

# Crystal-chemistry of alteration products of medieval stained-glasses

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Studies of glass-water interactions are of fundamental interest to understand the rate and extent of chemical mass transfer as well as the chemical durability of glasses. At present, glass dissolution and mechanisms of alteration are mainly deduced from experimental studies. However, information on natural alteration of glass over longer periods of time are also essential to check the validity of experimental models of dissolution (Sterpenich *et al.*, 1994). In this paper we use the alteration of medieval stained-glasses to evaluate the crystal-chemistry of glass alteration products, global kinetics of weathering, elemental release rates as well as the influence of glass composition over a period of one thousand years.

## Methods and results

The samples studied are archaeological stained glasses excavated from different sites in France (Marseille, Digne and Rouen) which date from the IX to the XIIIth century. All glasses are rich in silica, calcium and alkalis. Depending on the flux, the samples can be classified in either a sodic or a potassic family; the sodic glasses are richer in silica ( $\approx 70$  wt.% SiO<sub>2</sub>) than potassic glasses ( $\approx 50$  wt.% SiO<sub>2</sub>). ICP-MS analyses also reveal significant amounts of trace elements which correspond either to impurities in the starting materials (e.g. Ba, Sr, Pb, Zn, REE) or colour forming elements (e.g. Co, Cu, Fe, Mn).

Each sample is characterised by the presence of an altered layer which has developed on its surface. The thickness of this altered layer is strongly dependent on the chemical composition of the glass and ranges from 15 to 90  $\mu\text{m}$  for the sodic glasses, and from 300 to more than 1500  $\mu\text{m}$  for the potassic family for a same duration of burial. In contrast to medieval stained-glasses weathered on windows (Libourel *et al.*, 1994), the altered layer of archaeological samples show a laminar structure devoid of fracture.

The bulk chemical composition of the corroded crust was determined by ICP-AES and ICP-MS whereas the behaviour of elements between the

pristine and the leached glass was studied by electron and ion microprobe. The altered layer consists mainly of an hydrous silica gel with water content ranging from 14 to more than 20 wt.%. In comparison to the pristine glass, the altered layer is enriched in silica, aluminium and iron and severely depleted in potassium, sodium and magnesium, while calcium and phosphorus are only moderately depleted. Trace elements similarly show a dual behaviour: titanium, zirconium or light REE are enriched in the altered zone whereas barium, caesium, rubidium are strongly depleted.

The influence of the chemical composition on the durability of the glass can be estimated from the mean rate of corrosion defined by the thickness of the weathering crust formed during a known duration of burial. For a same archaeological site, a linear relation between the mean rate of corrosion and the degree of polymerisation of the glass (NBO/T) can be calculated. It appears that the more the glass is polymerised, the less it is leached.

It is possible to calculate the release rate not only for major elements but also for trace elements assuming that i) the initial surface of the studied glasses is still present as confirmed by the presence of initial decoration (vitrified paint), ii) the density of pristine and weathered glass can be determined and iii) the composition of pristine and weathered glass are known. The normalised kinetics of alteration, based on mobile elements such as sodium or potassium, show that the sodic glasses are 40 times less leachable than the potassic ones under the same conditions of alteration. The release rate of major and trace elements can also be expressed as a stoichiometric ratio related to mobile elements (sodium or potassium). When this ratio is equal to unity, the element considered releases in a similar manner to the alkalis, i.e. it is very leachable and thus strongly depleted in the altered layer. On the contrary ratios close to zero indicates stable or re-incorporated elements. For example, Fig. 1 shows that alkalis and alkali-earths are mainly leached, whereas Ti, Al, Fe and REE remain in the altered layer.

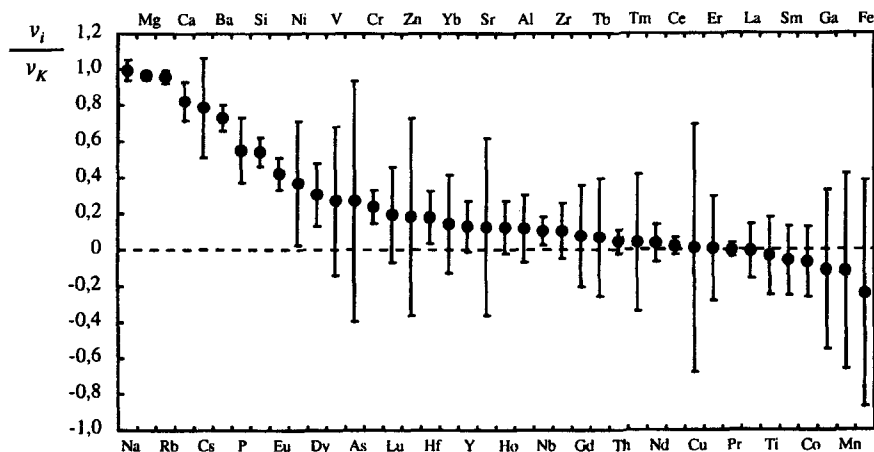


FIG. 1. Stoichiometric ratio related to potassium. Values correspond to the average for seven potassic samples of archaeological glasses. Error bars correspond to the variability recorded in these samples.

In order to better understand elemental behaviour during alteration processes, crystal chemistry of the corrosion products was determined using SIMS, electron microprobe profiles and TEM observation as well as X-Ray mapping. In agreement with observations from Cox and Ford (1993), these studies show that the corrosion crust of archaeological stained-glasses is made of three main phases: an hydrous silica gel, an hydroxyapatite like phase and a manganese oxide. Partition coefficients between these phases can thus be quantified and show, for instance, that As and Pb are strongly compatible in the phosphate, whereas Ni, Cu and Co are preferentially enriched in the manganese phase.

### Conclusion

Medieval stained-glasses provide important information on the durability of a glass under conditions of burial over periods of time up to more than one thousand years. Because these glasses are well dated and because the altered layer is well preserved, it is

possible, i) to determine the crystal-chemistry of major and trace elements, ii) to establish a chemical budget and to quantify the kinetics of glass weathering under natural conditions, and consequently iii) to determine the protective character of the leached layer. Moreover, due to their complex compositions, these archaeological glasses provide constraints on the release of pollutants into the biosphere.

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### References

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