Understanding Glass Deterioration in Museum Collections through SIMS analysis

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Introduction

SIMS is being applied complementarily to Raman spectroscopy to study the deterioration processes of glass by organic pollutants from show case materials in museum collections. While Raman spectroscopy provides information about changes in the chemical structure of the glass SIMS measures the changes in elemental composition as a function of depth.

Deterioration of soda and potash glass is known from study of both modern and historic glass. This is normally attributed to reaction between the glass surface and moisture in a two-stage process. The first stage is an ion exchange process between penetrating H+ and/or H3O+ ions from the moisture and an alkali metal ion (typically Na+), which is removed from the glass. At this stage, the silica network remains unchanged but an alkaline film containing NaOH and H2O forms on the glass surface. This film becomes increasingly alkaline and above pH 9 the second stage occurs with decomposition of the silica network.

Wine Glass from the 19th Century with white corrosion crystals of sodium formate

Study of glass collections within the National Museums of Scotland (NMS) showed that a higher proportion of the historical glass collections had deteriorated than expected and that alteration was enhanced by high concentrations of organic pollutants (acetic acid, formic acid and formaldehyde) in the display and storage cabinets. These pollutants influence the corrosion products formed at the glass surface, but their effect on the glass structure is unknown. In the current work, artificial corrosion experiments set up at ambient temperature have been used to increase understanding of the processes involved in the alteration of soda glass by organic pollutants. Thus, the effect of acetic and formic acids at 40, 50, or 60 % relative humidity has been investigated and compared to non-polluted atmospheres. The formation of formic acid from reaction of CO_2 with silicate rocks in the presence of water and light, possibly catalysed by metal ions, has been described (Otha K. et al. 2000[1]) and the reaction of silicate glass in a similar environment was examined. A synthetic soda glass was used for the experiments with percentage composition 71.8 SiO_2, 18.4 Na_2O, 3.3 K_2O, 2.7 CaO, 1.2 Al_2O_3, 0.3 FeO, 0.4 MnO, 0.8 MgO obtained by electron microprobe analysis with a Cameca SX100.

Experimental

In this study, SIMS was used to observe the concentration of elements as a function of depth in aged glasses over nanometre scale. Depth profiles were obtained using a Cameca ims-4f. Before analysis the samples were cleaned with dry ethanol to remove any corrosion products on the surface, as the salts cause loss in depth resolution, and were then coated with gold. Samples were sputtered using a 60nA, O⁻ beam at 10 keV. Positive secondary ions of H, Na, Al, Si, K and Ca were collected. The depths of the final sputtered craters were measured using stylus profilometry. The concentration variation of each element was plotted and the alteration depth was defined as the depth at which the

Na_2O profiles reach the bulk value obtained by electron microprobe analysis. The first 50 nm were not considered as this corresponds to the gold layer.

Results

The analyses showed that volatile organic acids play an important role in the modification of soda glass in humid atmospheres. After 6 weeks exposure to different environments, SIMS revealed varied depletions in the sodium concentration accompanied by an increase in the hydrogen content, which confirmed that the ion exchange process has taken place. However, the results showed that both the depth and the amount of sodium depletion must be considered when assessing surface alteration.

The increase in humidity resulted in an increase in sodium depletion in the glass for all samples. However, at identical humidity, the presence of acid-pollutants in the atmosphere, presently formic and acetic acids, compared to non-polluted atmosphere, result in increased loss of sodium from the glass. In addition, the presence of the pollutants modified the SIMS profile shape (Figure 1). In the sample not exposed to pollutants, the Na_2O content has been reduced from the bulk value of 18.5 wt% to a minimum of 8 wt%. In contrast, for the polluted atmospheres the minimum Na_2O content was 2 wt%.
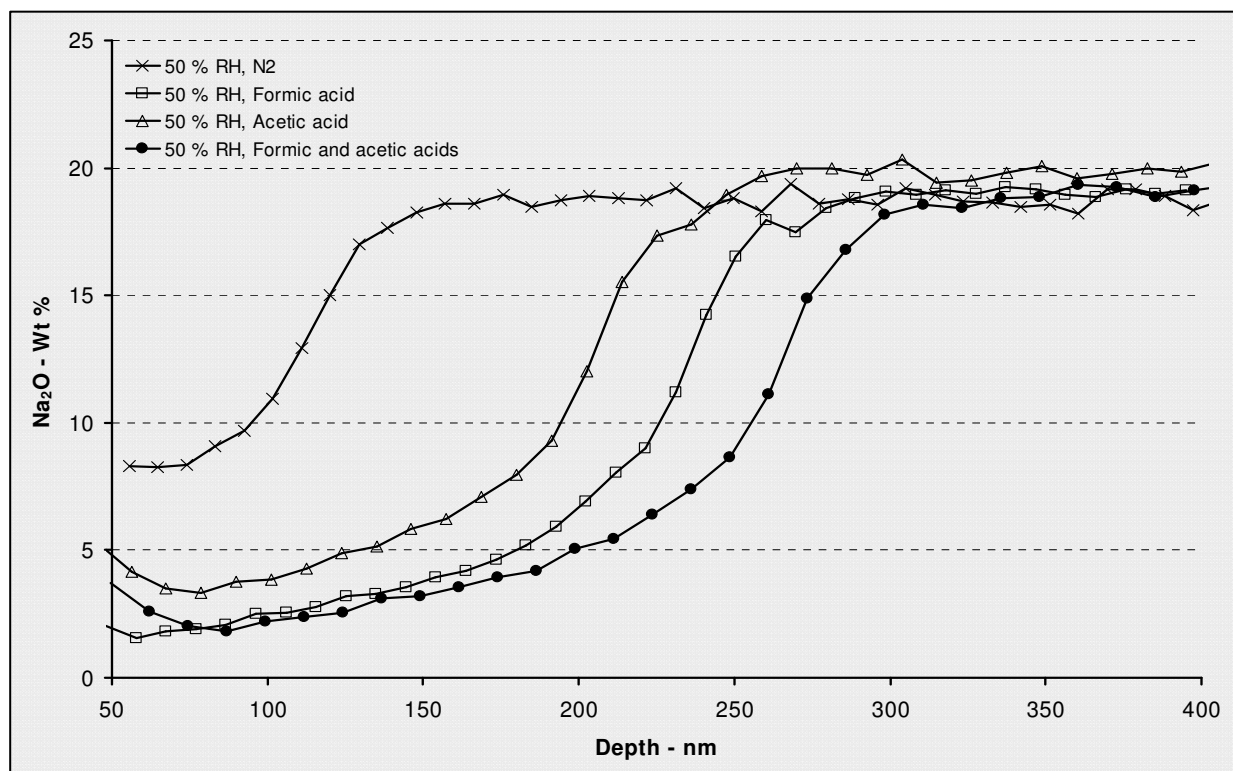
Figure 1. Influence of pollutants at 50 % RH : sodium depletion depths measured by SIMS on glass exposed to non-polluted atmosphere (nitrogen), formic acid, acetic acid or a mixture of both.

The presence of high levels of CO_2 greatly increased the sodium depletion from the glass. However the slight difference observed between light and dark experiments in all atmospheres suggests that the presence of light does not have a significant effect.

Further work will focus on the evolution of glass alteration as a function of time in similar polluted and non-polluted environments.

Reference

Otha K., Ogawa H., & Mizuno T. 2000. Abiological formation of formic acid on rocks in nature. *Applied Geochemistry* 15, 91-95.