

SEM-EDS, EPMA and MRS analysis of neo-crystallisations on weathered glasses

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2010 IOP Conf. Ser.: Mater. Sci. Eng. 7 012009

(<http://iopscience.iop.org/1757-899X/7/1/012009>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 93.58.200.4

The article was downloaded on 12/05/2012 at 07:33

Please note that [terms and conditions apply](#).

SEM-EDS, EPMA and MRS analysis of neo-crystallisations on weathered glasses

R Falcone^{1,5}, M Nardone², A Sodo³, G Sommariva¹, M Vallotto¹ and M Verità⁴

¹ Stazione Sperimentale del Vetro, Via Briati 10, IT- 30141 Murano-Venice, Italy

² Università dell'Aquila, Dipartimento di Fisica, IT-67100 Coppito-L'Aquila, Italy

³ Università di Roma Tre e ICPAL, Dipartimento di Fisica, IT-00146 Rome, Italy

⁴ Università IUAV di venezia, Laboratorio Analisi Materiali Antichi, Palazzo Badoer, San Polo 2468/B, IT-30125 Venice, Italy

E-mail: rfalcone@spevetro.it

Abstract. When a glass is exposed to the atmosphere the combined action of water and environmental elements leads to the weathering of the glass surface. Both the chemical composition of the glass and the environmental parameters influence the mechanism of glass weathering mainly consisting in the formation of a layer of hydrated leached glass and salt deposits. The study of these phenomena is very important for both industrial and cultural heritage applications. In order to study the weathering mechanism of glasses exposed outdoor the chemical composition of the glass and the chemical and mineralogical nature of the reaction products should be determined. X-ray micro-analytical techniques such as scanning electron microscopy and X-ray microanalysis (SEM-EDS) and electron probe microanalysis (WD-EPMA) are traditionally employed in this type of investigation. Nevertheless particular compounds are hardly detected with this technique (for ex. nitrates) and no direct information can be obtained on the mineralogical features of the reaction products. Moreover, X-ray diffractometry (XRD) cannot be successfully used because of the very low amounts of deposited material. This work reports the results of a combined complementary X-ray fluorescence spectrometry (WD-XRF), SEM-EDS, WD-EPMA and μ -Raman spectroscopy (MRS) investigation on the surfaces of an industrial float glass and a glass reproducing the low-durable glass of ancient stained windows exposed sheltered outdoor for 6 months. The investigation enabled the identification and characterisation of different reaction products (soluble salts) confirming the need of this analytical approach for the study of the glass weathering process.

1. Introduction

Glass is ordinarily considered to be a durable material. Nevertheless when exposed to the outdoor environment the combined action of water and other atmospheric elements (gases, particulate, etc.) leads to the weathering of the glass surface. The chemical durability (i.e., the resistance of glass against the attack by aqueous solutions) of different types of glass has been extensively studied in the last decades, mainly under laboratory conditions [1-3]. The results of these investigations agree upon the conclusion that two mechanisms of attack occur, depending on the solution pH. Leaching is the dominant reaction at $\text{pH} < 9$ and consists of ion exchange between the alkali and alkaline earths

⁵ To whom any correspondence should be addressed.

network modifying ions of the glass (namely Na^+ , K^+ , Ca^{2+} and Mg^{2+}) and H^+ (and H_3O^+) ions of the water, leading to the formation of a hydrated glass layer depleted in alkali and alkaline earths (leached hydrated glass layer). Corrosion (or network dissolution) is the dominant reaction at $\text{pH} > 9$ and is due to the attack of the hydroxyl anions (OH^-) against the Si-O bonds of the network. This reaction leads to the dissolution of all the glass components (congruent dissolution) and to the formation of porous and brittle silica gel deposits. Therefore, glass chemical deterioration can be described either as a leaching or a corrosion process (or as a combination of both) depending on the pH of the solution and on several other parameters such as exposure time, composition of the glass and of the solution and temperature.

The study of the behaviour of flat glass exposed outdoor is very important for both industrial and cultural heritage applications. In the case of modern soda-lime-silica float glass, weathering is responsible for the hazing and for the decay of optical properties (transparency, reflectance, etc.) of architectural glazing. Moreover the deterioration of ancient stained windows, generally consisting of silica-potash-lime glass, is a critical problem for the conservation of these important cultural heritage items. The “simple” mechanism of attack by aqueous solutions cannot be used to describe the weathering of glasses exposed to the atmosphere. In the “real” exposure conditions a more complex system of several interlinked phases has to be considered: glass, modified glass surface, deposits layer and atmospheric components. Recent investigation on float glass exposed outdoor have evidenced that, in a polluted urban environment, soiling (i.e., a combination of anthropogenic particles deposition and soluble salt neo-crystallisation) is the most important factor for the loss of optical quality whereas only a limited superficial de-alkalisation (leaching of Na from few tens of nm) was also detected [4, 5]. Instead, for ancient low-durable stained glass windows leaching is a very active phenomenon that, associated to glass corrosion, leads to the formation of thick weathered glass layers crossed by fractures where deposits of different origin give rise to the formation of crusts [6, 7]. In the early stage of weathering soluble salts neo-crystallisations are the most abundant deposits responsible for soiling of glasses exposed outdoor, in particular when glass is exposed in sheltered conditions. Soluble salts can either form directly in air and deposit on the glass surface transported by environmental droplets or form by the evaporation of fog droplets and condensed water on the glass surface; in the latter mechanism the reaction of cations leached from the glass and atmospheric gases has to be considered [5, 8]. Therefore the chemical and physical characterisation of neo-crystallisation is fundamental for the study and understanding of glass weathering mechanisms.

This work reports the results of a multi-analytical chemical and physical characterisation of neo-crystallisations deposited on a modern soda-lime-silica float glass and on a silica-potash-lime glass simulating a typical ancient stained window composition. The glass samples were exposed outdoor in sheltered conditions for 6 months in a polluted urban environment (Paris). The sheltered condition was chosen in order to eliminate the disturbing action of rainwater. After exposure samples were analysed by scanning electron microscopy equipped with an energy-dispersive X-ray spectrometry systems (SEM-EDS) and electron probe microanalysis (WD-EPMA). μ -Raman spectroscopy (MRS) was also applied in order to get complementary information on the deposits, particularly on those compounds that are hardly detected by X-ray micro-analytical techniques.

2. Experimental and analytical techniques

2.1. Glass samples

An industrial soda-lime-silica float glass (sample FLA) and a potash-lime-silica glass (KCA) were exposed outdoor in sheltered condition in a polluted urban environment for 6 months. The potash-lime glass was prepared in laboratory by melting a batch of high purity raw materials in an electric furnace at $1450\text{ }^\circ\text{C}$ for 2 hours in a platinum crucible. After melting the glass was cast on a metallic plate and annealed at $550\text{ }^\circ\text{C}$. The quantitative chemical compositions of the glass samples determined by WD-XRF are reported in table 1. Glass pieces of $10 \times 10\text{ mm}$ were cut and the exposed surfaces were previously polished using cerium oxide powder as abrasive.

Table 1. Chemical compositions of the glass samples (analysis by WD-XRF).

wt%	SiO ₂	Al ₂ O ₃	Na ₂ O	K ₂ O	CaO	MgO	Fe ₂ O ₃	SO ₃	P ₂ O ₅
FLA	71.7	0.6	13.5	0.1	9.5	4.2	0.1	0.3	
KCA	50.0	2.0		25.0	18.0	3.0		0.1	2.0

2.2. SEM/EDS

A Jeol JSM-5900 scanning electron microscope was used to study the morphology of the phases deposited on the exposed surface and to determine their chemical compositions. Since glasses are poor conductors of electrons samples were vacuum coated with carbon to prevent localized charging of the specimen and the consequent distortion of the electron beam.

Observations of the glass surfaces were performed both in secondary electron (SE) and backscattered electron (BSE) modes. The analytical conditions varied as follows: magnification 100x - 5000x; energy of the electron beam 5 - 15 kV; beam current 0.5 - 2.0 nA.

The semi-quantitative chemical compositions of the deposits were analysed using an energy-dispersive X-ray microanalyser (EDS) (Oxford Instruments Link ISIS 300) associated to the SEM. The analyses were performed at 7 - 10 kV to reduce the penetration of the electron beam and the counting time was 100 s.

2.3. WD-EPMA

A Cameca SX-50 X-ray electron microprobe equipped with three wavelength-dispersive X-ray spectrometers and TAP, PET, LIF crystals and a multi-layer crystal (Cameca PC2) for the analysis of light elements. EPMA was used mainly to analyse light elements such as C and N. Particular attention was devoted to the analysis of C because of the carbon coating previously applied to the samples. The presence of C in the deposits was therefore detected by comparing the net count rates (cps) of the C-K α line measured on the deposit particles to those measured on a sample of the same glass not exposed outdoor (reference), on which only the C of the coating was present. For this reason the exposed samples and the reference glass were carbon coated simultaneously. Quantitative analyses were performed using the Cameca QUANTITOOL analytical programme, calibrated with reference standard, applying a PAP matrix correction.

2.4. MRS

A Labram system by Dilor-Jobin Yvon equipped with three different laser sources at 632.8 nm (He-Ne), 514.5 nm (Ar⁺ ion) and 785.5 nm (diode laser) was used. After several preliminary tests, measurements were carried out using the He-Ne source to minimize fluorescence. The focussing and collecting optics of the system consists in a microscope in confocal configuration. Long distance (20x and 50x) objectives were used to illuminate and collect signals. The detector is a cooled 1024 x 256 pixel CCD. The dimensions of the pixels (about 24 μ m) determine the ultimate resolution of the instrument, which turns out to be of the order of 1 μ m⁻¹; the analyzed spot area was 2 - 3 μ m wide. Raman measurements were performed directly on the glass surface and on deposits without any preliminary sample preparation. On each sample several different points have been investigated covering the whole sample surface.

3. Results

After 6 months exposure both FLA and KCA glass samples displayed the presence of abundant deposits producing a diffused hazing and a general decay of the optical properties. Most of these deposits consist of neo-crystallisations whose shape and composition varied significantly; in some

cases, characteristic crystal habits were observed. SEM observation and X-ray micro-analytical investigations were focussed on the characterisation of the neo-crystallisations in order to define their chemical compositions and morphological features.

3.1. SEM/EDS and EPMA analysis

On the FLA sample abundant Na-sulphates/carbonates (figure 1) and lower amounts of Ca-sulphates were observed (figure 2). The formers are present in two different types of crystallisations: diffused small round-shaped dried drops ($< 2 \mu\text{m}$, figure 1a) and rounded aggregates of dendritic crystals (20 - 30 μm diameter, figure 1b). Ca-sulphates also feature different crystal habit: needle-like crystals (20 - 30 μm in length, figure 2a) and squat prisms and hexagonal tablets (20 - 30 μm large, figure 2b). NaCl crystals were not detected.

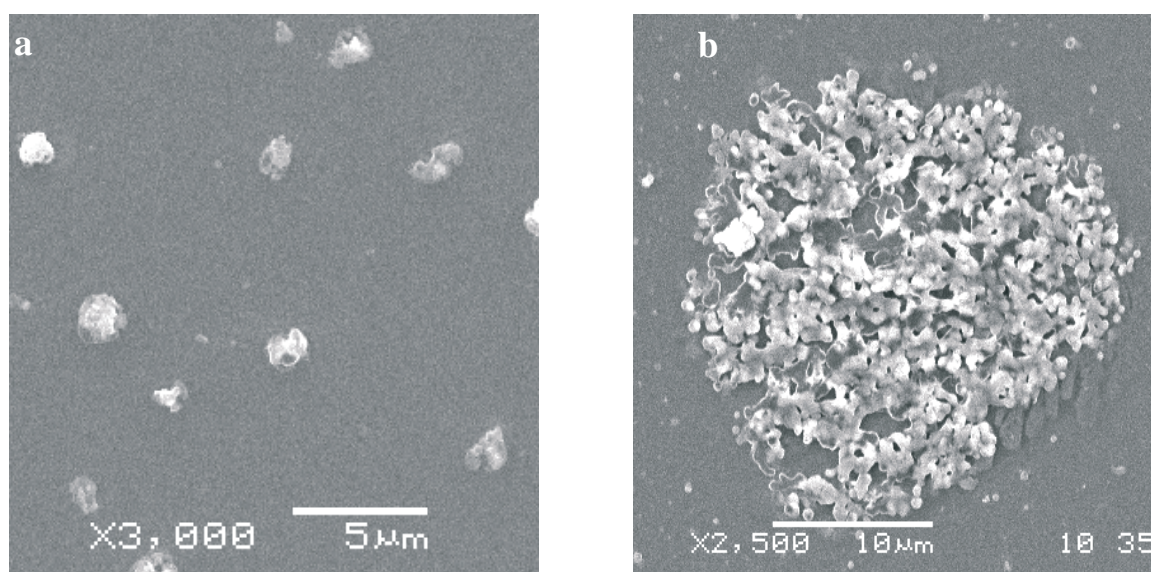


Figure 1. SEM micrographs of neo-crystallisations on sample FLA. Na-rich sulphates/carbonates: diffused small round-shaped dried drops (a) and rounded aggregates of dendritic crystals (b).

On the KCA sample more abundant neo-crystallisations were detected. In particular, spindle-shaped crystals of K-Ca sulphates were detected (10 - 20 μm , figure 3a) and frequent aggregates of flattened and/or prismatic crystals of Ca-sulphates (figure 3b) were identified. Furthermore, rare cubic K-chloride crystals were also found. These results are in good agreement with the results of similar investigation reported in literature [8, 9].

3.2. MRS analysis

Due to a broad fluorescence band generated by the sample, the collection of Raman spectra was quite difficult. However, the diffused presence of nitrate salts was detected on the spectra collected on both samples. In particular FLA spectra display a peak centred at 1070 cm^{-1} that is characteristic of sodium nitrate (NaNO_3) as reported in figure 4 where it is compared to the MRS spectrum of a pure NaNO_3 from a standard database [9]. The good matching is evident although the less intense band centred at 725 cm^{-1} is not so evident in the collected spectrum due to the low signal/noise ratio. The spectrum collected from the KCA sample show peaks at 717 and 1052 cm^{-1} , that can be unambiguously

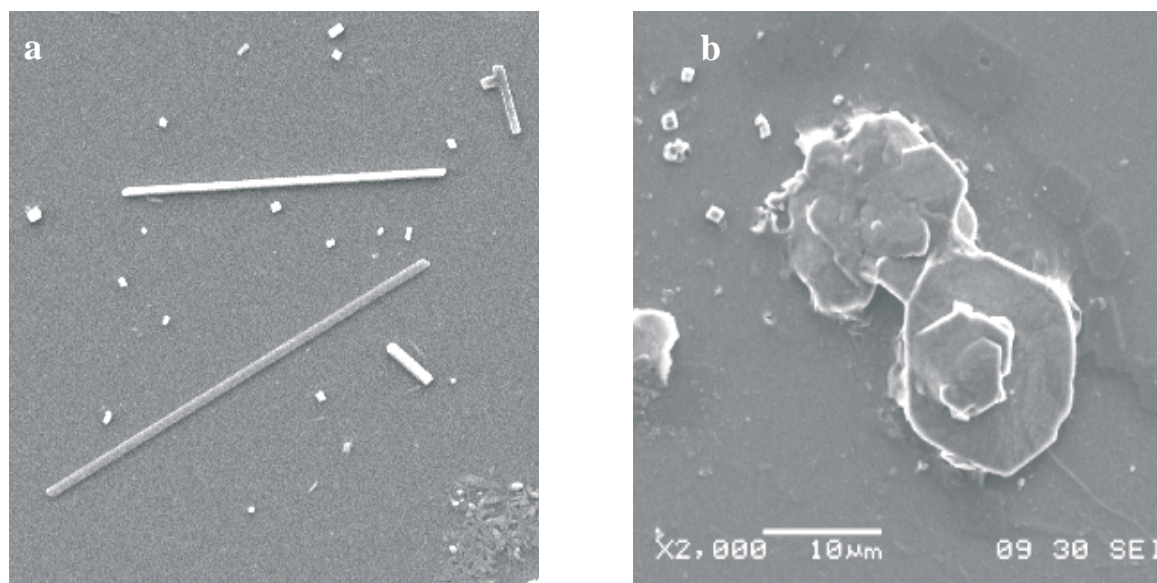


Figure 2. SEM micrographs of neo-crystallisations on sample FLA. Ca-sulphates: needle-like crystals (a) and squat prisms and hexagonal tablets (b).

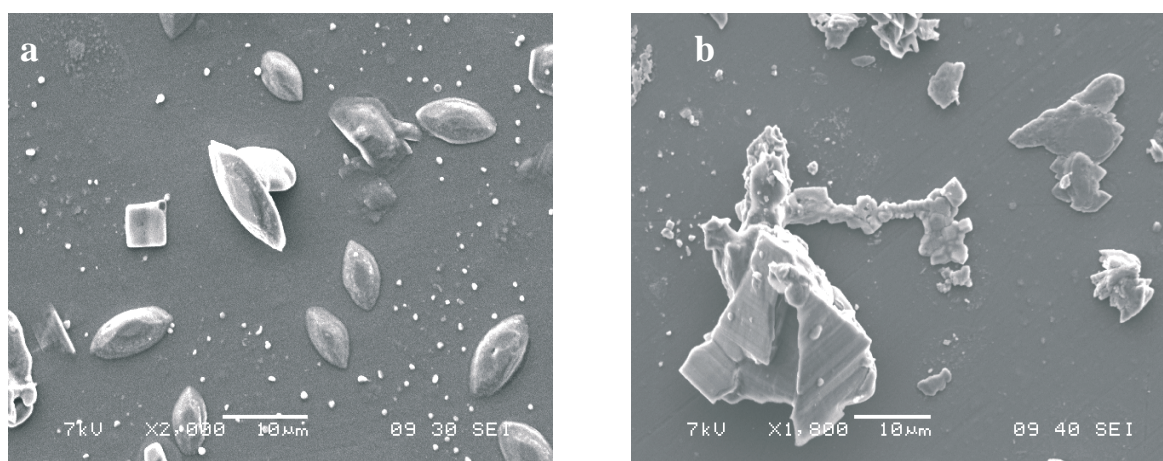


Figure 3. SEM micrographs of neo-crystallisations on sample KCA. Spindle-shaped crystals of K-Ca sulphates and cubic K-chloride crystals (a) and aggregates of flattened and prismatic crystals of Ca-sulphates (b).

ascribed to the presence of a potassium nitrate (KNO_3) as reported in figure 5 compared to a standard spectrum of KNO_3 [10]. No other compounds were detected by MRS.

4. Discussion

Soiling of glass exposed outdoor is a combination of particle deposition (mainly of anthropogenic origin, particulate organic matter and elemental carbon) and soluble salt neo-crystallisations on the glass surface. Soluble salts are the most abundant particles and can crystallize in air and deposit on the glass transported by environmental droplets. Nevertheless, the most probable mechanism is neo-crystallisation by reaction of aqueous solutions condensed on the glass surface with glass components. Depending on parameters such as relative humidity (RH) and temperature, atmospheric

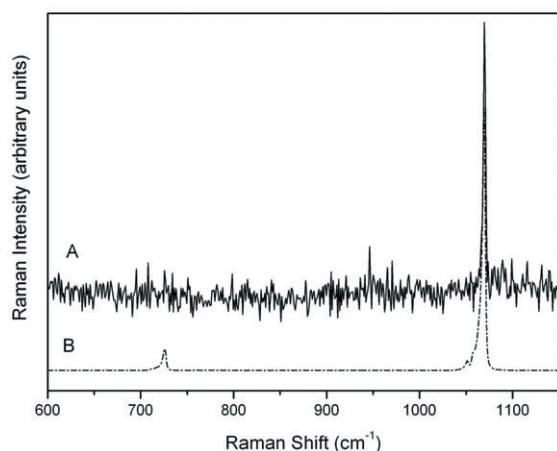


Figure 4. Raman spectra of the deposit on sample FLA (A) and standard NaNO_3 (B). For a better visualisation, spectra are arbitrary stacked.

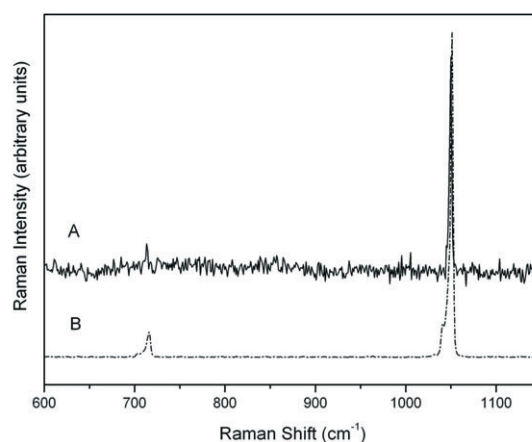


Figure 5. Raman spectra of deposit on sample KCA (A) and standard KNO_3 (B). For a better visualisation, spectra are arbitrary stacked.

humidity can condense on the glass surface forming a thin layer of adsorbed water. Due to its acidity the adsorbed water is able to extract alkali and alkaline earths ions from the glass (leaching) that can react with the atmospheric gases (CO_2 , SO_x , NO_x , HCl) forming the respective salts (carbonates, sulphates, nitrates, chlorides). These salts are crystallized or solubilized, depending on their concentration and solubility. When RH decreases water evaporates from the surface and salt deposits crystallize on the glass surface.

X-ray micro-analytical techniques (SEM/EDS and EPMA) and MRS spectroscopy apparently provided contradictory results. The formers enabled to detect the present of alkali and alkaline earths sulphates, carbonates and chlorides. Nevertheless, nitrates were not found, although N was specifically searched by EPMA-WDS analysis. On the contrary, the diffused presence of nitrates was clearly detected by MRS, but no sulphates, carbonates and chlorides were found with this technique. This contradictory result can be explained by the high solubility of nitrates which do not allow the development of well crystallized particles and probably leads to the formation of a diffused and very thin film of nitrates on the glass surface, not detectable by EPMA-WDS.

In previous works, chemical analysis carried out by ion chromatography (IC) on the salts deposited on the surface of a float sample revealed that sulphates followed by nitrates were the most abundant anionic species, while Ca^{2+} followed by Na^+ are by far the most abundant cations. Traces of chlorides were also detected by IC but no carbonates were found [9, 11].

These results demonstrate that none of the discussed techniques (SEM/EDS, EPMA, MRS and IC) enables the complete characterisation of the neo-crystallisations which develop on the surface of glasses exposed outdoor and, therefore, a multi-analytical approach involving different surface techniques is required.

The results obtained confirm the proposed mechanism. In particular the presence of Na-Ca compounds on the FLA (soda-lime) sample and K-Ca compounds on the KCA (potash-lime) sample indicate that in the early stages of the weathering process atmospheric humidity condensed on the glass surface extracts alkali and alkaline earths ions from the surface (leaching process, more evident in the potash-lime glasses). Then these cations react with atmospheric gases (CO_2 , SO_x , NO_x , HCl) to form the respective salt deposits (carbonates, sulphates, nitrates, chlorides).

5. Conclusions

This work demonstrated that a multi-analytical approach is required to reach complete identification and characterisation of the salts deposited (neo-crystallisations) on glass exposed outdoors in a polluted urban environment. X-ray micro-analytical techniques (SEM/EDS and EPMA) and μ -Raman spectroscopy (MRS) proved to be complementary techniques. Sulphates, carbonates and chlorides were detected by X-ray micro-analytical techniques, while MRS enabled to detect the presence of nitrates on both types of glass, which also confirmed the results obtained by IC analysis in previous works.

This study confirms that in the early stages of the weathering process soluble salts (carbonates, sulphates, nitrates, chlorides) are formed as the reaction products of cations (Na^+ , K^+ , Ca^{2+}) extracted by water (atmospheric humidity) condensed on the glass surface with atmospheric gases (CO_2 , SO_x , NO_x , HCl).

References

- [1] Scholze H 1991 *Glass, nature, structure and properties* (New York: Springer Verlag)
- [2] Barton J and Guillemet C 2005 *Le verre – Science et technologie* (Paris: EDP Sciences)
- [3] Varshneya A K 2006 *Fundamentals of inorganic glasses* (Sheffield: Society of Glass Technology)
- [4] Lombardo T, Chabas A, Lefèvre R A, Verità M and Geotti-Bianchini F 2005 Weathering of float glass exposed outdoors in an urban area. *Glass Technol.* **46** 271
- [5] Chabas A and Lefèvre R A 2002 Soiling of soda-lime-silica float glass in the polluted atmosphere of Paris. Proc XIX Int Cong Glass (Edinburgh, July 1-6 2001) *Glass Technol.* **43C** 79
- [6] Verità M 2006 *Modern and ancient glass: nature, composition and deterioration mechanisms. Scienze e materiali del patrimonio culturale 8, The materials of cultural heritage in their environment* (Lefèvre R A, ed.) (Bari: Edipuglia) 119
- [7] Roemich H 1999 Historic glass and its interaction with the environment. *The conservation of glass and ceramics* (London: James & James) 5
- [8] Munier I, Lefèvre R A, Geotti-Bianchini F and Verità M 2002 Influence of polluted urban atmosphere on the weathering of low durability glasses. *Glass Technol.* **43** 225
- [9] Verità M, Geotti-Bianchini F, Falcone R, Zangiacomì G, Chabas A, Lombardo T, Caveau S, Ausset C, Cachier H, Pertuisot M H and Oikonomou K 2007 Analysis of self-cleaning and float glass: a comparative study of pollution on the glass surfaces under real conditions. *Glass Sci. Technol.* **48** 183
- [10] Ruff R - Database of Raman spectroscopy, X-rays diffraction and chemistry of minerals. <http://rruff.info>
- [11] Chabas A, Lombardo T, Cachier H, Pertuisot M H, Oikonomou K, Falcone R, Verità M and Geotti-Bianchini F 2008 Behaviour of self-cleaning glass in urban atmosphere. *Building and Environment* **43** 2124