

Study of sea water influence on chemical and physical degradation of Roman glass^(*)

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Summary. — From ancient times to today glasses, generally based on siliceous oxides cooled to a hard condition to avoid crystallization, have been extensively used, for their chemical-physical durability. Indeed, glass is one of the materials most frequently discovered during archaeological excavations. The degradation induces the loss of brightness and transparency, and the formation of pits, crystals and patinas. Sometimes peeling layers may appear, too. All these phenomena alter irreversibly the aesthetic appearance of the glassworks. The research in this field, initially focused on the knowledge of history, composition and technology of the manufacture of works of art is trying now to rationalize the problems connected with degradation processes through, both, very sensitive characterization techniques and model experiments simulating degradation phenomena. In this work we deepen the analyses of glass degradation regarding samples coming from the Roman ship *Julia Felix* found on the seabed of Grado lagoon (Italy) and dated to the II century A.D. Their surfaces have been investigated through XPS (X-Ray Photoelectron Spectroscopy) and SIMS (Secondary Ion Mass Spectrometry) to understand water effects on glass degradation and interesting considerations on the mobility of the present ionic species are proposed. We also report the results of micro-XRF and synchrotron-XRD analyses that will allow us to single out the various crystallization species present resulting from the degradation phenomena of these glasses.

PACS 61.43.Fs – Glasses.

PACS 61.10.-i – X-ray diffraction and scattering.

PACS 68.49.Sf – Ion scattering from surfaces (charge transfer, sputtering, SIMS).

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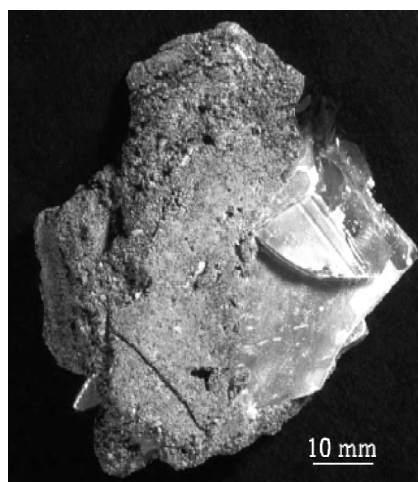


Fig. 1. – Picture of fragment IF2.

1. – Introduction

Seawater glass alteration and/or corrosion involve many different processes like surface adsorption of water, leaching reactions, localized increasing in pH , dissolution reactions, crystallization of insoluble carbonates and sulphates, biological deterioration. There are a number of physical and chemical processes that occur in the interface region ranging from the effect of contacting atmosphere up to the aqueous layer coating the glass fragment itself; for this reason the investigation is focused on glass surface.

The most important reactions that can take place when silicate glasses are in contact with an aqueous environment at $pH < 9$ are ionic exchange reactions between alkali ions of glass and protons of the solution, while aqueous solutions at $pH > 9$ induce the destruction of the bridging oxygen bond of the silica network. The interaction of gaseous CO_2 and SO_2 species with the vitreous surface can involve the formation and co-precipitation of many alteration products like calcium carbonates and calcium sulphates. These phenomena favour the decrease of alkaline-earth ions concentration in the glass. The substitution of alkaline or alkaline-earth ions with protons also causes a volume contraction of the vitreous matrix that induces fracture, collapse of the structure and pit formation. In pits crystallization causes a break-up action similar to the one of ice inside rock fractures.

2. – Experimental

The examined glass fragments (called IF1–11) composition is typical of the Roman era, with a large use of “natron”. In fig. 1, a picture of the fragment IF2 is represented. All the analyzed samples show visible thin exfoliation layers. They are very fragile, easily breakable and removable. In some samples the thin layers are iridescent, while in others they present a white colour [1].

All the samples (sample surfaces and thin sections) were analyzed by optical microscopy, XPS and micro-XRD. Samples were analyzed also through SIMS and XPS depth profiles to point out the element concentration trends in depth.

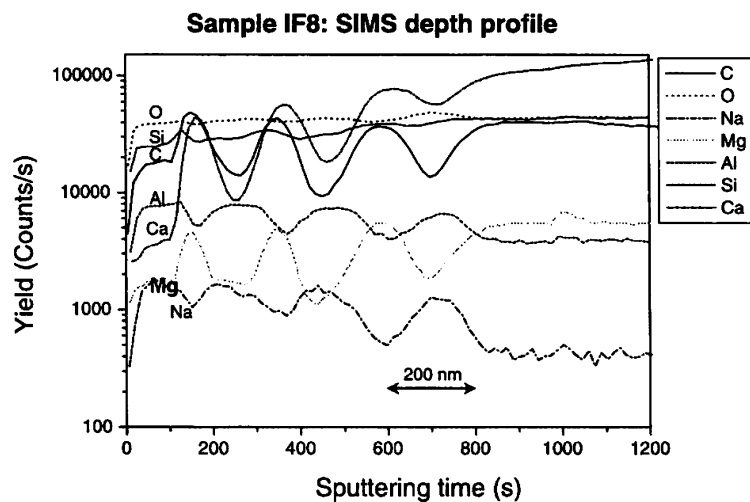


Fig. 2. – SIMS depth profile (Sample IF8).

An XPS spectrometer was equipped with Al/Mg anodes working with $\text{AlK}\alpha$ (1486.6 eV) and $\text{MgK}\alpha$ (1253.6 eV) sources at 20 mA and 14 kV. Also an Al monochromatic source (1486.6 eV) with the same parameters, and a charge neutralizer were used. The working pressure was in the range of 10^{-7} Pa. Survey scans were obtained in the 0–1350 eV range (using $\text{AlK}\alpha$ source) or 0–1150 eV (using $\text{MgK}\alpha$ source) by steps of 0.8 eV. The pass energy was 187.86 eV. The depth profiles were obtained by sputtering with Ar^+ ions, operating at 3 keV, at a pressure of $5 \cdot 10^{-6}$ Pa. A raster size of 2×2 mm was used. The analyzed areas were circles 0.8 mm in diameter.

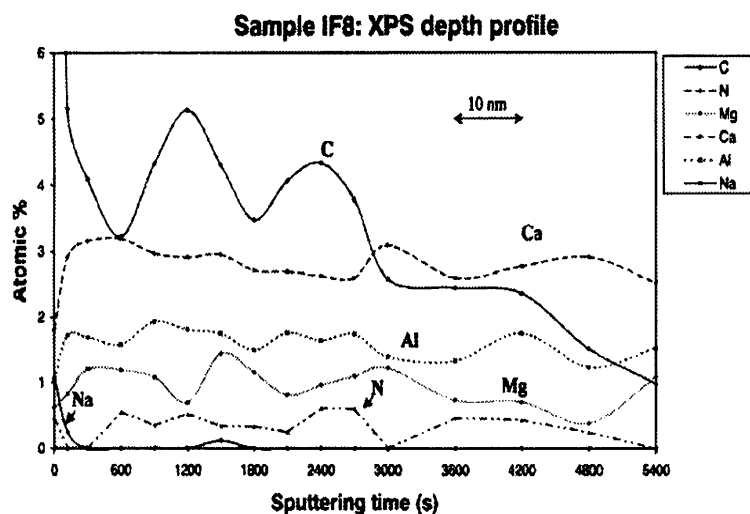


Fig. 3. – XPS depth profile (Sample IF8).

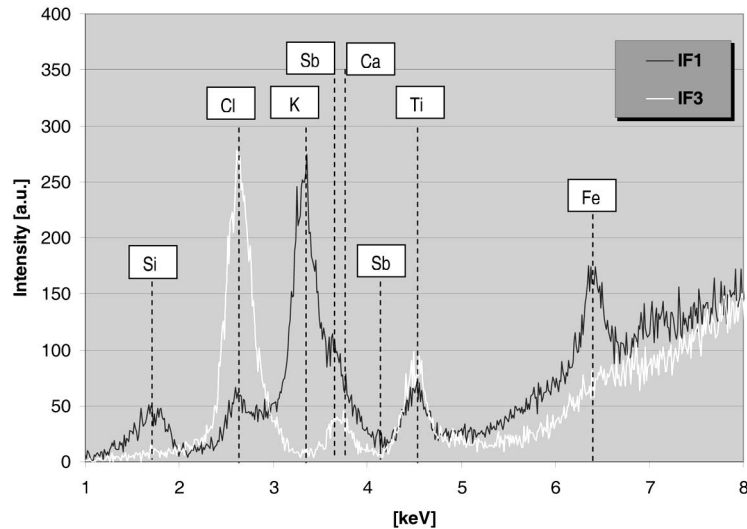


Fig. 4. – XRF spectra of samples IF1 and IF3.

The instrument used for SIMS analyses was an ionic microscope Cameca ims 4f. The compositional analysis was recorded with several primary beam current values (10, 20 and 40 nA, respectively) to optimize the measurement conditions and charge compensation. In the present paper the samples were bombarded with primary ions Cs^+ at 1–20 keV of power, an optimal current of 10 nA and the secondary ions emitted were analyzed by a mass analyzer made of magnetic and electrostatic sectors. A variable raster size of $125 \times 125 \text{ nm}$ was used. The working pressure was 10^{-7} Pa . A flood gun of electrons at 500 eV was used because the samples were insulators (better results were obtained by a 10 nA beam secondary current). The sputtering rate, estimated for flat glass samples, was about 60 nm/min.

XRF measurements have been carried out by means of a Unisantix XMF-104 micro-XRF system, equipped with a Kumakhov polycapillary lens. The measured area was about $100 \times 100 \text{ microns}$. Diffraction measurements have been performed on Daresbury Synchrotron Beamline 9.6, which provides a high intensity focused monochromatic X-ray beam at a fixed wavelength of 0.87 Å.

The station is equipped with an ADSC Quantum-4 CCD detector for data collection; data processing was made using the ESRF package FIT2D [2].

3. – Results

3.1. SIMS results. – As can be seen in the SIMS depth profile of sample IF8 (fig. 2) the sodium and aluminum signals change in yield in a synchronous mode and the trend is not attributable to mass interferences; even carbon, magnesium and calcium yields show a sinusoidal synchronous profile. The SIMS analysis suggests the presence, in this sample, of an outer portion characterized by a multilayered structure, with maxima and minima concentration sequence. The distance between two adjacent maxima is about 200 nm in depth. It is also easy to observe that the trend of sodium and aluminum signals is just out of phase with the carbon, calcium and magnesium one. These phenomena confirm a multilayered structure with alternating shells [1].

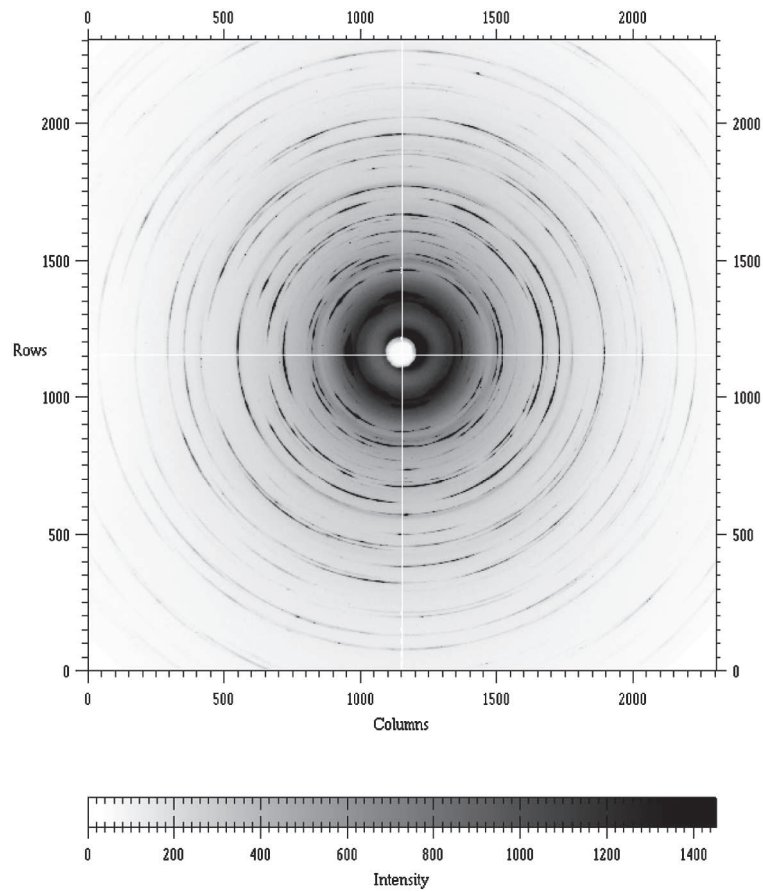


Fig. 5. – XRD diffraction spectrum of mopungite (Sample IF3).

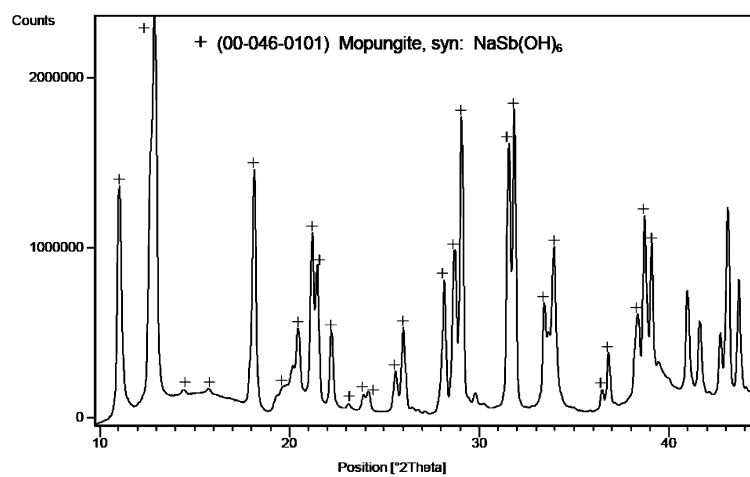


Fig. 6. – Sample IF3 - XRD diffraction pattern analysis.

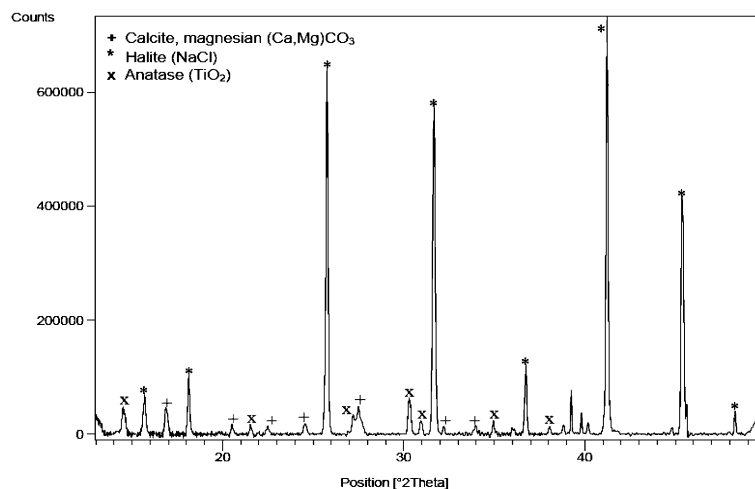


Fig. 7. – Sample IF1: XRD diffraction pattern analysis.

3.2. XPS results. – A very interesting trend is present in the IF8 sample depth profile (fig. 3). After 90 min of sputtering the carbon amount (exclusively hydrocarbon contamination) shrinks from 18 to less than 1% (atomic abundance). To reach this value, however, the carbon concentration follows a sinusoidal depth profile with alternated maxima and minima of carbon concentration below 5% of atomic abundance, which suggests the presence of a multilayered sample where hydrocarbon contamination piles up at the interface between two succeeding layers. These maxima are separated from 20 min of sputtering, and hence 20 nm in depth [1].

3.3. XRD and XRF results. – SIMS analysis showed the presence of titanium (IV) and antimony (V) traces in all samples; this is well established by XRF analysis too (fig. 4).

By means of micro-XRD measurements [3], it was possible to characterize the corresponding crystalline phases.

In particular, the presence of mopungite $\text{NaSb}(\text{OH})_6$ has been confirmed (figs. 5, 6); it was possible to detect mopungite in samples IF2 and IF3, not in IF1.

All the analysed samples show the presence of sodium chloride (halite).

Titanium (IV) compound has been identified as titanium dioxide (fig. 7); in sample IF1 traces of calcium and magnesium carbonate are present as well.

4. – Discussion and conclusions

Detailed XPS and SIMS analyses on Roman glass fragments from a seawater archaeological site have shown that the evolution of the glass submerged in marine water is similar to the one found in glasses from other terrestrial archaeological sites [4]. The alteration processes, like the ion migrations, the formation of calcium accumulation layers and carbonates near the surface, are mostly similar to the ones observed in other Roman and Early-medieval glasses. The only difference is that when the glass fragments remain for several centuries submerged in marine water, all the processes are faster and the final detectable results are more evident. So the presence of carbonates or hydrated layers inside the glass is very relevant and it produces a strongly visible exfoliation layer.

XRF analysis on samples IF1 and IF3 have shown the presence of silicon, potassium, chlorine, antimony, calcium, titanium and iron, according to previous XPS data.

The main difference is related to the presence of iron in sample IF1; this element was found also in sample IF11 [4].

By means of XRD analysis we could identify the crystalline phases associated to antimony and titanium, previously detected by means of ESEM analysis.

Antimony and iron were probably added by Romans to change the glass mixture appearance: antimony oxide was used as a decolorant and iron as a reduction treatment.

The origin of titanium is still unknown: it could be either a component of the glass, or coming from environment (external pollutants or crucible contamination).

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