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Medieval stained glass in a Mediterranean climate: Typology, weathering and glass decay, and associated biomineralization processes and products

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ABSTRACT

Medieval stained glass (13th–15th centuries) from three restoration works (Santa Maria del Mar and the Pedralbes Monastery church in Barcelona, and the Tarragona Cathedral in the northwestern Mediterranean area have been studied to characterize glass decay. Electron microprobe analysis gave evidence of two types of glass: an Na-rich type (stable, Mediterranean, of Roman-like tradition), and a K-Ca-rich type, similar to coeval Central European medieval stained glasses. The latter shows glass decay in the form of destructive (micro- and mesopitting) and constructive (patina and microcrust) glass surfaces. Nevertheless, this type of decay in the K-Ca-rich group of glasses is in terms of thickness reduction in flat glass an order of magnitude less than that commonly found in Central European countries with a continental climate. Macroscopic and microstructural studies (SEM-EDS, XRD) allowed us to identify biodeterioration decay with chemical effects similar to that for pure chemical hydration leaching and corrosion, associated with biomineralization with unspecific sulfate (gypsum, syngenite) and calcite mineralization as well as bioinduced (weddellite, whewellite, etc.) mineralization. Medieval-stained glass biodeterioration decay in the Mediterranean area shows patterns and products comparable to those developed on stone in the same historic buildings.

INTRODUCTION

Glassmaking has been an industrial activity for more than four thousand years. Flat glass, however, has been only extensively produced and used for architectural purposes for the last one thousand years, following the building of cathedrals and religious buildings in Central Europe in the early Middle Ages. Thus, the remnants of medieval stained glass windows constitute a part of our cultural heritage that has been exposed to environmental damage over centuries. This provides an exceptional opportunity to test glass durability and to understand long-term environmental corrosion processes on glass.

In addition, in historic buildings, both the rock and the glass have been exposed to the same atmospheric conditions, which allows for comparison of the mechanisms of decay on both materials. The main purpose of this paper is to provide new insights into the biodegradation processes of stained glass and associated mineralization. To do so, several European Mediterranean case studies have been chosen and studied, taking into account the fact that the decay of historic glass seems to appear at an earlier stage when compared with most Central European glasses.

State of the art

Glass is made up of several components: network formers, network modifiers (flux and stabilizers), and coloring elements (Fernandez Navarro 1985; Newton and Davison 1989; Römich 1999). The main network former of medieval stained glass is silica. Its content determines the physical and chemical behavior and the stability of silicate glasses. Flux decreases the temperature at which the mixture (essentially the silica) melts and is made up of alkaline elements (Newton and Davison 1989; Römich 1999). In medieval times, a flux was introduced into the mixture as vegetal ash. Stabilizers (lime, magnesia, etc.) make the glass strong and more water resistant. Phosphorus is a common component of medieval glasses (Pérez-y-Jorba et al. 1984); it can also act as a network-former (Römich 1999) and can be attributed to the ashes used as raw material to obtain alkali, especially potash (Freestone 1993). Furthermore, several metals (Cu, Co, Mn, etc.) were used to provide color to the glass (Bamford 1977; Newton and Davison 1989). If we consider the main elements in the glassy mesostase, historic glass can be classified, from a chemical point of view, into several types (Newton and Fuchs 1988; Brill 1999, and references therein). Most European medieval stained glass produced between the 12th and 15th century can be considered potassic in composition. Recent research on coeval European Mediterranean glass shows the continuation of a Roman-like sodium glassmaking tradition. Despite this, there is a mixture of pieces of glass of both compositions (usually restricted to different colors) in the same Mediterranean stained-glass windows (Julià et al. 2001; Garcia-Vallès and Vendrell 2002; Gimeno and Pugès 2002 in Spain; Gimeno, unpublished data, for Siena Cathedral, Italy).

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The main difference between current industrial glass and historic glass is the relative increase of flux in historic glass, a fact directly related to the kiln facilities available at that time (Hawthorne and Smith 1963). The relative increase of flux was made at the expense of silica in most cases, which enhances chemical weakness of the glass with respect to corrosion. Some detailed mediaeval recipes of potash-rich glass still exist (Theophilus in Hawthorne and Smith 1963).

A common feature of medieval stained glass is the presence of corrosion, patina development, and mineral crust growth over the glass. The combination of these (and other) factors has caused serious damage to many Central European stained glass windows, amounting to, in some cases, total decay of the glass. For this reason, studies on glass decay have become important in several countries (France, Germany, United Kingdom, etc.).

Most of these studies consider that glass corrosion and decay is mainly related to a physico-chemical process (Schreiner 1991, 2001; Schreiner et al. 1988; Newton and Davison 1989, and references therein). In spite of this, since the first quarter of 20th century there has been evidence of biological induction in stained glass decay (Mellor 1924 in Krumbein et al. 1995). Generally, the biological factor in the corrosion processes of historical glass has been underestimated. Microbial corrosion of glass is caused by an interaction of biophysical and biochemical processes induced by several factors (i.e., cell growth). Filamentous microorganisms provoke the stress that can propagate cracks in the glass surface and their metabolite products (organic and inorganic acids, enzymes, etc.) cause the biodestruction of glass (Callot et al. 1987; Müller et al. 2001). An overview of the topic of biodeterioration of glass can be found in Drewello and Weissman (1997), Drewello et al. (2000), Krumbein et al. (1991, 1996), Müller (1992), and Thorseth et al. (1995).

Whatever their origin, the two main environmental controls on stained glass decay are water availability and warm to hot environmental conditions. Time is of course another important variable. There are volumes of information on glass composition, environment, and decay of historic glass but it is very disseminated. Other important factors that enhance corrosion are environmental pollution (i.e., CO_2 and SO_x in urban areas, where most stained glass windows are located) and, in the case of biodeterioration, the presence of organic carbon on the glass. As far as we know, a comparison of decay effects between Central European and the driest Mediterranean climates has not been undertaken on historic glass, yet synthetic medieval-like potassium-rich glass has been extensively promoted as a glass sensor for monitoring environmental conditions (Römich 1999).

The result of glass decay is a sharp decrease of the flux and network modifiers on the surface and contiguous mass of glass (leaching). This leads to the genesis of a gel surface (or planar volume) of the glass depleted in practically all glass components except network formers (Perez-y-Jorba et al. 1978; Newton and Davison 1989; Sterpenich and Libourel 2001, and references therein). The leached elements can combine with others (i.e., atmospheric) components to form complex salts. The most soluble salts are removed by moisture and rain; the others remain on the glass surface as mineral products forming patinas and crusts (sulfates: gypsum and syngenite, calcite, etc., Bettembourg 1976). In K-Ca-rich medieval glasses, when the pH is greater than 9, advanced corrosion of the outer level of silica-rich glass occurs (Newton and Davison 1989 and references therein).

Sampling

A large set of samples from three different restoration and conservation projects in Mediterranean coastal cities of Northeastern Spain were studied (see representative samples in Table 1). This area has a Mediterranean climate with rainfalls mainly concentrated in spring and fall (around 580 mm/year). Barcelona and Tarragona are included in the Mediterranean climate, characterized by moderate weather, warm summers (21–30 °C), and mild sunny winters (6–14 °C). Two of the sampled sites are located in the city of Barcelona and the third in Tarragona, some 100 km south.

The two sites in Barcelona are the presbytery in the church in the Santa Maria de Pedralbes monastery and the large rosette from the main façade of Santa Maria del Mar church. The monastery and church of Santa Maria de Pedralbes was founded by the widowed Queen Elisenda de Montcada of Barcelona. The stained glass windows were built around 1330, and since that time the monastery and church have been under the auspices of the Barcelona municipality. The presbytery contains a very well preserved set of stained glasses with exceptional preservation of original glass pieces with their medieval lead framework (Ainaud de Lasarte et al. 1997; Julià et al. 2001; Gimeno and Pugès 2002). Santa Maria del Mar church is an important medieval building erected in the 14th century but the large rosette on the main façade was destroyed by the 1428 earthquake and the stained glass window was rebuilt during the 15th century. Over the centuries, later damage and repairs has led to a mixture of old glass panels with new ones, the most important modifications probably dating from the Spanish War of Independence (1808–1812) and the Spanish Civil War (1936–39) (Ainaud de Lasarte et al. 1985). The rosette of the transept from the Tarragona Cathedral might date from the beginning of the 14th century (Ainaud de Lasarte et al. 1992). It also evidences damage and repairs from the War of Independence. All the stained glass windows show original black-fired draws (grisailles), but our present study is only concerned with the composition and corrosion of the main pieces of glass.

All the samples were obtained during restoration works and therefore consist of small pieces of broken glass (in general smaller than 0.5 g) that have no possibility of being remounted in the panels.

Experimental methods

Several analytical strategies were adopted to characterize the chemical composition of the glass as well as to identify the decay pathologies and resultant mineral products. The samples were preliminarily observed through a stereomicroscope to obtain morphological information, to determine the structure and texture of the surface, and to observe the weathering products (patinas, crusts, pitting, loss of material, etc.) as well as the original inhomogeneous mesostase (if present) in the glass products. This was done to select the most suitable areas of the surface glass to be scraped with a diamond grindstone and to concentrate the neoformed phase powder, which was identified using a SIEMENS D-500 X-ray diffractometer. Diffraction patterns in the range 4–70° 2θ were obtained with 0.05° 2θ step scan and 5 s counting time, using Cu$K\alpha$ radiation, tube conditions 40 KV and 28 mA, and a graphite monochromator.

TABLE 1. Chemical composition of medieval glasses

Sample	T-1	T-2		T-3	T-4	T-5	T-6	T-7	T-8
Color	blue	colorless	red-plaque	blue	red-plaque	brown-yellow	brown-yellow	brown-yellow	blue
SiO_2	47.11	48.17	46.27	48.78	48.61	49.09	48.69	47.96	47.53
K_2O	18.47	18.26	17.9	16.08	18.84	18.75	18.1	18.06	20.6
Na_2O	0.33	0.38	0.37	0.35	0.36	0.3	0.43	0.32	0.37
P_2O_5	3.93	3.82	3.79	3.83	4.33	3.97	3.74	3.87	3.47
CaO	18.64	17.92	17.97	19.02	17.55	17.66	17.84	16.78	18.21
MgO	4.87	4.79	4.83	4.98	4.69	4.82	4.99	4.86	4.86
Al_2O_3	2.34	2.23	2.32	2.33	2.27	2.2	2.36	2.1	2.21
MnO	1.22	1.04	1.03	1.24	1	1.18	0.98	0.95	0
FeO	1.05	0.46	0.44	1.07	0.52	0.59	0.44	0.41	0
CuO	0.21	0.09	0.4	0.26	0.32	0.18	0.69	0.04	0.19
PbO	0.15	0.06	0.06	0.04	0.01	0	0.06	0.09	0.08
TiO	0.15	0.11	0.12	0.17	0.14	0.15	0.05	0.13	0.09

Sample	M-1	M-2	M-2	M-2	M-2	M-3	M-3	M-3	M-4
Color	blue	green	colorless	green	colorless	colorless	red	colorless	blue
SiO_2	48.1	47.74	50.06	48.37	48.44	49.21	48.54	49.14	52.6
K_2O	20.7	17.21	17.87	17.13	17.61	20.55	20.05	20.49	18.8
Na_2O	1.76	1.29	1.2	1.25	1.19	0.27	0.25	0.24	0.95
P_2O_5	5.18	4.65	5.31	4.87	4.91	1.3	1.64	1.69	4.51
CaO	13.2	13.42	14.33	13.5	13.81	16.59	15.9	16.52	12.7
MgO	4.97	4.53	4.83	4.51	4.79	3.15	3.09	3.15	5.03
Al_2O_3	2.09	1.93	2.02	1.88	2.08	1.93	2.02	1.9	1.81
MnO	1.31	1.12	1.22	1.04	1.21	1.11	1.42	1.28	0.78
FeO	0.42	0.52	0.5	0.57	0.55	0.53	0.38	0.27	0.51
CuO	0.04	3.58	0.09	3.75	0.03	0.62	0.85	0.05	0.16
PbO	0.01	0.09	0.1	0	0.07	0.7	0.86	0.83	0.01

Sample	VP-2		VP-3	VP-4	VP-6	VI-21	V-27	VI-34	CV-1	CV-2	CV-3
Color	colorless	red	turquoise	blue	pink-Mn	colorless	brown-yellow	pink	colorless	red-plaque	dark-green
SiO_2	46.75	45.31	48.38	46.87	47.98	55.51	55.98	48.03	62.42	53.9	58.89
K_2O	25.24	22.70	23.26	22.99	23.93	16.79	16.87	23.74	2.64	16.84	4.08
Na_2O	0.27	0.25	0.11	0.15	0.19	0.54	0.43	0.23	17.9	0.48	13.06
P_2O_5	2.47	1.32	1.22	1.15	1.31	3.06	0.00	1.04	0.87	4.33	0.61
CaO	17.72	20.40	19.01	19.08	17.94	14.04	14.17	17.85	6.57	14.08	9.08
MgO	3.50	3.13	3.22	3.23	3.65	4.27	4.29	3.53	2.08	3.48	1.81
Al_2O_3	1.19	1.46	1.13	1.27	1.45	2.26	2.23	1.45	4.04	2.28	3.67
MnO	0.70	0.71	1.07	1.07	1.41	0.89	0.89	1.35	1.01	0.9	1.75
FeO	0.39	0.38	0.51	0.96	0.46	0.41	0.41	0.44	0.64		
CuO	0.00	0.64	0.05	0.21	0.07	0.27	0.14	0.04	0.05	0.48	1.19
PbO	0.00	0.00	1.35	1.06	0.70	0.00	0.04	0.72			
TiO	0.07	0.10	0.06	0.10	0.09	0.16	0.15	0.08	0.21	0.17	0.22

Note: The samples M correspond to main of Santa Maria del Mar (Barcelona), the T come from lateral rosette of Tarragona Cathedral (Tarragona) and VP and CV come from the presbytery of the church from Pedralbes monastery (Barcelona). (See the text for explanation).

The glass samples were cut into two pieces. One was used to study the fresh fracture, including the glass and neoformed surface, by Scanning Electron Microscopy (SEM). The instruments used were a JEOL J3M-840 and a Leica 360, both served by a LINK Microanalysis energy dispersive spectrometry EDS system, including an energy-dispersed X-ray spectroscopy detector facility (LINK AN 10000 EDS). The other section, perpendicular to the surface, was set in an epoxy resin block, cut, and made into a thin polished section for preliminary examination under a petrographic microscope, and then by SEM-EDS. SEM was used to determine the structural changes in the surface, to evaluate the rate of corrosion within the glass, and to determine the composition.

The chemical composition of the glass was obtained using wavelength-dispersive spectrometry (WDS) microprobe analysis (CAMECA Camebax SX-50) at SCT-UB. Different natural and synthetic silicates and oxides of certified composition were used as standards (P & H Developments and Agar Scientific commercial standard blocks). The analyzing crystals were provided by CAMECA (LIF, TAP, and PET; and PC0 for instrumental determination of oxygen).

EPMA was used for the quantitative chemical characterization of the glass. This was achieved by random point microanalysis of the fresh glassy mesostase (in general $n = 15$ over each fragment). In most cases, glasses are very homogeneous and analytical differences are within the range of (or much lesser than) expected instrumental error. Zoned glasses (i.e., red glasses consisting of a deep red plate sandwiched between white glass) were studied also by acquisition of a profile of points orthogonal to the planar optical anisotropies. The analytical accuracy and precision was also controlled by means of internal standards (Corning Museum of Glass in Brill 1999).

The quantitative chemical analysis of medieval glasses does not differ in the main from the analysis of similar products (i.e., natural glasses). This topic has been the object of recent revision (Mass 1999). We must bear in mind some additional constraints: reduced number of available samples, high alkali content (i.e., much more than in obsidian), significant presence of certain volatile elements (i.e., chlorine related to the vegetal ash used as raw material). Furthermore, the presence of some elements (in most cases, metals) that acted as coloring agents can be useful not only in the determination of color origin but also in their potential activity with respect to weathering agents (i.e., biocides).

An analytical approach is an agreement between the available facilities and the expected results. X-ray fluorescence spectrometry (XRF) is a standard of quality in major-constituent element determinations, but commonly requires the destruction of large amounts of material (5–6 g of powdered material). This method provides good results for most elements and has the added advantage of good quantification of silica, an element that in other spectrometric procedures is otherwise commonly given by difference (see, i.e., Brill 1999). EPMA, on the other hand, requires very small quantities of material with comparable results, but data collection of alkali atoms, in particular Na, requires particular care because of the effect of migration under the electron beam (Gedeon et al. 2000). Moreover, EPMA also allows quantification of coloring metals (Cu, Pb, etc.) should they be present in glass at levels over several hundred μg/g.

In the end we decided to characterize the glass composition by EPMA, using a previously developed methodology for studying natural silica-rich glasses (Diaz et al. 1998). It warranted good recovery of alkali results, which was also controlled by means of a comparative study (XRF, EPMA, ICP, OES) of a set of 10 medieval stained glasses from the Pedralbes church (Gimeno and Pugès 2002; Gimeno unpublished data). This provided good data for the major components of the glasses including network formers (silica) and stabilizers, flux (Na, K), and common coloring agents. All these data were obtained with a mean loss of

glass less than 0.5 g. Glass composition is expressed as oxide percentage; the O atom content is obtained from stoichiometry or directly from the EMPA experiments with comparable results (Gimeno and Pugès 2002). Experimental results of the O atom content (when performed) allows for the evaluation of water content (in general, very low) and chlorine, a common constituent routinely detected by SEM-EDS (and, if required, by EPMA-EDS).

The reduced size and mineral composition of neoformed phases discouraged us from exploring them by EPMA, and therefore these phases were mainly characterized by XRD and SEM-EDS.

RESULTS

Glass characterization

Two main types of glasses can be identified according to their structure: those that are homogeneous with a uniform color throughout, and those composites formed by two or more layers of glass of different colors, normally a colored layer on or between colorless layers. These are the so-called plate glasses. In some cases, the color layer was clearly identified as formed by microcrystal dispersion in glass; hence, it could be considered an enamel (Fernández Navarro and La Iglesia 1994; Verità 2000). The most typical medieval plate glass is red, where the color is provided by Cu-containing phases. This red plate glass is present in the three sampled churches. The stained glass from the rosette of the Tarragona Cathedral consists of plate glasses of three different colors, namely blue, red, and green (Garcia-Vallès and Vendrell 2002).

Some representative chemical analyses of the three sets of studied glass are reported in Table 1. Two main compositional groups can be distinguished: Na-rich and K-rich (or K-Ca-rich) glasses. The Na-rich glasses typically show greater silica content (around 60%, ranging from approximately 55–65%) than the K-rich or K-Ca-rich glasses (around 45%, ranging from approximately 42–48%, Garcia-Vallès and Vendrell 2002; Gimeno and Pugès 2002). Al_2O_3, the other network-forming component, is present in all glasses at values in the same range (a few %) independent of their K- or Na-rich character. Therefore, Al cannot balance the detected difference in silica composition in terms of potential glass stability.

We can also consider the difference between samples in terms of their chronology and inner homogeneity. The Pedralbes glass represents the older type and shows a remarkable homogeneity in the soda glass group. This fact facilitates the understanding of elements implied in color generation, taking as an end-member white glass and considering the elements added (or removed) to obtain a determined color (Gimeno and Pugès 2002). According to this interpretation, it is clear, for example, that Cu, homogeneously added to white glass in a percentage of 5–6% CuO (avoiding iron addition), can produce a pale green color. On the other hand, a much smaller amount of CuO (1.6–2.2%) in a Cu-Fe salt gives a deep green color to the same glass. Our current state of knowledge does not allow us to infer whether the colored glasses were the product of successive batches of glass from a parental white one or a direct product of fusion.

Some of the studied samples of soda glasses from Santa Maria del Mar (Barcelona) and the Tarragona Cathedral can be interpreted as relicts of glass similar to the Pedralbes glass. This is not surprising since recycling of glass (i.e., in the case of Santa Maria del Mar) was a widespread practice among medieval window glassmakers. Nevertheless, we must point out that we mainly studied the K-rich compositions (Table 1). Here again, we can note a great homogeneity in the Pedralbes glasses, with two types of glass: one characterized by higher contents of K_2O (23–25%), CaO (17–19%), and lower contents of SiO_2 (around 48%), the other 16.5–17% K_2O, CaO 14%, and SiO_2 55–56%. This wide range of compositions does not allow for a common origin (especially if we consider the relative contents of some minor elements). Thus we can infer that probably the vegetal ashes used as raw material and the relative proportions of silica (as quartz sand) might have been different in the two cases. The potential decay rate might also be slightly higher in the first group. These two sets of K-Ca-rich glasses are also detected in the Santa Maria del Mar glasses, while the Tarragona Cathedral glasses seem, at first sight, much more heterogeneous (Garcia-Vallès and Vendrell 2002). Also in Santa Maria del Mar, the main trends of color incorporation in the K-Ca-glass are comparable in terms of metal coloring agents, to those of the Na-rich glasses from Pedralbes Monastery (Garcia-Vallès and Vendrell 2002; Gimeno and Pugès 2002).

Macroscopic and microstructural glass decay characterization

The analyzed external surface shows evidence of the following degradation typologies: chemical, physical, and biological. The chemical degradation is associated with corrosion and (or) the formation of neoformed mineral phases, namely patinas and crusts. Normally, the patinas are in the external part of the glass. When these are located indoors, we attribute them to an old reversion of the glass fragment during previous restoration. The color patinas are beige or orange. The physical decay of the glass pieces in the studied windows is mainly macroscopic and can be mostly related to impacts (i.e., star-like radiate fractures) or to deformation and bending of the lead framework. Therefore, most of the modifications of the glass surface (morphology and characteristics) can be related to chemical or biochemical processes, the resultant surface being either destructive or constructive.

In some cases, the macroscopic observations of external surface glass show small pits (destructive surface, Fig. 1). The pitting occurs only in certain pieces of glass of the window even taking into account the same color (a fact a priori attributable to different compositions). For example, in Figure 1, there is a selective pitting process, in this case in an old red glass located in the lower part of that panel of the window. Normally, these pits have a random distribution but they tend to coalesce (Fig. 2), in this case forming a weathered uniform surface, where the pits are filled with neoformed minerals (Fig. 3). However, the pits tend to laterally enlarge. In Figure 2, we observed the uniform size of the pits. Despite this, two sets of preferential near to orthogonal directions of pitting development can be detected. This pitting, called mesopitting, has an average size of between 30 to 300 micrometers on the surface of the glass and is characterized by a circular or oval morphology of the pits (Fig. 3).

The mesopitting was also studied by microscopy, in thin section perpendicular to the glass surface, showing penetration into the glass with a diameter of around 4–5 times larger than the depth (Fig. 4).

FIGURE 1. Macroscopic photograph of a medieval stained glass window (from Pedralbes Church), the arrow marks the small pits in the red glass (destructive surface).

FIGURE 2. Detail from Figure 1 of pits in a macroscopic photograph. Note evidence of two orthogonal sets of old scratches (see text for explanation).

SEM analysis of the glass surface corroborated the morphology and the lateral aggregation of the pits, showing how small pits increase in size and group together to form larger craters (Fig. 5). On the other hand, pit development is related to glass composition. For example, Figure 5 corresponds to a sample of red plate glass (a red plate sandwiched between colorless glass), where the pits start in the colorless part of the glass and stop at the red level, which is rich in copper. This destructive surface can be also filled (constructive activity) with new phases (Fig. 6 and see below).

The study of thin sections under SEM provides additional information of the 3D arrangement of mesopitting (the third dimension being perpendicular to the glass surface). In fact, we can observe initial development of curved-branched irregular micropitting (Fig. 7) not directly related to micro-cracking of the surface. Each of the micropits can show an incipient nodular-like glass-decay form overprinted on the curved branch of micropit progression. These branches of micropits tend to coalesce and to provide a deeply penetrated upper film of the glass, sometimes associated with an external surface patina (Fig. 8). It is worth noting the gradual hiding of micropit evidence with advanced development of coalescence associated with thicker patinas and microcrusts. SEM-EDS gives good evidence of the microchemical environment associated with the micropitting development. In general, we can establish the following succession of bands from unaltered glass to the sur-

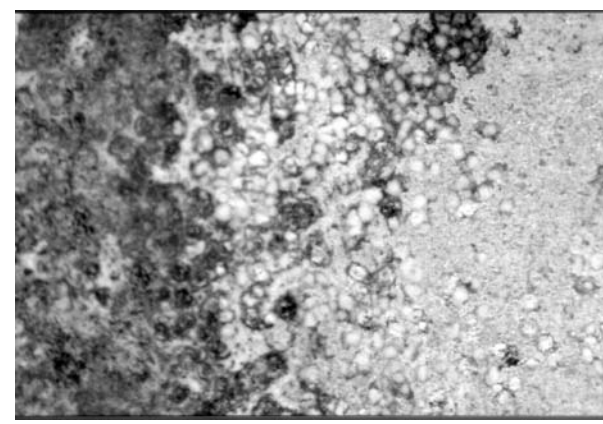

FIGURE 3. Detail of morphology of pits developed in the external surface.

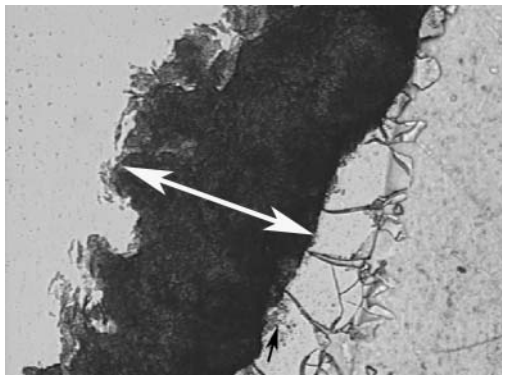

FIGURE 4. Decayed surface of developed micropits, observed under the microscopy in the thin section perpendicular to the glass surface. The simple-arrow shows the pit penetration in the glass and the double-arrow the decayed glass.

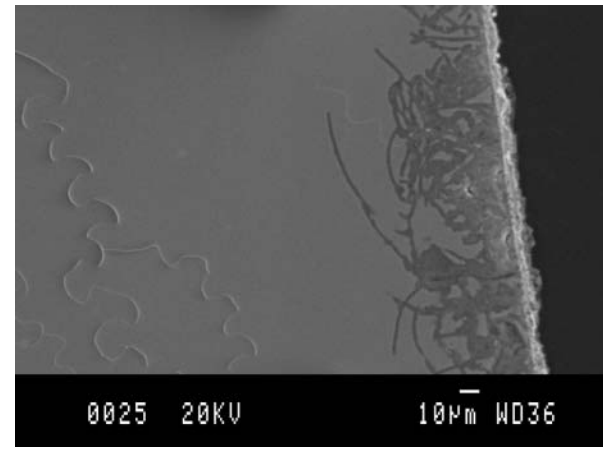

FIGURE 7. SEM picture of glass decay. Note initial development of curved-branched irregular micropitting.

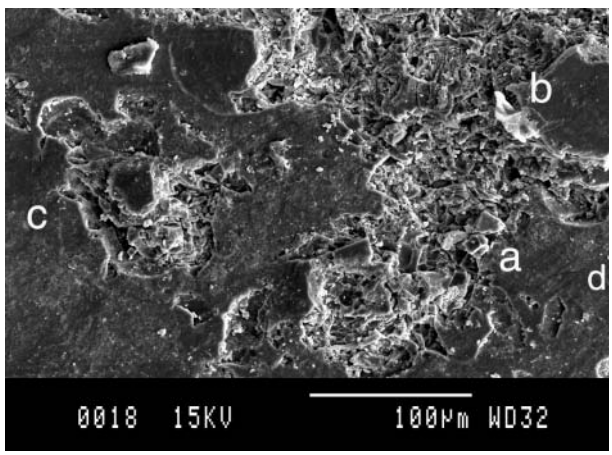

FIGURE 5. SEM image of a red plate medieval stained glass, the colorless layer is irregularly destroyed by biological activity. (**a**) Uncorroded bulk glass. (**b**) Hydrated silica layer. (**c**) Corrosion zone, pit. (**d**) End of the corrosion at the red Cu-rich layer.

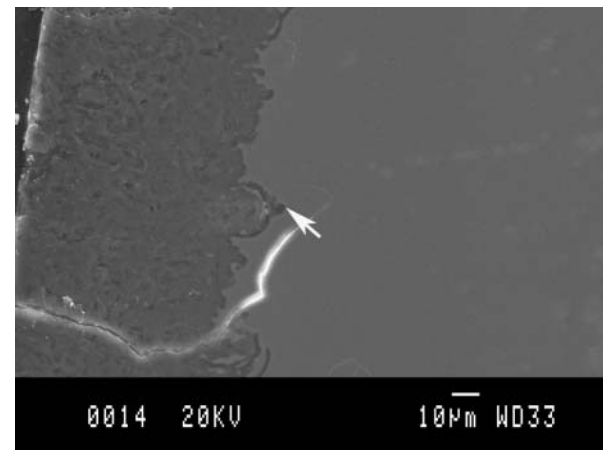

FIGURE 8. SEM picture of advanced glass decay, note the curved-branched irregular micropitting. The arrow marks the front of the decay, locally marked in Mn-rich glass (pink and purple glass) with high Mn concentration.

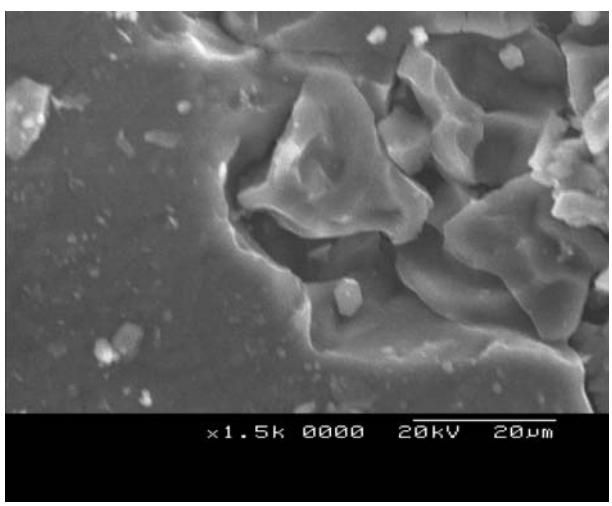

FIGURE 6. SEM picture of detail of Figure 5 point c. Note the morphology of the holes and the new phases partially filling the cavity.

face: a gel-like hydrated silica glass (depleted in most elements), beige-orange patina, and a sulfate weathering crust mostly consisting of gypsum and, locally, with interstitial K-Ca (syngenite) or K-Mg sulfates (Fig. 9). Frequently, only the outermost weathered crust consists of gypsum, a fact probably correlated by the high solubility of other sulfate phases. In the more Mn-rich glasses (i.e., the pink-purple ones), there is evidence of a high concentration of Mn in the deeper part of the individual micropits located within the glass (see Fig. 8).

As previously stated, other aspects of the surface are constructive, corresponding to patina formation, with new material accumulating on the surface of the glass. The patina textures are uniform in the analyzed samples, leading to generalized moderate opacification of the glass piece, but their compositions vary. Sometimes there are important developments of patinas or microcrusts (i.e., Fig. 4), but since they are associated with destructive surfaces and weathered crusts, it is difficult to quantify a mass or volume balance on the glass surface.

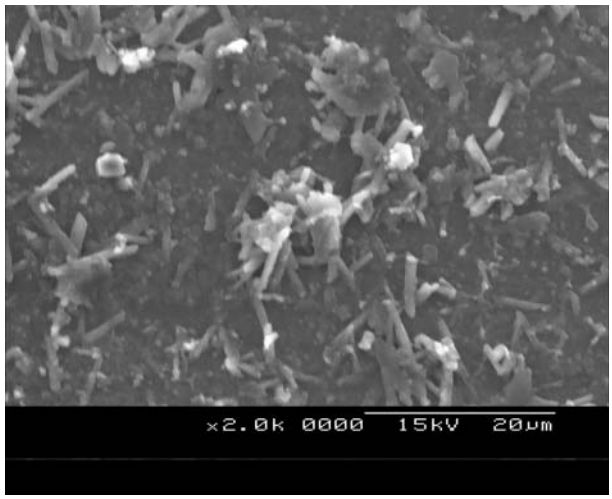

FIGURE 9. SEM picture of a neoformed prismatic or needle-like forms of Ca-oxalate and syngenite.

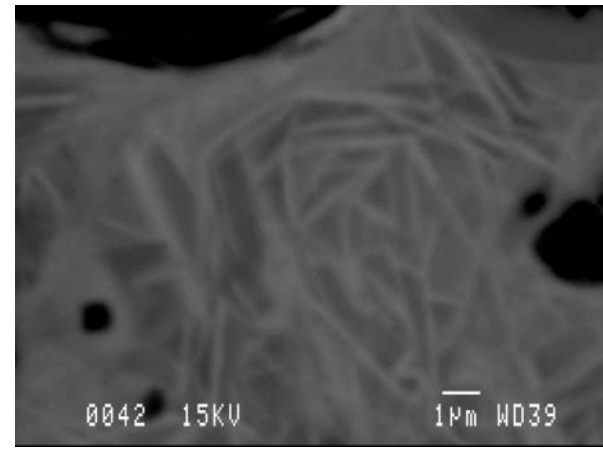

FIGURE 10. SEM picture with a close-up of sulfate crystals, gypsum, and syngenite. The later occupies the central darker sectors between idiomorphic crystals and is locally associated with Mg-rich sulfates.

The glasses rich in potassium show uniform corrosion, with a thin gypsum and syngenite layer. We observe, for example, a surface of weathering crust, with characteristic prismatic or needle-like forms of Ca-oxalate and syngenite (Figs. 9 and 10). Locally some traces of other possible soluble salts such as polyhalite have been detected by SEM-EDS. By comparison with the Na-rich glasses, the presence of patinas in the former, solely or mainly constituted by gypsum, is also of interest. In leached glass surfaces (therefore with the destructive surface mainly exposed), there is also evidence of a gel with a silica composition.

XRD analyses confirmed that the patinas and weathering crusts are made up of gypsum ($CaSO_4 \cdot 2H_2O$) (Fig. 11), bixbyite (Mn_2O_3), syngenite [$K_2Ca(SO_4)_2 \cdot H_2O$] (Fig. 12), calcite ($CaCO_3$), and quartz (SiO_2), and revealed the presence of clay minerals and Ca-oxalate (weddellite, $CaC_2O_4 \cdot 2H_2O$) (Fig. 13) and whewellite ($CaC_2O_4 \cdot H_2O$) in some patinas.

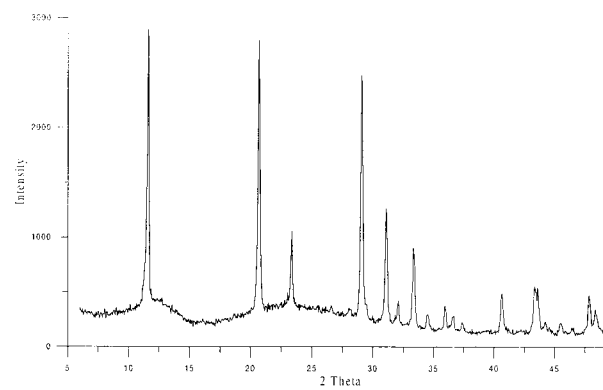

FIGURE 11. X-ray spectra of the weathered crust composed of gypsum.

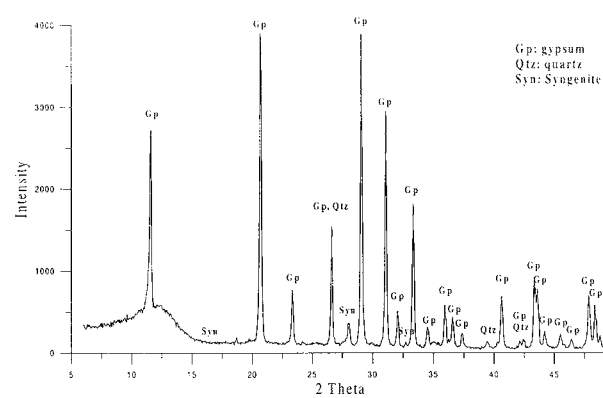

FIGURE 12. X-ray spectra of the weathered crust made up of three neoformed minerals.

DISCUSSION

A first result of this study is that the state of conservation of Mediterranean medieval stained glasses is much better than that of most coeval Central European glasses. Some extreme pathologies such as dramatic thinning of glass pieces, significant physical decay, and development of generalized corrosions and associated thick crusts are absent. Several factors can be invoked to explain it. Widespread use of Na-rich glass, characterized by silica contents around 60% in weight, is a primary factor that explains the good preservation of the stained glass pieces; the role of silica as a network-forming agent has been clearly shown (Newton and Davison 1989 and references therein).

Therefore, it seems useful to concentrate on the K-rich (or K-Ca-rich) glasses present in the same stained glass windows to determine if the decay processes and pathologies are comparable to those described for Central European medieval windows. Therefore, the lesser degree of decay in the Mediterranean area can be interpreted in terms of different stages of the same processes. This may imply that differences in decay are related to different kinetics of similar processes related to the same agents.

The basic chemistry of the process of stained glass decay is well known: first, attack by water allows for the formation of

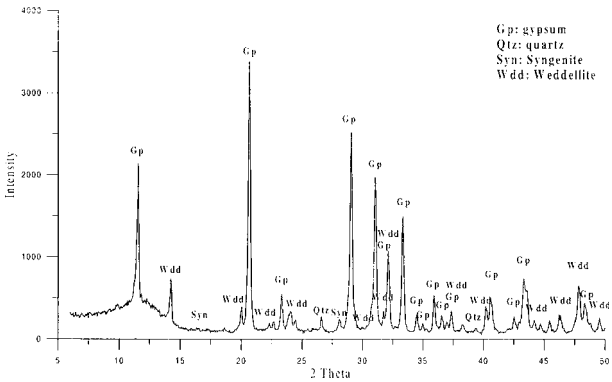

FIGURE 13. X-ray spectra of beige patina.

hydroxides, cation migration, and loss by leaching and hydration of a superficial film. Then, subsequent conversion of these hydroxides to carbonates by carbon dioxide in the atmosphere, and finally, the conversion of those carbonates to sulfates (Newton 1979; Newton and Davison 1989 and references therein). During this process, the surface of the glass can develop several microchemical environments from case to case, as a function of the different chemistry of stained glasses (Newton and Davison 1989 and references therein).

From a chemical point of view, available evidence suggests that all these processes have developed in the K-Ca-rich stained glasses of the three sites sampled, to varying degrees. This intensity of decay is generally lesser than that in coeval Central European medieval stained glasses. It is not easy to quantify the decay in medieval stained glasses, since they do not display a homogeneous thickness like current industrial glass. In spite of this, the measured thickness of the K and K-Ca glasses is around 2–3 mm on average, while Na glass can be somewhat thicker (3 to 4 mm). This can be correlated to the production time of glass during flat glassmaking (Newton and Davison 1989). In Central Europe and in a continental climate, K- and K-Ca-rich glass decay can lead to the total elimination of this thickness, and full-holed glass is not uncommon (as in the case of the severely damaged glass of the Leon Cathedral in Central Spain). In contrast, the pit penetration in K- and K-Ca glasses under a Mediterranean climate is in most cases in the range of 1 mm or less. Thus, the decay effects are on the of 20 to 30 times greater for glasses in continental climates with Atlantic influence where the mean rainfall is in the range of 750–900 mm/year.

The main factors of degradation in the studied medieval stained glasses are water and microorganism activity. Biological activity in all the studied sites is fossil. Therefore in the glasses studied, only remains associated to their activity have been observed, not living organic bodies themselves. These remains are corrosion forms (biopitting) and mineral precipitates. The new minerals formed under biological control are calcite and gypsum (locally also syngenite) as well as oxalate calcium (patinas). This leads to changes in the optical qualities of the glass (opacification and partial discoloration).

The biodeterioration of glass has been reported by several authors. The microbial colonization of glass surfaces modifies and generally accelerates physical-chemical processes by biologically catalyzed reaction (Krumbein et al. 1995). Some authors (Tennent 1981; Callot et al. 1987 and others) have described pitting and cracking decay by fungi. Bundles of hyphae of epilithic lichens can also contribute to mesopitting (Krumbein et al. 1995). The organisms play an important role in the mineral dynamics of the glasses. It can be stated that biopitting and microbial redeposition of some of the elements in the form of films and crusts is one of the major activities in this type of glass deterioration. Many different microorganisms have been shown to leach, enrich, and redeposit very different and even rare cations selectively (Krumbein et al. 1995).

The destructive surfaces in the Mediterranean glasses studied have the same characteristics as those previously described in the biodeterioration of stone (Garcia-Vallès et al. 2002 and references therein). The destructive bioactivity produces an important number of morphologies of holes, usually concentric, of variable diameter as a function of the organism that produces it, as well as of the composition of the glass (Fig. 5). The bioactivity also generates biomineralization, (i.e., weddelite and whewellite, and probably also calcite). The mineral record states that the dissolution of some mineral phases (i.e., sulfates by rain water) can be also associated with local supersaturation of bioinduced mineral phases. Thus, we can conclude that in this case, the chemical alteration of glass is invariably accelerated in the presence of microbiota. On the other hand, comparison with other described chemically corroded glass surfaces (Hogg et al. 1999) shows that the obtained morphologies are quite different from those reported here.

The building stone of the Tarragona Cathedral façade presents a similar destructive surface and constructive or beige-orange patina. In this case, the calcite and Ca-oxalate (weddellite and whewellite) and the biopitting are also associated with bioactivity (Garcia-Vallès et al. 1997). Experimental work corroborates this origin (Urzí and Realini 1998; Urzí et al. 1999; Garcia-Vallès et al. 2000). Previous research on the stone of monuments, natural outcrops, and old quarries in Mediterranean area has recognized the presence of this patina directly in contact with the rock surface (Garcia-Vallès et al. 1996, 1997, 2002).

In the Mediterranean areas, seasonal and environmental climate variations correspond to significant changes in the ecological dynamics of microorganisms colonizing rock surfaces, which can be related to mineral deposition (Garcia-Vallès et al. 2000, 2002).

The biological activity is more significant in the external glass face, the one that is usually more altered. Normally bioactivity is related to environmental conditions (i.e., moisture), glass composition (as this study clearly shows, where the K-rich glasses are the most selectively damaged), and textural characteristics (ruggedness, fissures, stings, bubbles, etc.). The silica-leaching layer is produced by hydration of silica network-formed glass after hydrolysis of Si-O-Si bonds, a consequence of the reaction of the Si-O bonds with water to form new hydroxyl groups.

In addition, we have found evidence of a direct relationship between the chemical composition of the glass substrate (i.e.,

the markedly different behavior of poorly altered Na-rich glass with respect to the more advanced degradation of K-rich glass) and biological activity. This fact has been explained not specifically in terms of biota activity but simply by taking into account the intrinsic deficit in the network components of the glass (silica) with respect to the flux (Newton and Davison 1989).

More specifically, in the case of biopitting corrosion in red plate glass, there is evidence of a specific, selective biologically related chemical behavior toward the interior of the glass. Small pits increase in size and coalesce, forming craters with an unequivocal bioactivity zone (Fig. 5 and magnification in Fig. 6) that significantly differ from the ones related to pure chemical corrosion (Hogg et al. 1999). In this example the bioactivity starts in the colorless glass that forms the external level of the glass (Cu content is very low, in the range of instrumental noise) and progresses as far as the level of the red plate (Cu content in a range of 0.32 to 0.85%), where it suddenly stops. Cu is not an element that can act as a glass network former. In fact no reported activity as a stabilizer has been observed. Thus we can conclude that in this case, the Cu-rich portion of the glass acts as a barrier to bioactivity, allowing us to infer that Cu behaves as an efficient biocide. Other evident chemical barriers to the biological decay of the glass are, e.g., old repairs with mortar or the grisaille-fired draw (Garcia-Vallès and Vendrell 2002). Also, when the drawings are made from yellow silver, the biological attack delays the destructive action considerably, as described by Krumbein et al. (1991).

Biological activity on glass can be developed by lichens, algae, bacteria, and fungi. The bio-deterioration is at the expense of certain ions that the organisms extract from the glass, a fact that must be related to their metabolic needs. In a simplified way, we can say that these organisms "eat" glass. This phenomenon has also been described for natural volcanic glasses (Thorseth et al. 1995). In the case of medieval stained glass, their metabolic activity depletes the glass of several ions (K, Mg, Ca, etc.). Therefore, it provokes the same succession of events and the same result (decay and corrosion of glass) as purely chemical degradation of glass reproduced in the laboratory (Newton and Davison 1989 and references therein) and also that described elsewhere for Central European medieval glasses.

Neoformed cavities in glass surfaces can also be the site of selective crystallization of sulfates such as gypsum and syngenite. The hygroscopicity of these sulfates maintains the humidity at the glass surface, facilitating the continuity of degradation processes. Furthermore, the precipitation of other minerals, such as weddellite or whewellite, leads to the self-generation of a protective film against water leaching.

There is a relationship between constructive surfaces (patina and crust development) and bioactivity. We have found evidence for a direct spatial relationship between mineralization (constructive) and biological (destructive) activity, involving several mineral phases: gypsum, syngenite, calcite, quartz, clay minerals, and oxalates (weddellite, whewellite), as well as an undetermined (poor-crystalline) silica phase. Some mineral phases (clays, quartz, and some of the calcite) can be easily interpreted as non-significant mineral phases, which, for example, can be supplied by wind as dust. According to Newton (1975), the sulfate production does not need to result from direct attack of SO_2 in the atmosphere. The microchemical (SEM-EDS) test showed that in K-rich glass Ca and K (as well as most other glass components except silica) are leached in association with micropitting activity. The next stage is the formation of carbonates, nitrates, etc. due to their reaction with CO_2, NO_2, etc. Finally, these intermediate products are converted to sulfates as they react with atmospheric SO_2. Of course, dense traffic in urban environments and industrial activities involving fossil fuel burning provides a greater presence of CO_2 and SO_2, which in turn increases the rate of glass decay. This is true in case of biodeterioration at least from the moment atmospheric contamination kills the organism acting on the glass (i.e., a common fact with lichen acting on stone in Mediterranean cities). The described succession of mineral phases is coherent with the microstratigraphy revealed by the glass study, especially in the less developed stages of glass decay. Weddellite and whewellite (and to some degree, also calcite) are ascribed to reactions with organic substances arising from bioactivity (Perez-y-Jorba et al. 1980, 1993; Tennent 1981; Krumbein et al. 1996; Garcia-Vallès and Vendrell 2002) since microorganisms excrete organic acids. As a general rule, we can point out that advanced decay of the glass by microorganisms and associated mineral reactions (with increased percentage of sulfates related to other mineral phases) tends to obscure the biological origin of the process.

There is also evidence of the role played by other elements essential for microorganic life. Mn enrichment regarding microbiopitting (only detectable under SEM-EDS when the original glass substrate shows a multiplication factor of 2 in its Mn content) may be considered relevant in terms of biological activity. Perez-y-Jorba and Bettembourg (1989) also describe local concentrations of Mn in microfissures in leached glass surfaces. Drewello and Weissman (1997) verify that purple glass with high amounts of MnO showed an increased number of colony-forming units of fungi growing on them.

One factor of decay that is not easily discernable is anthropogenic influence related to restoration. In the case of biodeterioration of glass, organic fresco painting or protective organic films are a potential source of nutrients for microorganisms. Old mechanical cleaning with metallic or hard brushes can be directly related to orthogonal sets of old scratches preferentially followed by microorganism pitting (Fig. 2). Similar cases have been described by Newton and Davison (1989).

An issue that largely exceeds the scope of this paper is the systematic comparison of Mediterranean and Central European climatic environmental conditions, but we can detect their effects on the mechanisms of glass decay considering glasses of the same age and range of composition. In general, due to humidity in Barcelona and Tarragona, the two main products of corrosion are the formation of a layer of silica gel and the leaching of potassium and calcium that produce the formation of hydrated sulfates of potassium and calcium (Fig. 8). Potassium cations (and the potassium phases as syngenite) are more sensitive (and soluble) to humidity than sodium cations. There is no evident difference in glass decay with respect to the distance of the site from the marine coast (Santa Maria del Mar is

nearest, then the Tarragona Cathedral, and finally the Pedralbes Monastery). The main differences with respect to continental European climate are that the winters are warmer (a fact that can play in favor of bioactivity) and that water availability is appreciably less. Under continental climates, this last factor may enhance chemical solution of the glass and, related to cold winters, physical decay of the glass (microfracturation).

The comparison between Central European and Mediterranean decay processes in glass remains an open and suggestive field of research. Several questions arise from this study: Is the prevalence of chemical or biological processes mainly related to environmental aspects (i.e., water availability) correlated with climate? Has biodeterioration been underevaluated in Central European glasses? Are the K-Ca-rich Mediterranean glasses less similar than those claimed by major element chemistry for coeval Central European glasses? Finally, it seems clear that further research on biocide effects of some metals in medieval stained glasses can be very useful nor only in the preservation of our cultural heritage but also in the field of dangerous waste management.

Glass has been prospected as a toxic waste encapsulator in environmental management; direct glassmaking of metal-rich toxic materials has been also considered a potential inertization method (i.e., in the case of metals released by mine tailings). Some studies try to quantify the rate of chemical corrosion of glass under buried conditions (see Sterpenich and Libourel 2001), taking as a reference material medieval stained glass. This kind of glass was buried for centuries, thus it records the decay taking into account the only factor that usually we cannot reproduce in the laboratory, which is time. In contrast to this, we think that this paper provides new criteria to be considered in glass duration assessment: biological attack on glass must be taken into account as a potential risk in safe toxic waste management. Several biological experiments might be conducted to clarify metal toxicity against microorganisms, since addition of little amounts of some heavy metals (as Cu) might be of great interest to ensure durability of the glass containers.

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