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The glasses of the transept's rosette of the cathedral of Tarragona: characterisation, classification and decay

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The glasses of the rosette forming the main window of the transept of the Gothic Cathedral of Tarragona have been characterised by means of SEM/EDS, XRD, FTIR and electronic microprobe. The multivariate statistical treatment of these data allow to establish a classification of the samples forming groups having an historical significance and reflecting ancient restorations. Furthermore, the decay patterns and mechanisms have been determined and the weathering by-products characterised. It has been demonstrated a clear influence of the bioactivity in the decay of these glasses, which activity is partially controlled by the chemical composition of the glasses.

Keywords: glass, gothic, decay, bioactivity, colour

Los vidrios del rosetón del transepto de la catedral de Tarragona: caracterización, clasificación y alteraciones

Se han caracterizado numerosas muestras de los vidrios que forman el rosetón del transepto de la catedral de Tarragona mediante SEM/EDS, XRD, FTIR y microsonda electrónica. La aplicación de análisis estadístico multivariante permite establecer una clasificación de las muestras que refleja anteriores intervenciones de restauración. Además, se han estudiado los mecanismos y procesos de degradación, y se han determinado los productos de alteración. Ha quedado demostrada una clara ifluencia biológica en la alteración de estos vidrios, cuya actividad es parcialmente controlada por su composición química.

Palabras clave: vidrio, gotico, alteración, bioactividad, color

1. INTRODUCTION

The characterisation of glasses is one of the most important criterion to be considered in order to take decisions on how to restore and which are the best methods to be applied on them. Furthermore, quite often it is not easy to know the relative age of different pieces of a window after the restorations undertaken along the time. In the case of this rosette of the cathedral of Tarragona, the original drawing were practically lost after the destruction during the Independence War and the window was rebuilt with some of the original fragments plus many new ones.

During one of the phases of restoration of the cathedral affecting the transept, a complete restoration of the window was decided and thus, the different pieces forming it were dismounted and transported to the restorer's workshop. So that, before the intervention it was the opportunity to analyse samples of many fragments, including the grisaille, remains of ancient paintings and weathering layers formed along the time. Simultaneously, each of the pieces was studied to understand how they were mounted and the drawings more or less reconstructed. Most of the original pieces were mounted at the contrary of their original position, namely with the grisaille in the outer part. The glass windows exhibited a variety of decay forms occurred throughout the years since their first placement in the window's pieces.

The aim of this work is the characterisation of glasses forming the rosette of the transept of the Cathedral of Tarragona, including the decorative elements (namely grisaille and old paintings) as well as the identification of the decay forms, the diagnosis of the state of conservation and the recognition of the weathering layers. So that, the objectives of this paper are i) to identify the composition of the glass matrix (glass former, stabilizers and chromofor elements); ii) to determine, as far as possible, the production techniques of the different coloured glasses, including those so-called flashed glass; iii) to study the decay patterns and mechanisms; and iv) to use the chemical composition as a chronological tool and a technological and conservative criterion.

2. MATERIALS AND METHODS

Samples of different coloured glasses of the rosette were collected in the restorer workshop with the criteria of minimum affectation of the pieces (already broken fragments, etc.). The sampling criteria were to collect different glass colours, external and internal coatings (weathering layers and paintings), and grisaille types. So that, the set of samples studied cover the complete range of colours present in the rosette, the different types of grisaille, the ancient paints and the weathering layers.

During the sampling campaign complete and exhaustive in-situ stereomicroscopic studies of the whole set of glasses forming each piece was carried out in order to better understand the decay patterns, the position of the grisailles and the ways of application and conservation of ancient paints.

The samples were studied by using the classical analytical tools used in these kind of investigations, namely X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) with a dispersive energy analysis (EDS), wavelength analyses of dispersed X-ray (Electronic Microprobe) and Infrared Spectroscopy (FTIR). These different analytical methods are complementary and give a good characterisation of the glasses and of the new layers, including man-made paintings.

The samples were cutted with a low deformation diamond saw to prepare transversal polished cross sections once embedded in epoxy resin, to be analysed in the electronic microprobe (EM) and SEM/EDS to determine the chemical composition of the glasses. Several profiles crossing the samples were measured in order to have a picture of the homogeneity of the glass.

The surface of the glasses with grisaille was studied and analysed by SEM/EDS, which also allowed to see the weathering corrosion and the layers formed on the surfaces. Power scratched from these layers was analysed by XRD and FTIR to determine the new mineral phases (the crystalline corrosion products) generated by weathering, and the organic compounds, respectively.

3. RESULTS AND DISCUSSION

3.1. Glasses

3.1.1. CHEMICAL COMPOSITION

The chemical composition of the glass samples is given in table I. The data correspond the to the average of the points measured in each sample, except for the red flashed glass samples, in which the composition of each layer (red and colourless) is given.

The main component or network former of these glasses is silica (SiO_2), which values range from 40.18 to 73.84 %wt, while alumina (Al_2O_3) with contents from 0.65 to 3.75%wt, could be considered as stabilizer incorporated in the network in the silicon positions, and could be due to the addition of clays for the glass production. Sodium, potassium and calcium oxides act as fluxes, depending of each case. Jackson (1995) related the CaO with a common glass additive as limestone. And the chromofor elements are iron, manganese, copper, silver (as colloidal particles).

The P_2O_5 (from 0 to 4.3%wt) is always present (except in one sample) and its values can be considered as usual for medieval glasses. Its concentration is always related to the high amounts of potash and can be attributed to the ashes used as raw material to get potash (Freestone 1993). Together with these main components, some others element were also determined in lower proportions, such as PbO (0.01 to 0.36%wt), NiO (under 0.15%wt), TiO_2 (under 0.3%wt).

In order to classify the samples analysed by their chemical affinity, a statistical multivariate treatment was carried out considering the chemical concentration of glass former and fluxes elements (Si, Al, Ca, Mg, K and Na) as variables. The results as a dendogram show two different groups (Figure 1), one of which divided in two subgroups. These three sets of samples are in agreement with those showed in the ternary diagram of Figure 2 and correspond to the three typical compositions of silica glasses with different fluxes described by different authors. The average chemical composition of these three groups is given in Table II, and each group can be described as follows:

• Soda glass domain is characterized by a Na_2O contents higher than 11%, SiO_2 between 55-65% and K_2O over 4.8%. This composition is related by Schreiner and Grasserbouer (1985) and Gratuze et al. (1992) to medieval glasses. In general, the glasses of the 12th century have a high silica content, approximately 60% (Fernández-Navarro, 1996). They are considered as more water and humidity resistant due to the higher sodium proportion.

TABLE I. CHEMICAL COMPOSITION OF THE GLASS SAMPLES. THE NUMBERS BETWEEN BRACKETS CORRESPOND TO THE STANDARD DEVIATION.

		PbO	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO	MnO	FeO	NiO	CuO
Blue	T-22	0,08 (0,06)	0,34 (0,02)	4,65 (0,09)	2,15 (0,10)	43,22 (1,65)	3,62 (0,11)	17,13 (0,53)	17,83 (0,31)	0,14 (0,02)	1,13 (0,08)	0,99 (0,06)	0,02 (0,02)	0,17 (0,04)
	T-3	0,12 (0,11)	2,29 (0,44)	3,09 (0,09)	1,03 (0,06)	73,84 (1,06)	0,27 (0,09)	0,84 (0,12)	7,30 (0,10)	0,11 (0,03)	0,36 (0,04)	0,91 (0,05)	0,15 (0,03)	0,03 (0,02)
	T-2	0,06 (0,06)	0,33 (0,03)	4,78 (0,04)	2,26 (0,09)	45,77 (1,81)	3,39 (0,09)	15,49 (0,53)	18,12 (0,34)	0,16 (0,02)	1,13 (0,07)	0,99 (0,06)	0,03 (0,02)	0,21 (0,03)
	T-41	0,08 (0,05)	0,37 (0,07)	4,86 (0,1)	2,21 (0,07)	41,99 (0,77)	3,47 (0,24)	17,74 (0,17)	18,21 (0,09)	0,15 (0,03)	0,00 (0,05)	0,00 (0,05)	0,01 (0,02)	0,19 (0,05)
Blue turquoise	T-33	0,04 (0,05)	15,86(0,19)	3,46 (0,04)	1,62 (0,07)	56,96 (1,24)	0,59 (0,10)	2,07 (0,04)	7,30 (0,08)	0,12 (0,02)	0,27 (0,06)	0,62 (0,04)	0,02 (0,02)	2,22 (0,09)
Brown-yellow	T-42	0,10 (0,11)	11,65(0,15)	2,68 (0,05)	3,64 (0,03)	61,56 (0,31)	0,44 (0,07)	2,44 (0,04)	9,52 (0,15)	0,30 (0,02)	3,27 (0,07)	3,62 (0,13)	0,02 (0,02)	0,04 (0,02)
	T-32	0,03 (0,05)	0,33 (0,03)	4,68 (0,20)	2,18 (0,06)	47,91 (2,39)	3,53 (1,29)	18,95 (2,44)	17,32 (0,49)	0,15 (0,03)	1,00 (0,07)	0,45 (0,05)	0,01 (0,02)	0,06 (0,04)
Colour-less	T-5	0,06 (0,09)	0,38 (0,17)	4,79 (0,07)	2,22 (0,05)	48,17 (1,04)	3,82 (0,16)	18,26 (0,76)	17,92 (0,25)	0,15 (0,03)	1,04 (0,08)	0,46 (0,06)	0,01 (0,01)	0,09 (0,05)
	T-27	0,36 (0,20)	15,70(0,18)	0,12 (0,04)	0,63 (0,12)	63,11 (1,08)	0,00 (0,01)	0,13 (0,02)	11,41 (0,7)	0,07 (0,02)	0,01 (0,02)	0,09 (0,03)	0,02 (0,02)	0,03 (0,03)
Green	T-36	0,02 (0,03)	14,77(0,12)	0,09 (0,02)	2,01 (0,05)	59,13 (1,41)	0,04 (0,03)	1,34 (0,02)	9,86 (0,06)	0,04 (0,03)	0,19 (0,06)	0,34 (0,06)	0,02 (0,02)	1,39 (0,06)
	T-29	0,04 (0,04)	13,22(0,18)	2,57 (0,03)	3,75 (0,08)	55,35 (1,31)	0,88 (0,09)	4,85 (0,06)	6,48 (0,09)	0,16 (0,02)	0,07 (0,04)	1,68 (0,18)	0,00 (0,01)	3,28 (0,12)
	T-21	0,07 (0,06)	16,85(0,19)	3,77 (0,06)	2,75 (0,07)	54,71 (1,01)	0,46 (0,09)	2,08 (0,17)	9,55 (0,15)	0,19 (0,02)	0,90 (0,07)	1,02 (0,07)	0,02 (0,02)	0,01 (0,02)
Purple	T-23	0,08 (0,09)	4,18 (0,96)	3,85 (0,05)	3,05 (0,07)	62,31 (1,29)	0,53 (0,06)	2,19 (0,22)	8,46 (0,13)	0,15 (0,03)	2,34 (0,08)	1,14 (0,06)	0,01 (0,01)	0,03 (0,03)
	T-4	0,01 (0,02)	8,07 (6,41)	0,08 (0,02)	0,75 (0,02)	58,77 (9,54)	0,04 (0,03)	0,23 (0,02)	11,10 (0,24)	0,05 (0,03)	4,17 (0,20)	0,22 (0,06)	0,03 (0,03)	0,04 (0,02)
	T-17	0,04 (0,05)	17,53(0,22)	3,34 (0,07)	3,54 (0,05)	60,78 (0,77)	0,39 (0,13)	2,29 (0,04)	8,32 (0,06)	0,21 (0,03)	1,40 (0,08)	0,76 (0,07)	0,01 (0,01)	0,02 (0,03)
Purple (dark)	T-28	0,02 (0,03)	15,29(0,14)	0,24 (0,05)	1,97 (0,07)	65,31 (0,36)	0,64 (0,10)	4,39 (0,10)	7,17 (0,074)	0,11 (0,03)	0,93 (0,07)	0,48 (0,08)	0,02 (0,02)	0,03 (0,03)
	T-40	0,04 (0,06)	0,38(0,14)	4,42 (0,10)	0,65 (0,09)	40,18 (1,57)	1,24 (0,08)	15,59 (0,22)	22,41 (0,2)	0,10 (0,02)	0,64 (0,08)	0,26 (0,04)	0,01 (0,02)	0,00 (0,02)
Red-flashed glass	T-6	0,06 (0,07)	0,37 (0,03)	4,83 (0,09)	2,32 (0,04)	46,27 (1,16)	3,79 (0,25)	17,90 (0,43)	17,99 (0,29)	0,14 (0,03)	1,03 (0,09)	0,44 (0,05)	0,02 (0,02)	0,40 (0,39)
	T-31	0,01 (0,03)	0,36 (0,04)	4,69 (0,15)	2,27 (0,05)	48,61 (0,32)	4,33 (0,16)	18,84 (0,40)	17,54 (0,30)	0,17 (0,02)	1,00 (0,04)	0,52 (0,05)	0,01 (0,02)	0,32 (0,42)
	T-35	0,08 (0,08)	0,41 (0,03)	4,49 (0,13)	2,30 (0,07)	41,53 (1,83)	3,45 (0,34)	17,43 (0,42)	17,15 (0,50)	0,16 (0,04)	1,07 (0,05)	0,47 (0,07)	0,03 (0,03)	0,39 (0,33)

TABLE II. AVERAGE CHEMICAL COMPOSITION OF THE THREE GROUPS. THE NUMBERS BETWEEN BRACKETS CORRESPOND TO THE STANDARD DEVIATION.

	PbO	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO	MnO	FeO	NiO	CuO
Group I	0,06 (0,02)	0,36 (0,03)	4,69 (0,15)	2,06 (0,53)	44,85 (3,18)	3,40 (0,86)	17,48 (1,25)	18,27 (1,59)	0,15 (0,02)	0,89 (0,36)	0,51 (0,31)	0,02 (0,01)	0,20 (0,14)
Group II	0,09 (0,12)	15,1 (1,91)	2,04 (1,61)	2,49 (1,12)	59,61 (3,77)	0,43 (0,30)	2,45 (1,53)	8,70 (1,67)	0,15 (0,08)	0,88 (1,08)	1,07 (1,13)	0,02 (0,01)	0,88 (1,28)
Group III	0,04 (0,05)	4,85 (2,94)	2,34 (1,99)	1,61 (1,25)	64,97 (7,88)	0,28 (0,25)	1,09 (1,01)	8,95 (1,95)	0,10 (0,05)	2,29 (1,90)	0,76 (0,48)	0,07 (0,08)	0,03 (0,01)

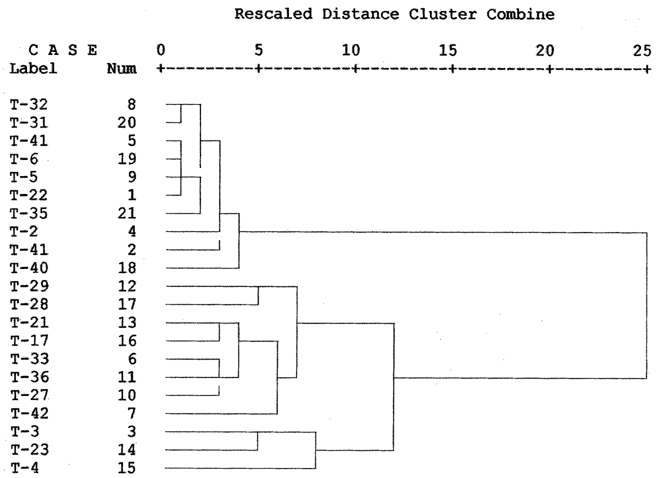

Figure 1. Dendogram showing the presence of three glass populations.

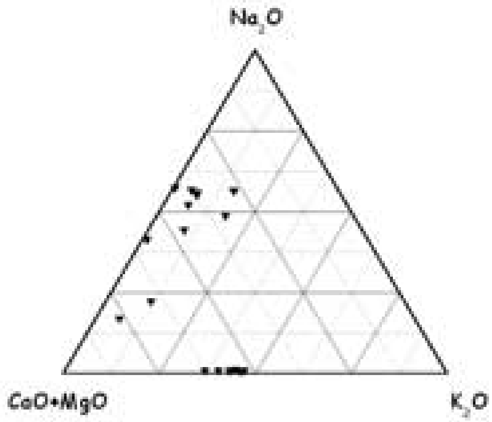

Figure 2. Ternary diagram with the different domains according to their main composition.

• Lime-potash glass domain is characterised by a poor silica contents, 40-48.6% contributing to decrease their chemical stability. The main elements in this group are 17-22% of CaO, 15-18% of K_2O and 0.4% of Na_2O. Normally, this composition is attributed to glasses from 13th to 15th centuries (Cox and Ford, 1993) and these type of glasses were used during the Romanesque and Gothic periods (Schreiner, 1988). The observations on this window seem to show a correlation between the development of an external weathering crust with the potash content of the glass.

• Lime glass domain is constituted by 7-11% of CaO, high a silica proportion 59-74%, between 2-8% of Na_2O and 0.2-2% of K_2O. The increase in silica and the decrease in potash represent an improvement of the glass quality. Generally, this composition corresponds to glasses produced since the 15th century.

3.1.2. COLOURING AGENTS

Two types of coloured effects were determined in this glasses. The first obtained by the presence of the oxides of transition metals such as iron, manganese and copper (Table I) in the silica network, dissolved in the glass matrix. The iron is the main colourant for green, green-yellow and yellow glasses. Other chromatic effect is due to the colloidal dispersion of insoluble metallic particles such as those of silver stains. The colour obtained depends not only of the ions, but also of the presence of other oxides, their state of oxidation and the temperature and conditions in the kiln. Mirti et al. (2000) affirmed that the hue is determined by the Fe^{+2}/Fe^{+3} ratio, while the saturation depends on the iron concentration.

• purple glass colour: in this case the colour is due to the Mn^{2+} ion. Increasing the manganese content, the colour of the glass becomes more saturated. Some authors (Pérez y Jorba and Bettembourg, 1989) related this element with glass opacification and brown coloration, probably with higher concentrations that those find here.

• turquoise blue glass colour: in this case the colouring agent is copper, about 2% of CuO and some iron, in agreement with the colour generation by copper in alkaline glasses (Bamford, 1977).

• blue glass colour: the cromphor oxides are FeO and MnO (Fernández-Navarro, 1997). All the blue glasses studied here are K-rich.

• green glass colour is due to a combination of two elements, copper and iron (probably as Fe^{+2}). In this case the CuO proportion is higher than 1.4%, reaching 3.28% in some cases. The saturation of green is attributed to different proportions of FeO and Fe_2O_3 (Newton and Davison, 1997; Heck and Hoffmann, 2000).

• brown-yellow glass colour results of the combination of Mn^{2+} and Fe^{+3} as chromophers.

• the red glass colour due to Cu_2O. Copper is present in amounts between 0.4 and 0.9 wt%, being the Cu_2O colloids responsible for the red colour. This is why the thickness has to be very low and thus, the red glasses are formed by two layers (flashed glass), one red and one colourless. According with Freestone (1993) the medieval red enamels coloured by copper present a high content of phosphorus (in this case approximately 4%), attributed to woodash glass.

• yellow glasses are coloured by a colloidal dispersion of metallic silver nanoparticles. The images obtained with backscattered electrons in the SEM (Figure 3) show of a bright layer diffused from the surface to the inner part, which corresponds to the area of higher concentration of silver.

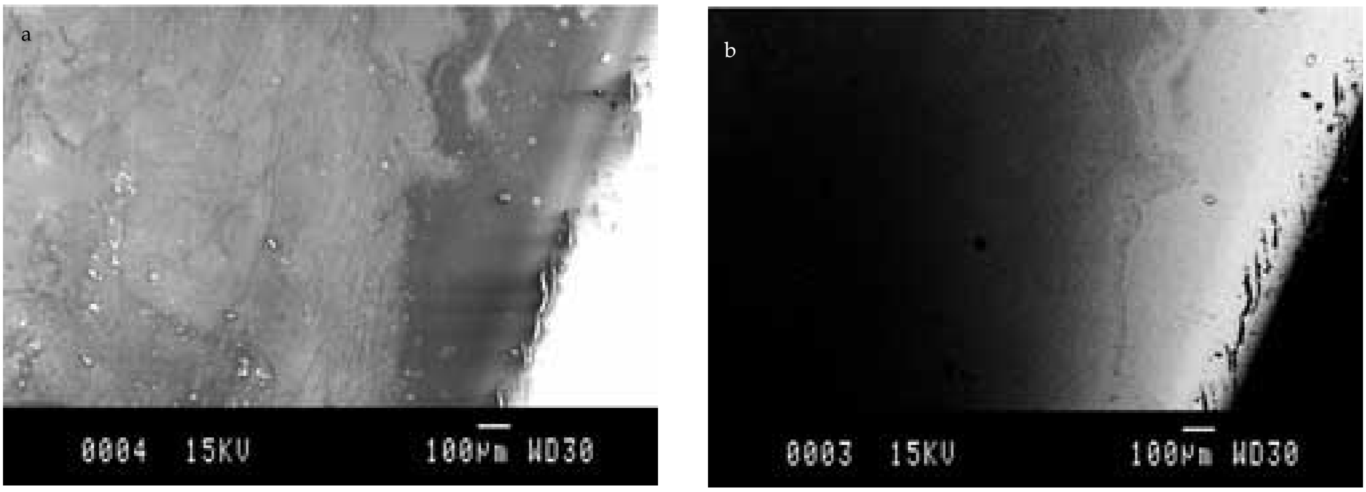

Figure 3. SEM photographs of silver stained glass cross section (left SEI image; right BSE image) There are some little cracks close to the surface. The BSE micrograph illustrates the silver dispersion into the glass network.

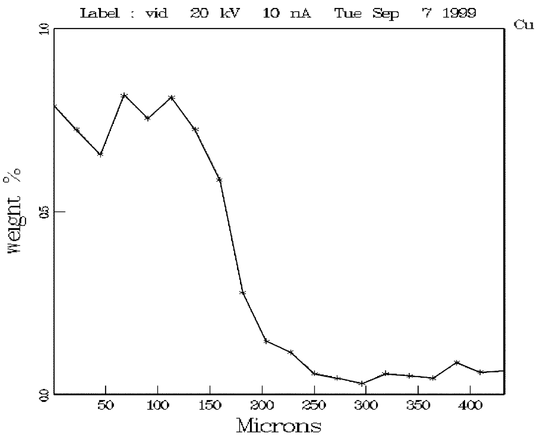

Figure 4. Compositional profile of copper concentration in the red glass *flashed glass*. The profile was obtained by measuring different points along a cross line.

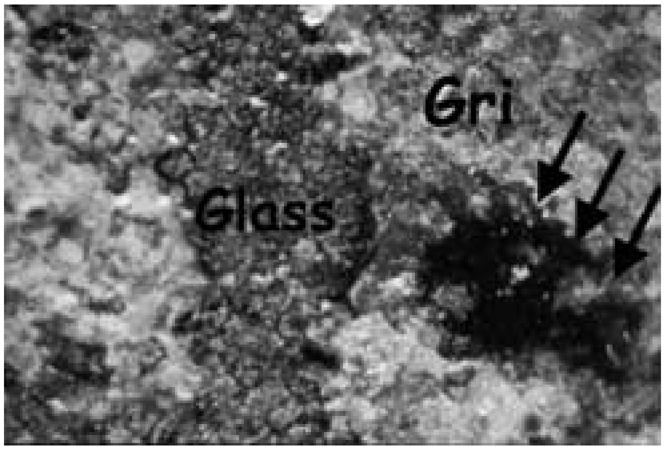

Figure 5 . Photomicrography (incident light) of grisaille (labeled Gri) partially affected by bioactivity (biopitting) (marked with arrows). All is coated by an orange patina.

3.1.3. STRATIGRAPHY OF GLASS

Two main types of stratigraphy (cross sections) have been found in this rosette. One corresponds to homogeneous glasses with the colour uniformly distributed through the glass mass. Some of the samples are coloured and other ones colourless, without any chromophor element. The other type is the so-called *flashed glass*, formed by two layer of glass, one red and an other one colourless.

The red layer has different thicknesses from 160mm to 200mm, while the colourless layer is about 2.5mm thick. From the chemical point of view the difference is the copper content of the red layer (see Table I). A profile of the copper content obtained by measuring several points along a cross line is shown in Figure 4. This typology is attributed to glasses made during the 16th century (Spitzer-Aronson, 1974; Bettembourg, 1976).

3.2. Grisaille

Some glasses are decorated with grisaille consisting in a black opaque glass (with silica as main component), coloured by iron oxide for the black grisaille and copper oxide for the brownish one. The grisaille, together with the silver yellow stain of some glasses, compose the drawings that form the decoration of the window.

In most of the cases studied, the grisaille has a good state of conservation except some pieces, which grisaille is located in the external part of the windows (outdoor due to an erroneous restoration) and has been partially affected by organic activity (Figure 5).

In this study we determined two types of grisaille, attributed to different dates, which main difference is their homogeneity. In the SEM observations (Figure 6) the typical heterogeneity characteristic of the grisailles having a good firing process can be seen.

The contact between glass and grisaille is clear and does not present new mineral phases or corrosive elements (Figure 7). Only in few points gypsum has been determined as neoformed into the pore system of the grisaille (Figure 8). Sometimes the grisaille is coated by a patina and occasionally it is coated by an ancient painting (which also coats the glasses), applied in the 20th century to darken the nave of the cathedral.

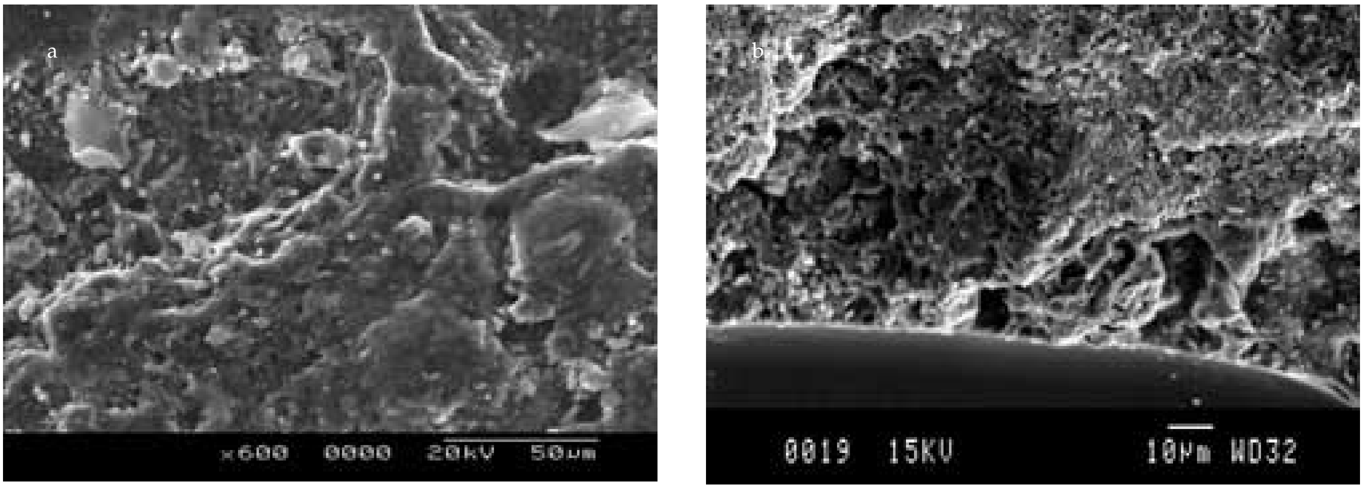

Figure 6. SEM observations showing the typical heterogeneity, characteristic of the grisailles having a good firing process.

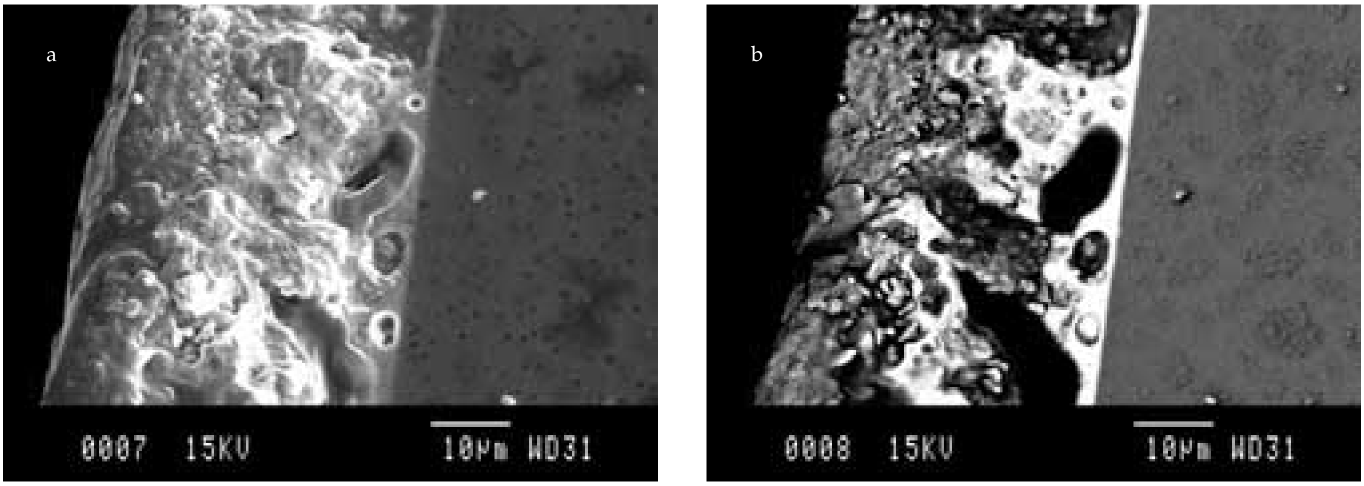

Figure 7. SEM photography of the contact between grisaille and the glass. Left: SEI image; right: BSE image. The contact between both is clean and flat. In the outermost part (darker in the BSE image) can be recognised the weathering layer.

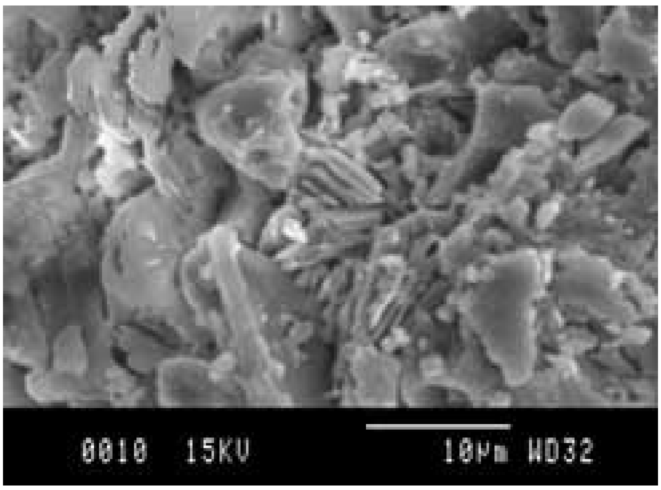

Figure 8. SEM image corresponding to gypsum neoformed into the pore system of the grisaille.

3.3. Weathering

Many glasses exhibited a "weathering crust" external or internal, which were removed from the glass by a diamond tool in order to be analysed by XRD and FTIR.

3.3.1. EXTERNAL CRUST FORMATIONS

Sometimes, the external part of glasses of the rosette show a layer of new mineral phases. The thickness of this authigenic layer depends on both, the glass composition and the environment conditions. In some pieces this layer was found in the external and the internal glass faces. Since these layers are formed in the outer part, it confirms that these pieces were inverted from their normal position in an ancient restoration.

Depending of the degree of adhesion we established two types of crust or patinas, all of them orange and formed by a single layer. Different origins are proposed for both.

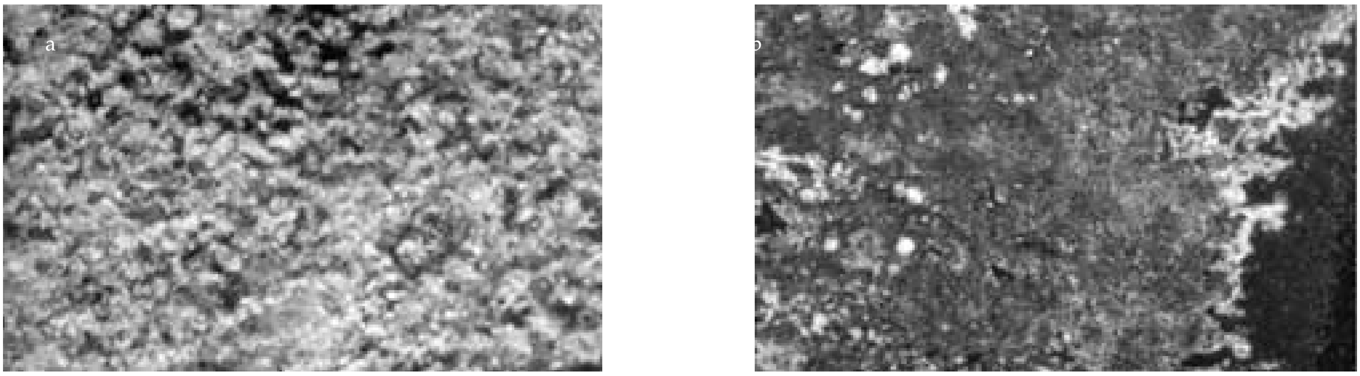

Figure 9. Photomicrographs (incident light) of an orange patina type I. In the right image one can see the effects of the lixiviation (right part of the image) of the glass as well as some pitting produced by microorganisms (left part of the image).

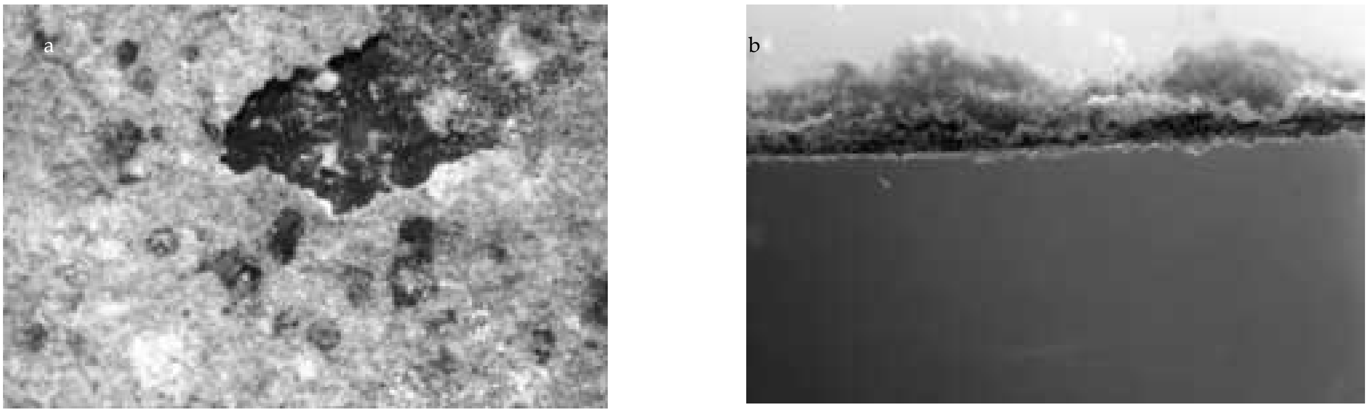

Figure 10. Microphotographs (incident light) of an orange patina type II. Left: observation of the surface; right: cross section. In the cross section can be appreciated the effects of biopitting in the glass surface, below the patina. Some pitting cal also be observed on the surface of the patina (left image)

- Type I: orange layer with high adhesion, extremely hard and that cannot be mechanically separated from the glass subtract. It is homogeneous, uniform and compact. Its surface exhibits a botryoidal texture and sometimes, pits. Investigations carried out by XRD and FTIR showed that in many cases, the main minerals forming these layers are quartz [SiO_2] and gypsum [Ca $SO_4 \cdot 2H_2O$], with few calcite [$CaCO_3$] and weddellite [Ca $(COO)_2$ $2H_2O$]. The origin of quartz could be attributed to glass lixiviation, consequence of an hydrolytic attack or to a dry deposition from the atmospheric dust.

When this patina is removed by cleaning, the surface of underlying glass appears roughness and the glass loss transparency. In this cases we determined remains of bioactivity, which provoked pits responsible of the decreasing of transparency of the glass. The biogenic formation of calcite, weddellite and perhaps gypsum is a process influenced by micro-organisms colonizing the surfaces (Krumbein, 1986; Garcia-Vallès, et. Al., 1996a; Garcia-Vallès, 1996b; Garcia-Vallès, 1997). In a case we determined the relative age of this patina, which was developed on a glass corresponding to a repair from twenty years ago. Micro-organisms could be the possible responsible of its formation, as the image showed in Figure 9 suggests.

- Type II: orange layer poorly attached to the substrate, in contact with the unaltered glasses. This deposit is formed by two minerals: quartz and gypsum, and their extension is not uniform (Figure 10). According to the composition, it could be a remain of some ancient paintings on the glasses of the windows.

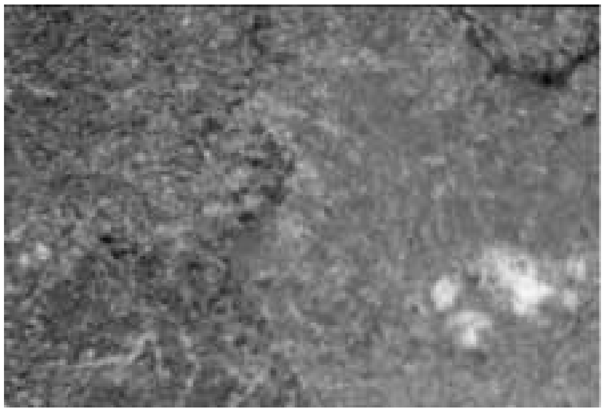

Figure 11. Microphotograph (incident light) of internal layer type I, mainly formed by gypsum, showing its botryoidal aspect.

3.3.2. ANCIENT PAINTINGS

In the inner glass faces (indoor) we determined two different types of man-made coatings applied in some epoch to create a dark atmosphere in the naves. The morphology and composition of both types depend of the glass composition.

- Type I: black or dark-brown layer with a good adhesion to the glass. The mineral composition is quartz, gypsum, calcite, weddellite and syngenite [$K_2Ca(SO_4)_2 \cdot H_2O$] (neoformed mineral phase produced by a secondary reaction between gypsum and the lixiviate solutions of the K-rich glasses) (Figure 11).

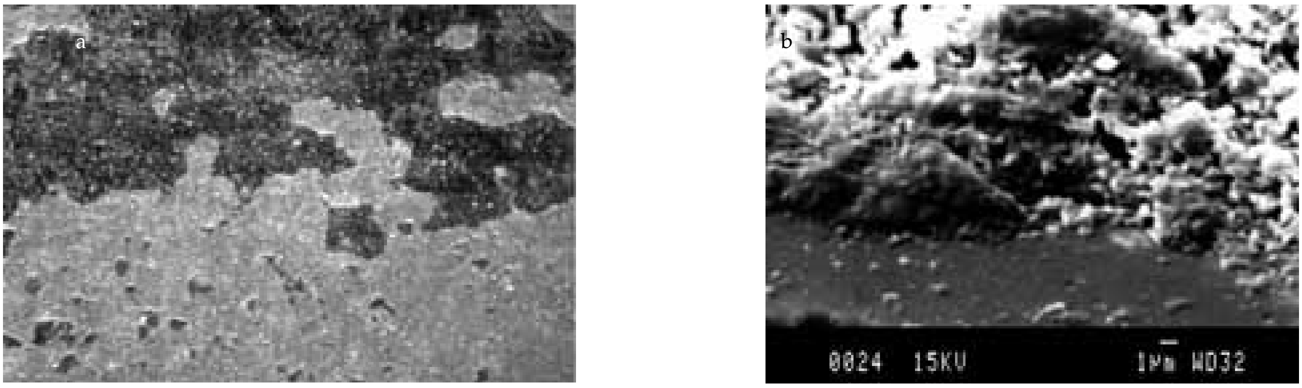

Figure 12. Microphotograph (incident light) and SEM of an internal layer type II.

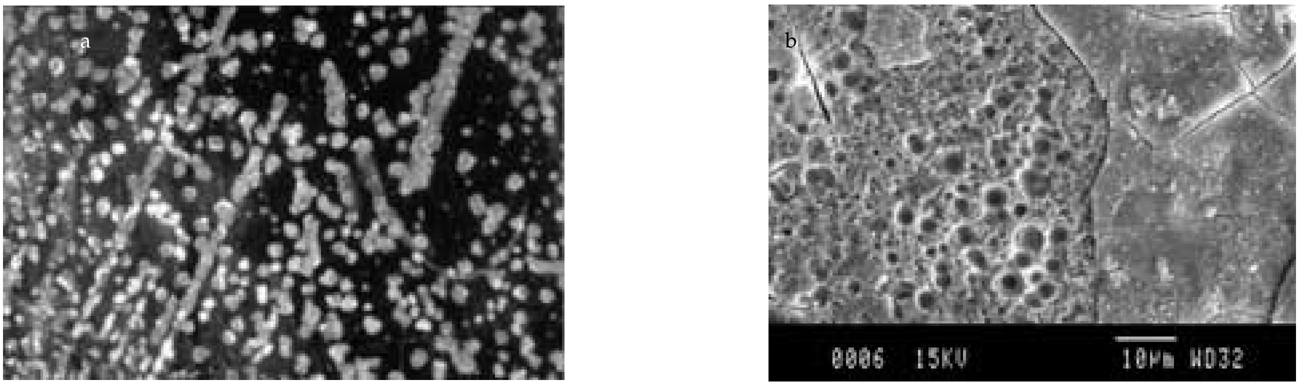

Figure 13. Bioactivity developed in the red part of the *flashed glass* glass. Observe the corrossion figures.

- Type II: dark coating badly adhered to the glass. It was applied on the glass and on the grisaille as a painting. Mineral composition are quartz, gypsum and calcite (Figure 12) with an undetermined organic binding.

3.4. Decay

In general, the glasses forming this rosette are well preserved and unaltered. The glasses made with potash flux are more easily decayed by atmospheric corrosion. The only decay phenomenon observed is related to bioactivity. Some authors, Callot et al. (1987), Ehrlich (1990), Krumbein et al., (1991, 1996) among others, established the importance of biological activity in the alteration of glasses, as processes developed at low temperature.

This attack leads to the glass opacification in combination with the orange patina type I, as well as biopitting or small holes more or less developed depending of the glass composition. In some cases the bioactivity affected the glass and also the patina.

A quite modern piece of purple glass (sample No. 40) was relatively affected by sun exposition (12 years), and/or multiple interaction of biological and physic-chemical phenomena; along this short time itsr colour changed to become blue. This fact could be related to the destruction of the colour centres by the UV radiation, however this aspect has not been analysed in this paper.

The penetration of the bioactivity in these glasses is related with the chemical composition. Some elements play a role as inhibitors of the bioactivity (like Cu, for instance). In the red flashed glasses, the bioactivity is stopped when the organisms reached the Cu-rich layer and thus, they stopped their destructive activity that only affected the colourless layer. In those samples showing ancient bioactivity, it occurs a non-uniform spatial distribution of pitting on the surface of the glass. In some cases, the biopitting formed a pattern of channels like those shown in Figure 13.

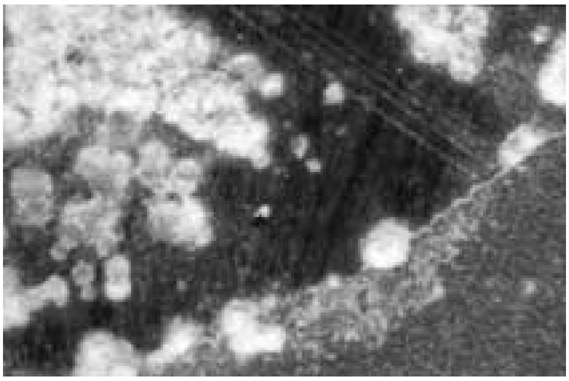

Figure 14. Microphotograph (incident light) of selective bioactivity. In this case when the organism reached the grisaille stopped its activity.

An other example supports the conclusions of Krumbein et al. (1991): when the drawing were made with silver yellow, the biological attack delays the destructive action considerably. In some other pieces, the bioactivity shows a important development on the glass but it was stopped when the grisaille was reached (Figure 14).

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