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Application of atomic force microscopy to the study of glass decay

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Abstract

Conventional methods such as scanning electron microscopy with energy dispersive X-ray spectrometry are commonly used to characterize corroded glasses. However, their use is often restricted when glass pieces come from historical artworks and may not be damaged. Atomic force microscopy can be an alternative method for characterizing such glasses since it is an essentially non-destructive technique which allows their topographic analysis with good vertical and lateral resolutions. In addition, samples do not require any previous manipulation. The application of atomic force microscopy to study glass decay is reported in this paper. The main goals of the research were to study the corroded texture of both historical glass pieces and model glasses weathered in the laboratory, and to determine and compare the chemical corrosion mechanisms which occurred in both cases. The resulting data suggest that atomic force microscopy can be a useful technique for characterizing decay mechanisms in historical glasses.

Keywords: Glass; Decay; Microscopy; Weathering; Chemical resistance

1. Introduction

Corroded glasses usually present a delicate surface with abundant craters and pits frequently filled with products of an ion-exchange which form crusts of variable thickness and density [1]. Such glasses are commonly analyzed by scanning electron microscopy (SEM) with energy dispersive X-ray spectrometry (EDX) [2]. However, the study of corroded glasses through these techniques is often a difficult task, especially when samples come from historical stained glass windows or some other kind glass artwork from the cultural heritage, since they have to be preserved and cannot be destroyed or damaged. In addition, grisailles and other decorative superficial

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glazes and paints also pose serious difficulties since they are formed by glassy materials as well and, consequently, with the same microstructural features as those of the underlaying glass artwork. In light of this situation, it is clear that new characterization methods are needed [3,4].

Atomic force microscopy (AFM) may be a suitable alternative method for characterizing historical corroded glasses. AFM is an essentially non-destructive technique which allows the performance of topographic and textural analyses with good resolution (0.01 nm vertical and a few nanometers lateral) [5–7]. Besides, it presents the advantage that the samples to be observed do not require previous manipulation and do not have to be submitted to vacuum, thereby avoiding any kind of alteration on either the delicate surface or the corrosion crusts present on historical glasses. Although there are AFM instruments that can analyze the surfaces of large samples most instruments do in fact require relatively small samples, similar to those ones that would fit in an SEM specimen stage.

Medieval stained glass windows were commonly produced from potash–lime–silica glasses [8]. As is known [9], these glasses are very sensitive to weathering conditions, especially against humidity and atmospheric pollutants. Acid pollutants such as SO_2 and NO_x combined with a high relative humidity produce the phenomenon of acid rain. Under such aggressive environment, Medieval stained glasses experience a strong chemical attack which causes the leaching of alkaline ions, the formation of a superficial silica gel layer, the precipitation of insoluble salts as a result of the corrosion mechanism and, finally, the formation of interconnected craters and pits [10]. Under these environmental conditions, historical glasses lose mass, transparency, original colourings and brightness. In turn, grisailles and other glassy paints can be detached and then the aesthetic and iconographic value of the stained glass windows decreases dramatically.

Prior to the start of any kind of restoration or preservation work, knowledge of either the current state of conservation or the degree of corrosion of the glass pieces which form part of the historical stained glass windows is a key factor. Cleaning and repairing tasks depend on the kind of attack experienced by the glass and these attacks need to be investigated on the glass surface. In this regard, AFM arises as a non-conventional observation technique for delicate materials and can play an important role in the characterization of corroded surfaces from historical glasses, as well as in the study of glasses subjected to accelerated weathering processes. Comparison of the topography and morphology of artificially weathered model glasses and original historical pieces may enable the assignment and understanding of general chemical decay phenomena in glasses. Thus, the goals of the present work were, on the one hand, to study the corroded texture of both historical glass pieces and model glasses intentionally weathered in the laboratory by means of AFM. On the other hand, it was also aimed at assigning the chemical corrosion mechanisms experienced by the historical glasses from those produced in model glasses under controlled laboratory conditions.

2. Experimental

Corroded glass pieces from a historical stained glass window panel of the Cathedral of León (Spain, 13th century A.D.) and a model glass with similar composition prepared in the laboratory were studied. The model glass was melted in an electric furnace at about 1400 °C for 2.5 h, starting from Na_2CO_3, K_2CO_3, $CaCO_3$, $MgCO_3$, $AlPO_4$ and $MnCO_3$ pure chemical reagents. Washed quartz sand (99.5 wt.% of SiO_2) was the source for silica. After casting in a brass mould and hand pressing, plates of $1.5 \times 2.5 \times 0.4$ cm in size were obtained. These samples were annealed at 650 °C to avoid mechanical stresses and cracking.

Several samples of the model glass were artificially weathered following two different patterns:

a) under a humid SO_2 atmosphere in a Kesternich chamber for 25 time cycles. In each cycle 50 ppm of SO_2 were added. Each time cycle lasted 8 h and was carried out at 40 °C under a 100% relative humidity. After each cycle the chamber was opened and the SO_2 atmosphere was slowly exhausted during 16 h up to reach room conditions.
b) under an alkaline attack in liquid medium, undertaken by dipping the samples into a 2 M NaOH solution for 6 h at room temperature. After that, the glass samples were withdrawn from the solutions,

softly washed with distilled water and dried at room temperature.

All the samples were observed by optical microscopy (OM), scanning electron microscopy (SEM) and AFM. OM was carried out by means of an Olympus DP-11 conventional reflected light microscope and a Nikon Optiphot2-Pol microscope. SEM observations were undertaken with a Philips XL30 instrument.

AFM images were obtained with a Topometrix Explorer TMX 2000 microscope working in air and in the so-called "non-contact" mode. A stiff Si_3N_4 cantilever (NT-MDT Ultrasharp NSCS12) is oscillated at its resonance frequency (around 139 KHz) very close to (10–100 nm) but with no direct contact with the surface of the sample. Changes in the amplitude of the oscillation caused by the surface topography at every point are compensated by a feeback loop that approaches or retracts the probe until the non-perturbed reference signal is recovered. The compensating feedback signal is directly related to the height of the surface features (topography). The AFM image is constructed by scanning the surface in the X and Y plane by running 300 lines with 300 points each. Surface topography is represented in a 2D picture by a grey colour scale. Bright areas are above dark ones. In every figure, AFM images are plotted with the same Z scale to allow direct comparison. Quantitative data are presented in line profiles. Every profile is taken at the middle of each image (i.e. line 150 of 300). Surface roughness (RMS) is defined as the square mean of the deviation in height at every point from the overall surface height. The size of the pieces of glass observed by AFM in this research was generally no larger than 10–12 mm.

3. Results and discussion

3.1. Historical glass

The most common image of the external corroded surface of the historical glasses studied showed a variable amount and distribution of craters and pits (Fig. 1a) and an alteration layer which covers the

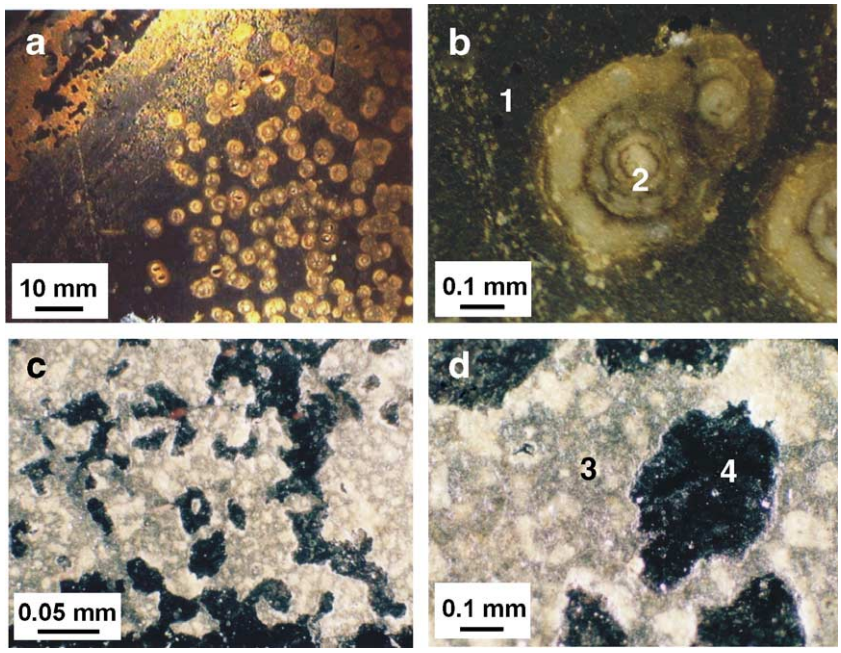

Fig. 1. OM images of a historical glass piece from a stained glass window panel of the Cathedral of León: a) External surface (outdoor the cathedral), general view. b) Detail of crater-shaped pits. c) Internal surface (indoor the cathedral), general view. d) Detail of altered (light) and less altered (dark) areas. Numbers indicate the zones in which AFM topographic images were taken.

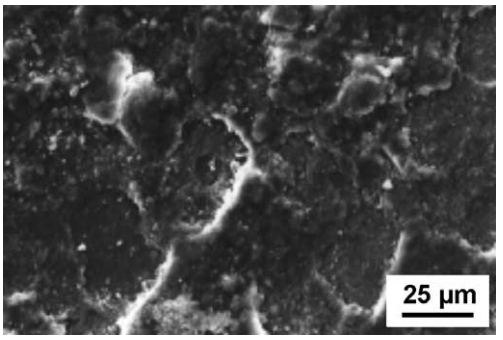

Fig. 2. SEM image of the external surface (outdoor the cathedral) of a glass piece from a stained glass window panel of the Cathedral of León.

majority of the glass surface (Fig. 1b, zone 1). The craters and pits appeared filled with insoluble salts deposits showing a circular morphology with central and border growing zones or *haloes* (Fig. 1b, zone 2). On the contrary, the internal surface presented some general areas of a porous and heterogeneous alteration (Fig. 1c; d, zone 3), together with other areas in which a less alteration has been taken place (Fig. 1d, zone 4). SEM observations on both external and internal surfaces (Fig. 2) determined a textured morphology of a porous and heterogeneous appearance as well.

AFM topographic images of the same historical sample shown in Figs. 1 and 2, are displayed in Fig. 3. These images correspond to the external surface of the sample (located in the outdoor side of the cathedral), which is covered by a thin alteration layer. The AFM image taken on the centre of a pit (Fig. 3b) revealed a rough texture with an overall grain height between 300 and 400 nm and an average RMS roughness of 201 nm (Table 1). This microstructure is probably related to the high crystallinity degree of the

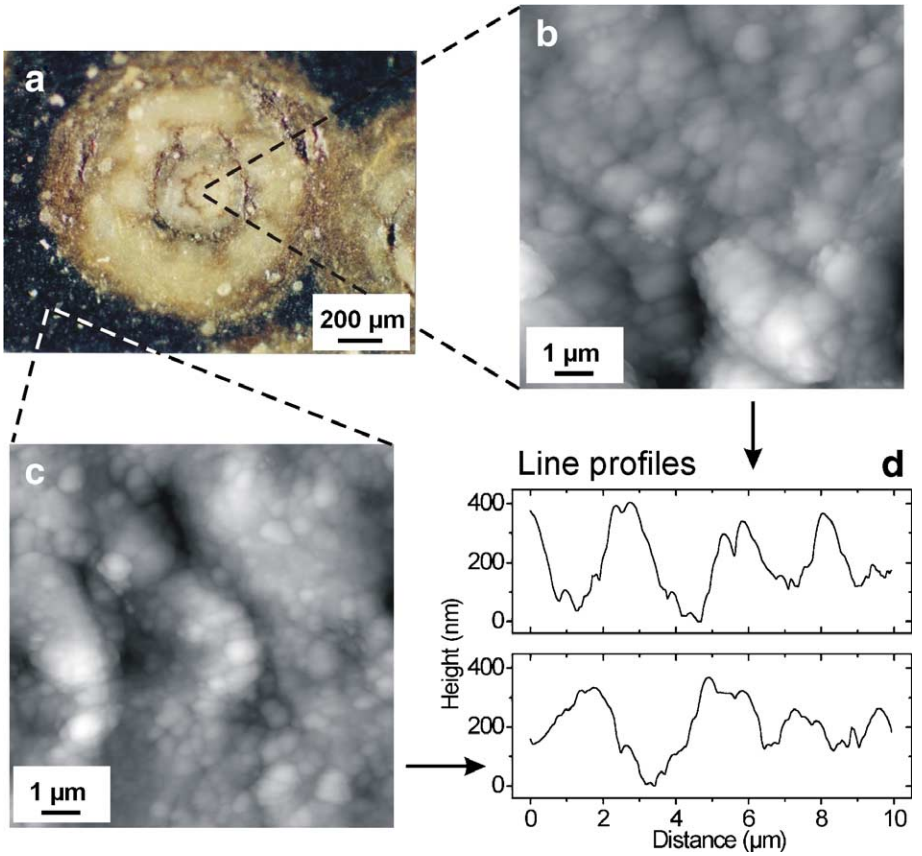

Fig. 3. External surface (outdoor the cathedral) of a historical glass sample: a) OM image of a crater-shaped pit. b) AFM topographic image of a pit center area. c) AFM topographic image of the thin alteration layer. d) AFM line profiles of images b) and c), respectively.

Table 1
Roughness (RMS) measured in the samples studied

Sample	Site for AFM observation	Roughness (nm)
Historical glass	External/outdoor surface (pit center)	201
	External/outdoor surface (thin alteration layer)	87
	Internal/indoor surface (altered area)	102
	Internal/indoor surface (less altered area)	38
Model glass (SO_2 atmosphere, acid conditions)	More attacked area	48
	Less attacked area	3
Model glass (alkaline solution)	General	266

insoluble salts precipitated at the bottom of the craters and pits (gypsum, calcium–potassium sulphate, calcium carbonate, calcium oxalate, etc.) [1,11]. On the other hand, the AFM image taken outside the pits, on the thin alteration layer (Fig. 3c), showed a lower grain height (between 180 and 380 nm) and a lower RMS roughness (87 nm, Table 1).

Fig. 4 displays some AFM topographic images from the internal surface of the historical glass sample (located in the indoor side of the cathedral). The AFM image taken on the more altered area (Fig. 4b) also revealed a rough texture very similar to that observed in the centre of a pit located on the external surface (Fig. 3b). In this case the grain height lies between 200 and 400 nm, whereas the average RMS roughness is cut by almost a half (102 nm, Table 1). The AFM image taken on the less altered area (Fig. 4c) showed, on the contrary, a practically plain topography which can be related to the original glassy matrix. This fact is roughly appreciated by the low height of grains (between 5 and 40 nm, approximately) and a low RMS roughness (38 nm, Table 1).

3.2. Model glass weathered under a humid SO_2 atmosphere

OM observations of the model glass submitted to a SO_2 atmosphere showed a heterogeneous surface with some white deposits, probably formed and precipitated as a consequence of the acid attack accomplished in the Kesternich chamber (Fig. 5a) [12]. The AFM topographic analysis of the dark zones (Fig. 5b) allowed the identification of a barely attacked area characterized by homogeneous grains of small height (8–12 nm) and a low RMS roughness (3 nm, Table 1) in comparison with pits and altered areas exhibited by the historical glass sample (Figs. 3b and 4b). On the other hand, the AFM topographic image of the white deposits (Fig. 5c) showed a higher RMS roughness (48 nm, Table 1), which is close to that measured on the less altered area (internal surface) of the historical glass sample (Fig. 4b), even though in this case the grain height is higher (between 100 and 290 nm). In this regard, it is important to note that the RMS roughness is calculated from the overall surface, while the line profile is only one of the 300 lines present in an image. Thus, although a relatively plain background can be observed, the presence of only a few large grains may considerably increase the roughness value.

3.3. Model glass weathered under an alkaline attack in a liquid medium

The model glass submitted to an alkaline solution presented a homogeneous rough surface in which some small pits, referred to the X and Y plane, appeared (Fig. 6a). As can be observed on the AFM topographic image of Fig. 6b, the rough surface is formed by small elongated shapes superimposed on an almost plain grain-like background. This fact is roughly measured in the line profile as well as in the value of the RMS roughness (266 nm, Table 1), which is close to that obtained in the centre of a pit of the historical sample (Fig. 3b), except for a few grains having nearly 800 nm in height. This result could be ascribed [13] to the alkaline attack experienced by the glass, which destroys the glass network. Thus, both alkaline and earth–alkaline elements, as well as silica, are leached from the glass body, dealing with a fragile surface in which different insoluble compounds are deposited.

Within this framework, chemical mechanism for historical glasses decay can be written as follows:

a) ion-exchange of the glass alkaline ions with the H^+ ions present as a result of humidity:

$$\equiv Si-O^-\ldots K^+ + (H^+ + OH^-)\ \text{water} \rightarrow \equiv Si-OH + K^+ + OH^- \quad (1)$$

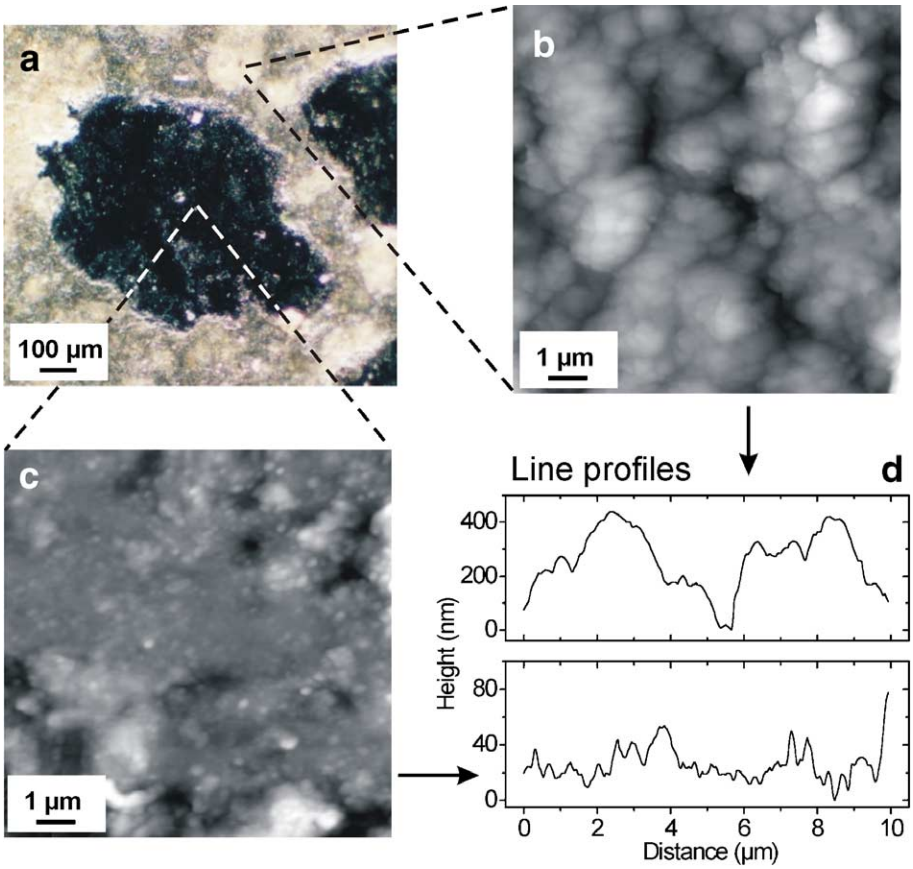

Fig. 4. Internal surface (indoor the cathedral) of a historical glass sample: a) OM image of altered (light) and less altered (dark) areas. b) AFM topographic image of an altered area. c) AFM topographic image of a less altered area. d) AFM line profiles of images b) and c), respectively.

b) Break down of the glass network through an alkaline attack carried out by the OH^- ions generated in the step a:

$$\equiv Si - O - Si\equiv + OH^- \rightarrow \equiv Si - OH + {}^-O - Si\equiv \quad (2)$$

c) leaching of the earth–alkaline ions from the glass network:

$$\equiv Si - O^- \ldots Ca^{2+} \ldots {}^-O - Si\equiv + 2H_2O \rightarrow \equiv Si - OH + HO - Si\equiv + Ca(OH)_2. \quad (3)$$

Under a humid environment, the leaching of alkaline ions from the glass surface takes place (step a). This process is enhanced by the presence of acid pollutants such as SO_2 and NO_x. The result of that acid attack is the formation of silanol groups (≡Si-OH) on the glass surface, which produces an often cracked silica gel layer very similar to that showed in Fig. 5a. The most dangerous damage for the glass is that caused by the OH^- ions generated as a consequence of the previous interaction glass/acid water [14,15]. Such basic ions destroy siloxane bonds (≡Si-O-Si≡), according to the step b, and favour the penetration of more water molecules (H^+ ions and OH^- ions) towards the inner layers of the glass (step c). The result is then a roughly damaged material whose microstructure corresponds to that of Fig. 6a and b.

The general superficial alteration showed by the historical samples (Fig. 4c) is somehow similar to

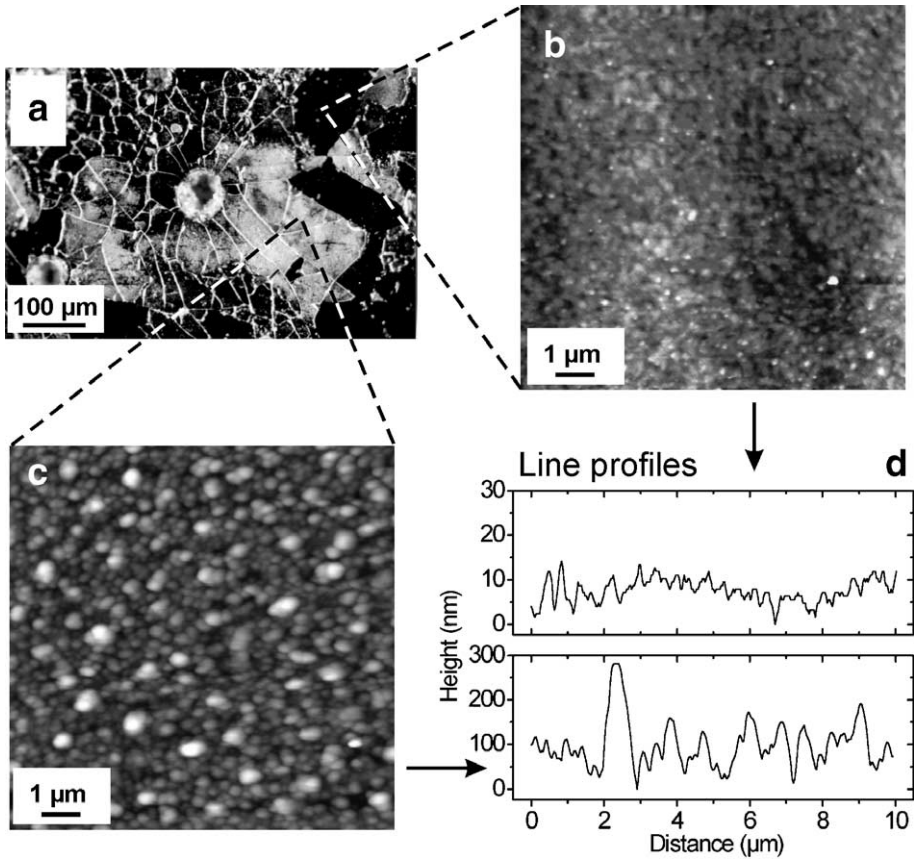

Fig. 5. Model glass sample weathered under a SO_2 simulated atmosphere (acid gaseous medium): a) OM image, general view. b) AFM topographic image of the less attacked area. c) AFM topographic image of the more attacked area. d) AFM line profiles of images b) and c), respectively.

that obtained after the accelerated weathering of a model glass under a SO_2 humid atmosphere (Fig. 5b), even though the sample from the model glass submitted to the Kesternich chamber showed a more homogeneous topography as a consequence of the controlled attack treatment. The topography of the crater-shaped pits on historical samples (Fig. 3b) is related to the model glass weathered into the NaOH solution (Fig. 6b), submitted to a more severe chemical attack with a higher pH. It is important to emphasize that certain differences in microstructure have been noted between ancient and model glass pieces, above all, beacuse in the historical samples, both acid and alkaline attacks have been identified together in many zones of the glass. Furthermore, it should not be forgotten that the initial weathering products of the ancient glass could have been themselves weathered and re-shaped many times during the corrosion process, giving rise to a somehow different microstructure in comparison with model glasses weathered in the laboratory. In any case, the AFM topographic images obtained both for historical and artificially weathered samples could be used as reference microstructures for further identification and diagnosis of decay signs and chemical damage on glasses.

Ideally, on a different note, non-destructive microscopy such as AFM should be coupled and complemented with non-destructive microanalysis (e.g., PIXE-RBS with an air path). However, given that this kind of microanalyses are commonly very punctual and specific, a sample-based analysis

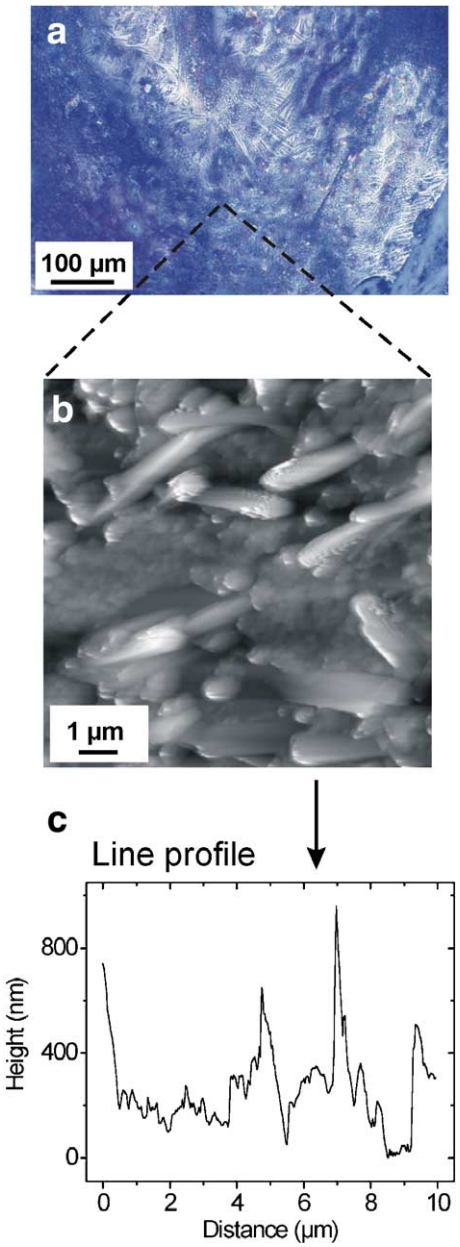

Fig. 6. Model glass sample weathered under an alkaline attack in a liquid medium: a) OM image, general view. b) AFM topographic image. c) AFM line profile of image b.

would always be advisable to study ancient glass corrosion, since weathering products of the ancient glass are, in general, very heterogeneous and they must be primarily approached from their macro and microstructural features.

4. Conclusions

Both original altered historical glasses (13th century A.D.) and artificially weathered model glasses have been superficially characterized by AFM. The study of the images obtained on model glasses revealed different textures depending on the conditions tested (under a SO_2 environment and submitted to an alkaline solution). The alteration layer of the historical glasses has been assigned to the interaction of humidity and acid environmental pollutants on the glass surface. The formation of pits filled with insoluble salts generated during the weathering process has been correlated with an alkaline attack that causes the destruction of the glass network.

The AFM technique, therefore, forms a powerful non-destructive and direct observation tool for delicate corroded glasses. Since it presents the advantage that samples do not require any previous manipulation and must not be submitted to vacuum, it is particularly suitable for characterizing valuable historical glasses. A set of AFM topographic micrographs were obtained, some of them showed in the present paper. Such micrographs will be used as reference microstructure images for further assignments of chemical decay processes and mechanisms related to historical glasses altered by real environmental factors or model glasses subjected to simulated weathering conditions.

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References

[1] Arman B, Kuban B. Corrosion products encountered on glass surfaces. Mater Charact 1992;29:49–53.
[2] Römich H, López E. Research on corrosion phenomena of archaeological glass. In: Kordas G, editor. Proc 1st Int Conf

Hyalos Vitrum Glass. Athens: Glasnet Publications; 2002. p. 241–7.
[3] Römich H, López E, Mees F, Jakobs P, Cornelis E, Van Dyck D, et al. Micro-computed tomography (mCT) as a new non-destructive tool for the characterisation of archaeological glasses. In: Van Grieken R, Janssens K, Van't Dack L, Meerman G, editors. Proc 7th Int Conf on non-destructive testing and microanalyses for the diagnostics and conservation of the cultural and environmental heritage. Antwerp: University of Antwerp press; 2002. p. 1–12.
[4] Müller E, Drewello U, Drewello R, Weissmann R, Wuertz S. In situ analysis of biofilms on historic window glass using confocal laser scanning microscopy. J Cult Herit 2001;2:31–42.
[5] Varatharajan R, Samanta SB, Jayavel R, Subramanian C, Narlikar AV, Ramasamy P. Ferroelectric characterisation studies on barium calcium titanate single crystals. Mater Charact 2000;45:89–93.
[6] Pailloux F, Gaboriaud RJ, Champeaux C, Catherinot A. AFM, SEM, EDX and HRTEM study of the crystalline growth rate anisotropy-induced internal stress and surface roughness of YbaCuO thin film. Mater Charact 2001;46:55–63.
[7] Lou S, Gao J, Xiao X, Li X, Li G, Zhang Y, et al. Studies of nanobubbles produced at liquid/solid interfaces. Mater Charact 2002;48:211–4.
[8] Valle FJ, Ortega P, Pascual L, Carmona N, Fernández Navarro JM. Chemical composition of Medieval stained glasses from the Cathedral of León (Spain). Glass Sci Technol 2002;75:152–7.
[9] Leissner J. The effect of corrosion on stained glass windows. Mater Constr 1996;46:27–38.
[10] Fernández Navarro JM. Alteration processes of Medieval stained glass windows. Study and protection treatments. Mater Constr 1996;46:5–25.
[11] Fernández Navarro JM. Causes for the physical and chemical deterioration of historical glasses. In: Fernández Navarro JM, Pastor P, editors. Jornadas Nacionales sobre Restauración y Conservación de Vidrios. La Granja; 2000. p. 17–37.
[12] Carmona N. Estudio de los procesos de alteración de vidrieras históricas y de los tratamientos para su restauración y protección. Ph.D. Thesis, Universidad de Valladolid, Valladolid, Spain; 2002.
[13] García-Heras M, Gil C, Carmona N, Villegas MA. Weathering effects on materials from historical stained glass windows. Mater Constr 2003;53:21–34.
[14] Fernández Navarro JM. El vidrio. Madrid: Consejo Superior de Investigaciones Científicas; 2003. p. 593.
[15] El-Shamy TM, Lewins J, Douglas RW. The dependence on the pH of the decomposition of glasses by aqueous solutions. Glass Technol 1972;13:81–7.