
Faculté des Sciences
61 Av. du Général de Gaulle
F-94010 Créteil Cédex