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# Deterioration of stained glass by atmospheric corrosion and micro-organisms

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Mediaeval stained glasses are characterized by a high content of modifier ions responsible for their sensitivity towards atmospheric corrosion. Sulphur dioxide associated with moist air is the main agent responsible for alterations and products involved in the corrosion are mainly sulphates. Micro-organisms are other destructive agents of the glass surface. Some of them metabolize iron and manganese and their intervention in the displacement of such elements is considered.

## 1. Introduction

The conservation of mediaeval stained glass has been the subject of multidisciplinary research since a phenomenon of accelerated degradation has come to light in Europe. Studies of this deterioration occurring in mediaeval stained glass are very complex because of the numerous factors involved, depending both on the glass characteristics (composition, colour, thermic history) and on external conditions (climate, exposure, environment). Ancient glasses are attacked by atmospheric pollution due to humidity, $CO_2$ and sulphuric effluents. Because the great majority of French glasses are very rich in modifying elements such as potassium and calcium, they are particularly vulnerable to environmental aggressions. Sulphuric anhydride which is present with water in the air is principally responsible for atmospheric corrosion.

Two different types of decay are observed on stained glass:

(a) in some cases the corrosion starts by a pitting of the surface, and as the pits increase in number and size, they join together to form craters with a deterioration of the glass bulk;

(b) in other cases, the whole surface of the panels turns opaque and is covered with a layer of corrosion products called "weathering crust". The corrosion products arise from the reaction of sulphuric anhydride with the modifying elements and are mainly sulphates. The composition of the glass is the primary factor which determines the durability and the appearance of the various sulphates. The pitted glasses are characterized by the presence of only gypsum $CaSO_4$, $2H_2O$, while the "weathering crust" is a mixture of gypsum and the double salt syngenite: $K_2SO_4 \cdot CaSO_4$, $H_2O$.

The alkali content rules the formation of the two sulphates.

Previous papers [1–3] deal with the chemical aspect of the atmospheric deterioration. Especially, the study of the specific behaviour of former and modifier ions observed by electron microprobe analysis allow an approach to the corrosion process.

Besides the sulphuric anhydride attack, it is also necessary to take into consideration the action of other destructive agents: micro-organisms [4]. Fungi, lichens and algae all favour the maintenance of humidity on the glass surface while many bacteria produce acid secretions.

The present paper describes some preliminary observations of the attack of the glass surface by micro-organisms. Two examples will be considered: the first is a purple glass from Evron (Mayenne) dating from the 14th century. The second is related to the panel of "The New Covenant" from Bourges Cathedral in the 13th century.

## 2. Experimental details

Corrosion products were identified by X-ray diffraction analysis. Some samples were coated with gold and observed in a scanning electron micro-

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TABLE I Analyses of two mediaeval glasses (wt%)

| | Evron | Bourges |
|---|---|---|
| $SiO_2$ | 50.8 | 53 |
| $K_2O$ | 15.32 | 17.9 |
| $Na_2O$ | 2.89 | – |
| CaO | 14.86 | 14.5 |
| MgO | 6.99 | 5.2 |
| $P_2O_5$ | 4.90 | 3.5 |
| MnO | 2.11 | 1.02 |
| CuO | 0.044 | < 100 ppm |
| CoO | – | – |
| $Fe_2O_3$ | 0.62 | 0.34 |

scope at 20 kV. On the other hand, the depth and the nature of the pits were determined by microprobe analysis. In accordance with the norms recently established for glasses rich in alkali, an area of 200 to 300 $\mu$m was scanned for less than 10 sec. The current intensity was 30 to 80 nA at 15 kV [5].

Both samples were analysed by X-ray fluorescence and chemical absorption. The compositions are given in Table I.

## 3. Results and discussion

Some isolated craters resulting from atmospheric corrosion are visible on the external surface of the stained glass from Evron. This kind of attack is characteristic of glass which has a moderate alkali content, where the pits are few and separate [3]. Fig. 1 shows the deterioration at the surface as well as at the bottom of a crater where numerous cracks have formed. Corrosion products are located in these cavities; since corrosion was minimal, X-rays detected only traces of gypsum.

An examination of the internal face of the window reveals another type of alteration, due to the presence of micro-organisms. Fig. 2 shows the difference in aspect of this surface deterioration. Numerous circular holes occur as the result of perforating action of the micro-organisms. The degradation then continues in the subjacent glass before resurfacing at the periphery, producing alteration in concentric zones around the original point of attack. The bottom of the crater is covered with filaments which indicate the presence of fungi.

The purpose of this research is not to identify these biological corrosion agents, but only to determine the effects of their proliferation on the structure of the glass.

Biological corrosion is accompanied by opacification of large black spots within the glass. Fig. 3 shows the beginning of an attack observed in cross-section by optical microscope. The affected zone is characterized by evenly-spaced concentric striations never before observed in the study of atmospheric corrosion. This rhythmic growth is linked to the progression of the micro-organisms.

Microprobe analysis (Fig. 4) allows the observation of the distribution of the different elements of the glass in a similar region.

(1) The zone of attack is enriched in network formers Si and Al, which confirms the decrease in modifying elements. Phosphorus, which is considered as a former, behaves differently from the above elements in that it is largely lacking in the affected zone, but is present in a slightly higher concentration at the centre.

(2) Modifying elements such as K and Mg are practically eliminated.

(3) Calcium is also extracted, although present at the centre in slightly higher concentration.

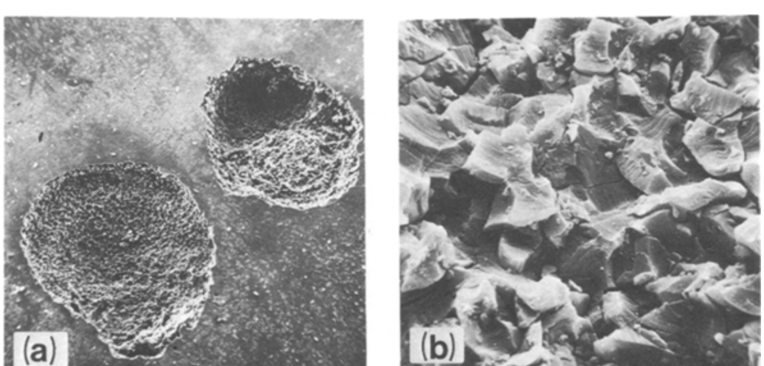


*Figure 1* Scanning electron micrograph of the localized attack by atmospheric corrosion. External face of stained glass (purple glass dating from the 14th century, Evron). (a) Deterioration of the surface by separate pits (× 50). (b) Bottom of crater with block decohesion and cracks (× 1000).

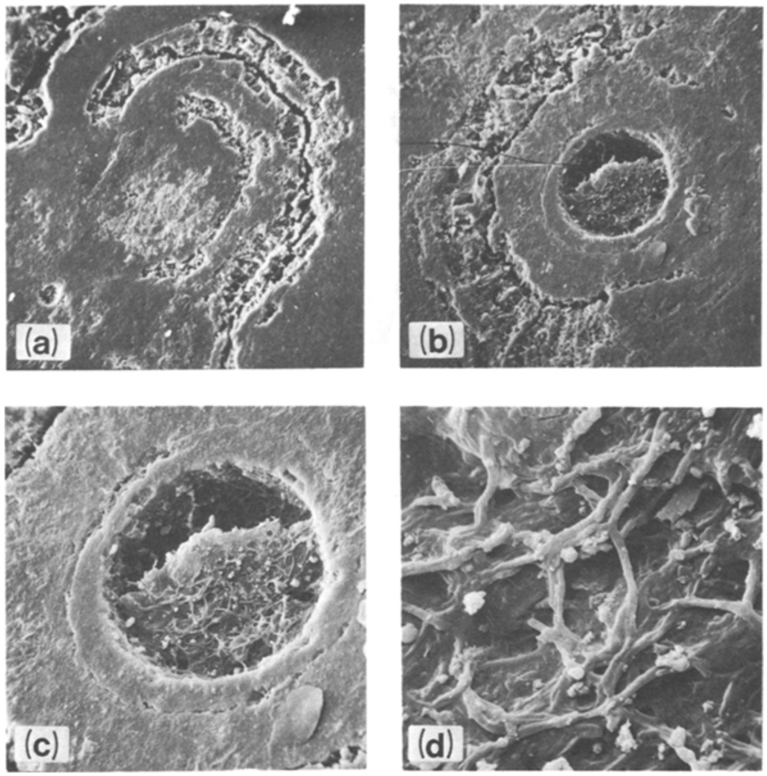


*Figure 2* Scanning electron micrograph of the biological corrosion. Internal face of the stained glass. (a) and (b) perforating action of micro-organisms and circular evolution of alteration (X 200). (c) X 400 and (d) X 2000, bottom of perforation with fungi.

(4) Traces of sulphur are visible in the cracks although without any obvious correlation with calcium.

These results are similar to those obtained on samples corroded by atmospheric pollution. It would seem, in particular, that there is an associated migration of calcium and phosphorus [6].

The observation of the minor elements shows a precipitation of manganese in the cracks, as seen in Fig. 4. On the other hand iron and titanium are not displaced. "In nature, the biogeochemistry of iron and manganese is manifested in a striking fashion" [7]. The ferrobacteria which metabolize iron are able to transform bivalent iron to a trivalent state. These same micro-organisms also metabolize manganese [7–9] and their intervention in the displacement of certain elements cannot be ruled out. However, it is difficult to separate the two types of corrosion, which in the majority of cases must act simultaneously. The almost complete disappearence of potassium and magnesium most probably can be attributed to the action of water.

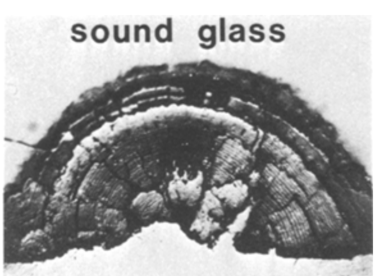


*Figure 3* Optical micrograph showing biological corrosion on the glass of Evron (seen edge-on X 160).

The examination of a panel of 13th century glass from Bourges cathedral supplies another example of biological corrosion. The corrosion features are different for the external and internal faces.

(a) Fig. 5 is related to the examination by microprobe analysis of the external face of a purple glass which has been altered in depth by multiple large diameter craters, resulting in a total

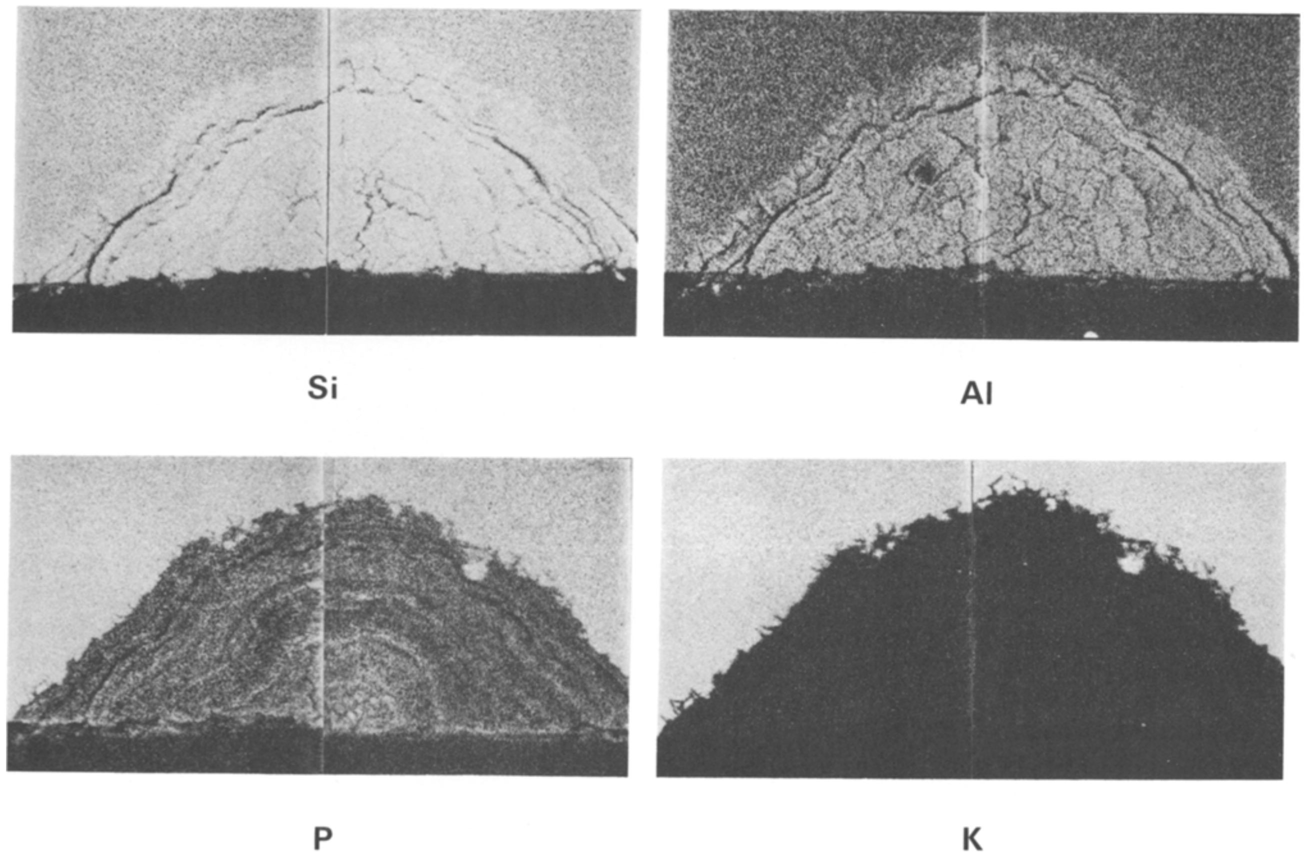


*Figure 4* Microprobe analysis of the beginning of an attack observed on the glass of Evron. Each picture is obtained with the $K\alpha$ radiation of the corresponding element ( 300 $\mu$m × 300 $\mu$m).

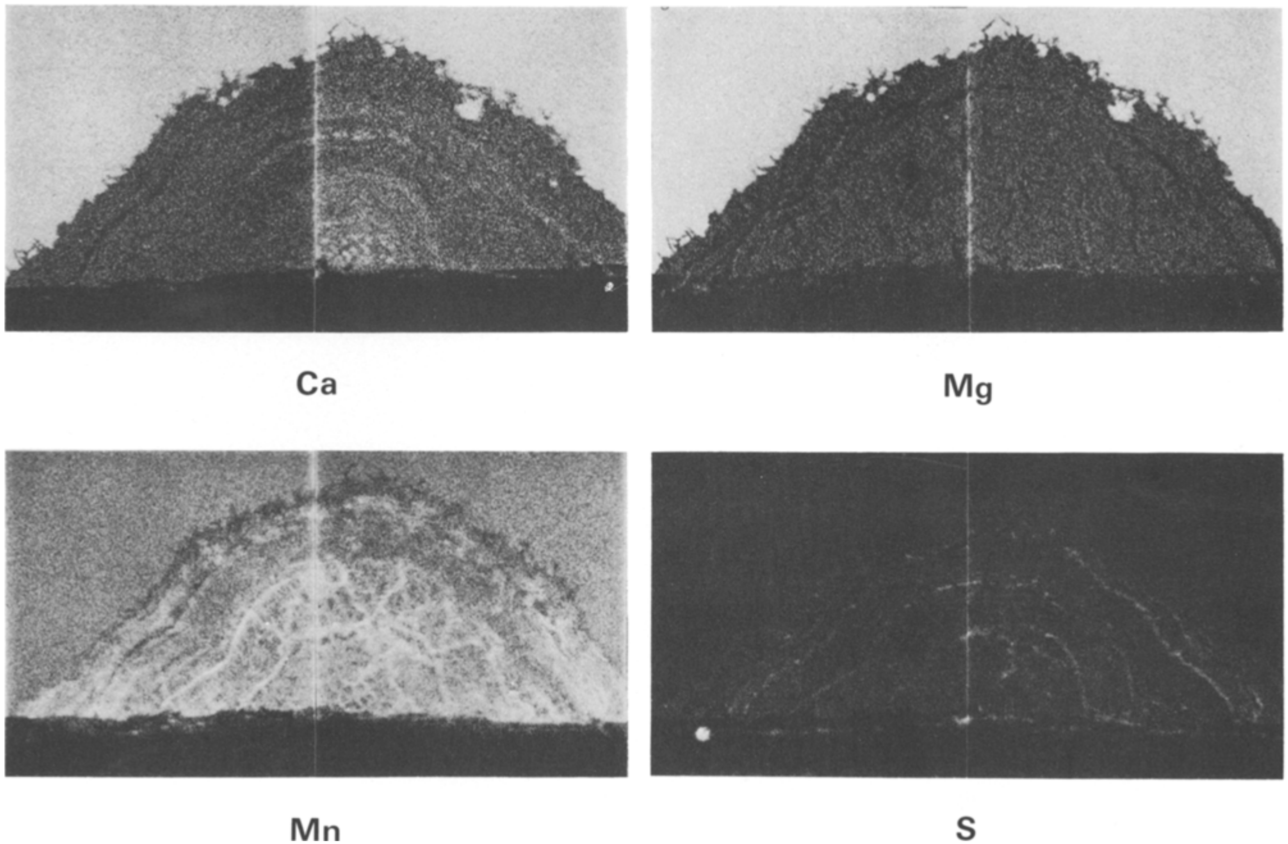


*Figure 4 (continued)*

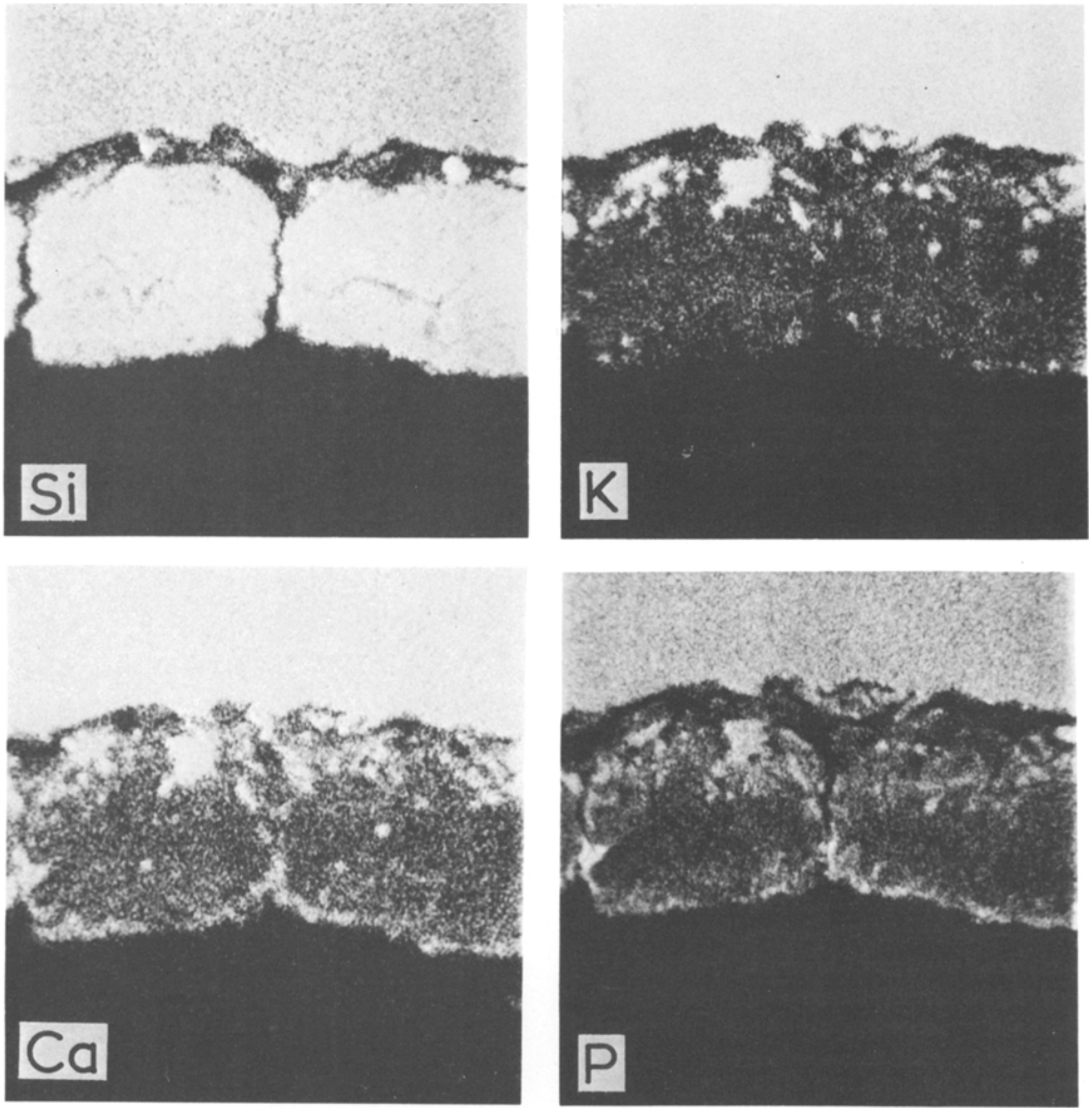


*Figure 5* Microprobe analysis of the external face of stained glass from Bourges cathedral (area 250 $\mu$m X 250 $\mu$m).

destruction of the surface. As indicated in Fig. 5, the constituent elements of glass follow the usual behaviour produced by atmospheric agents. Some remarks may be made concerning low-content elements.

(1) Manganese is lacking in the affected zone and is not found in the cracks.

(2) Iron is present in greater quantities at the edge of the healthy glass while at the same time a localization identical to that of sulphur is clearly detected.

The presence of sulphur unassociated with calcium suggests a possible intervention of sulpho-bacteria. These bacteria take their energy from oxido-reduction reactions using inorganic substances. The sulphur-reducing bacteria cause the reduction of sulphites and sulphates in an aqueous environment. In stained glass subjected to atmospheric corrosion the formation of more or less soluble sulphurated compounds should be an ideal place for their development.

(b) The internal face of the glass is covered by a hard, thick crust composed mainly of calcite $CaCO_3$ with a small amount of gypsum. In addition to these two compounds, another phase has been identified by X-rays: calcium oxalate

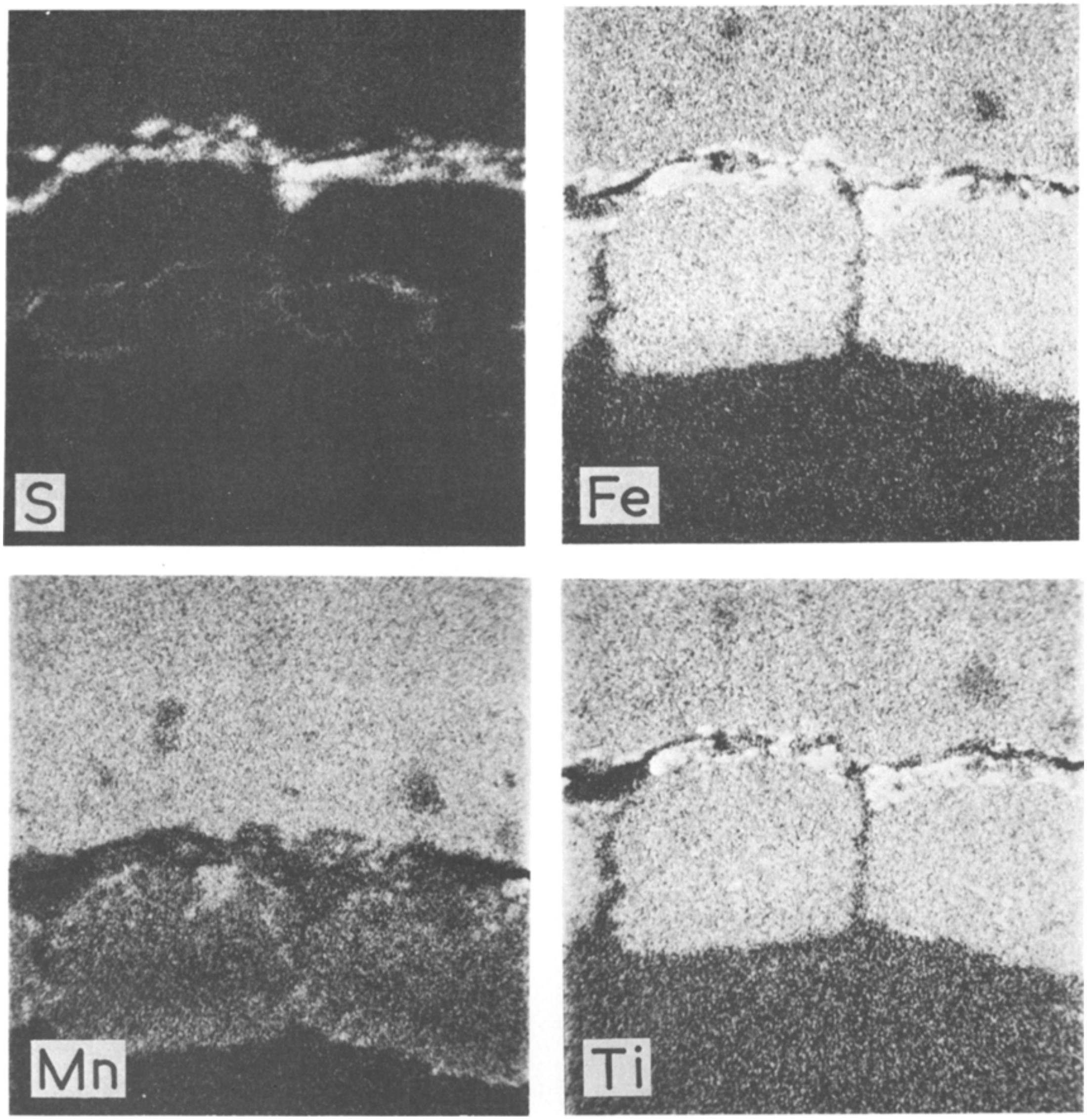


*Figure 5* (*continued*)

$CaC_2O_4$, $2H_2O$. Infra-red spectroscopy completed at the "Laboratoire de Recherches des Monuments Historiques" has confirmed its existence. Also, this same phase has often been demonstrated on stained glass from the cathedrals of Amiens and Le Mans associated with calcite. Calcium oxalate has been observed in the alteration products of the stones of several monuments in Italy [10–12]. Its formation can be attributed to the action of micro-organisms such as lichens or certain bacteria. An attact of calcite by oxalic acid secreted by some of these micro-organisms may explain its origin.

On the other hand, the large deposit of calcite often observed on the internal face of stained glass is not a corrosion product but an exterior deposit due to water dripping on the walls of the building. Thus biological corrosion would come into play only in the formation of the oxalate, which is the reverse of other forms of bacterial corrosion often associated with the effects of atmospheric agents.

The glasses from Bourges and Evron are purple with appreciable amounts of manganese, and therefore *a priori* favourable to the implication of ferrobacteria. The question arises whether the red glasses are equally the seat of this type of corrosion, since the copper salts known to be poisonous to numerous micro-organisms might inhibit the phenomenon [13].

## 4. Conclusions

Corrosion of stained glass may result both from the action of chemical atmospheric effluents and of biological agents. It is difficult for samples directly issued from ancient panels to separate their respective role in the corrosion process. Nevertheless, the following conclusions concerning different aspects of biological attack can be drawn from this study.

(a) Ferrobacteria are liable for the metabolization of manganese in some stained glass. The displacement of this element has been demonstrated on a purple glass from Evron. In this sample, micro-organisms are direct agents of surface decay and are probably responsible for the observed alteration of the purple colour.

(b) The presence of sulpho-bacteria is suggested by an identical localization of iron and sulphur as detected on a glass from Bourges. Sulpho-bacteria are well known to act on solutions of sulphurated compounds arising from atmospheric corrosion.

(c) The occurrence of calcium oxalate, identified on several panels, may be explained by the transformation of calcite by micro-organisms. Calcite is often deposited on the internal face of the glass without corrosion of the underlying glass [3].

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