Study Of The Corrosion Processes On Roman And Byzantine Glasses From Northern Tunisia

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The present investigation focuses on some glass objects among those discovered in an area around the ancient city of *Thugga* in northern Tunisia, particularly flourishing during the Roman and Byzantine periods (1). The Late Roman-Byzantine time is not characterised by elaborate vessel shapes derived from precious metal prototypes, but rather by simpler multifunctional forms, as beakers, goblets, and dishes with similar features in the whole Mediterranean world. Also the glass composition seems to change between the 4th and the 5th century, turning to a yellowish-green or olive green colouration of the glass instead of the typical Roman blue-greenish colouration of earlier times. This new glass colouration varies further drastically in the 7th century, when a characteristic light blue-turquoise glass becomes the most widespread. A complete chemical characterization of these objects was carried out in a previous study (2) aimed to investigate the production technology including the chromophores responsible for the different shades. In the present work we have investigated the degradation and corrosion processes affecting some of these shards. It is worth to note that to ascertain the composition of the glass surfaces the analyses have been carried out by means of non-destructive techniques such as XPS (X-ray photoelectron spectroscopy), SEM-EDX (scanning electron microscopy coupled with energy dispersive X-ray analysis) and laser-ablation ICP-MS ((Inductively Coupled Plasma – Mass Spectrometry).
Roman and Byzantine glass shards collected during excavation campaigns around the ancient city of Thugga in northern Tunisia (1) have been characterized by means of numerous analytical techniques (2). It was found out that the chemical elements responsible for the different shades were generally Fe for the green shades, Cu and Co for the blue ones, Mn (used as discolouring agent) for the transparent samples. As concerns the raw materials used for glass production a common local provenance of sands has been hypothesized. Roman and Byzantine glasses generally show a good standard of technology, particularly in terms of color control. Transition metal ions, such as iron (Fe^{3+}/Fe^{2+}), cobalt (Co^{2+}) and copper (Cu^{2+}/Cu^{+}) acted as coloring agents in the glass production process (2).
A very interesting aspect concerning archaeological glass analysis is represented by the study of the degradation and corrosion processes (3, 4, 5, 6). Surface alteration is due to burial conditions and depends on different parameters such as temperature, pH, glass-composition and pollution. In particular both soil and groundwater compositions, if the objects were buried, play an important role in the glass degradation phenomena. In Figure 1 some examples of degradation present on glaze surfaces are shown. The corrosion process might be generally due to leaching of alkali and alkaline earth ions that causes the destruction of the glass and iridescence formation (3).

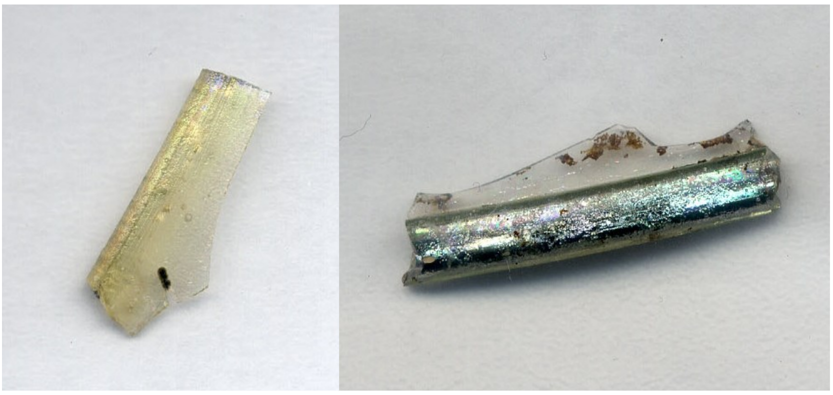

Figure 1. Samples GLR011 (left) and GLU034 (right) showing typical degradation layers .

The study of the morphology and the chemical composition of the iridescent and corrosion layers has been performed by SEM-EDX, XPS and laser-ablation ICP-MS.
At first SEM-EDX analyses were carried out aiming to a comparison between the chemical composition of the areas affected by degradation and those still intact. SEM allowed us to differentiate among various types of alteration: in some cases (sample GLB002) incrustations were present in the altered areas (see Figure 2) while typical lamellae (Figure 3) were observed on the iridescent surface – zones (sample GLU034).

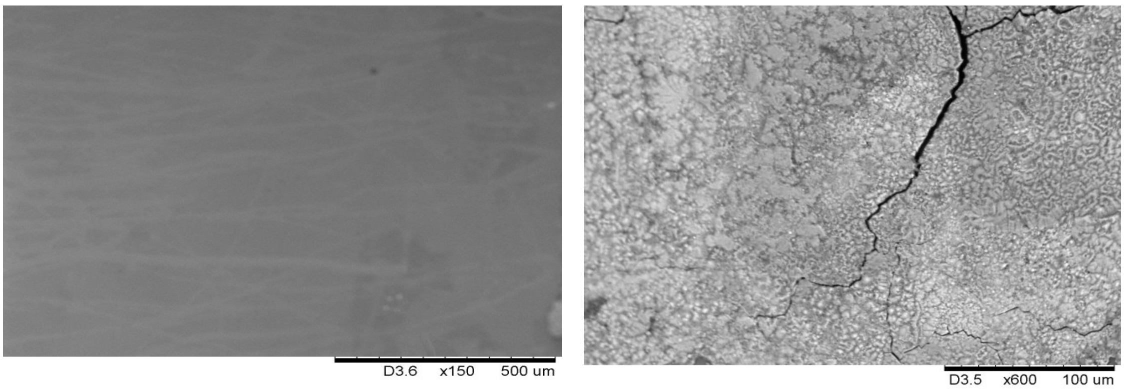

Figure 2. Comparison between SEM results on a not altered area (left) and on degraded area (right) - sample GLB002.

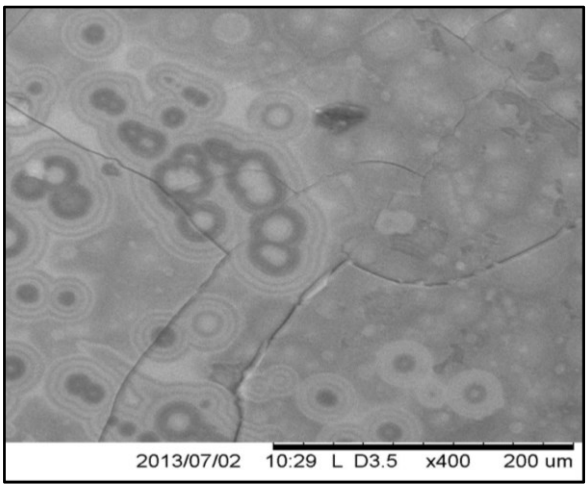

Figure 3. SEM picture of typical lamellae structure (sample GLU034).

Small-area XPS results, obtained using a monochromatic source Alk (300µm) present in a Thetaprobe spectrometer (Thermo Fisher), provided information not only on the elemental composition, that was uniform in all cases, but also on the atomic concentrations in the different areas. The surfaces of the iridescent areas resulted to be strongly hydrated and alkali depleted. The comparison of the Ca/Si and Na/Si ratios obtained on degraded and unaltered zones of the same sample substantiated a preferential dissolution of calcium and sodium ions that might be replaced by hydrogen ions (gel formation).

By using laser ablation ICP-MS a great number of trace and RE elements at a low concentration (10 ppb – 100 ppm) have been determined, allowing the complete chemical characterization of the glass shards and the corrosion layers.

The LA-ICP-MS analyses were conducted using an Elan DRCe (Perkin Elmer) spectrometer coupled with a New Wave UP213 solid-state Nd-YAG laser microprobe, operating at 213 nm wavelength. The spot analysis was 80 µm in diameter and 100 µm deep. Data were processed by using the GLITTER software and the calibration performed with the SRM612 standard (50 ppm) by NIST (7, 8).

The multi-analytical approach proved to be very useful for identifying the different degradation processes that might take place at the surface of glasses in various environments. These results lay the foundations to safely conserve the glasses and to suggest possible restoration interventions.

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