MODEL HISTORICAL GLASSES UNDER SIMULATED BURIAL CONDITIONS

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Introduction

The majority of archaeological glasses come from Roman contexts due to the high level of glass production in this historical period. They are beads, vessels, mosaics tiles and, sometimes, glass production wastes (Palomar *et al.*, 2009). The main composition of Roman glasses is soda lime silicate glass, which is characterized by a close and stable chemical structure against the external environment. In contrast, potash lime silicate glasses, which forms less durable chemical structures, were mainly produced in Medieval times.

Usual pathologies that appear on archaeological glasses are craters and dealkalinization layers. They show also dark deposits, whose formation is connected with the high content of manganese in the glass. Craters are frequent and appear as spherical or oval pits on the surface. They can be isolated or interconnected forming a crater network. Dealkalinization surface layers are associated with cycles of wet/drought. In the wet period, water hydrates the glass surface which transforms its microstructure. In the drought time, the surface layers are progressively dried and physical tensions in between different layers may crack and separate them. Their adherence depends on the hydration degree.

Simulation experiments can be useful to understand the degradation mechanisms on historical glasses. Up to now, such simulations have consisted in immersing the model glass into chemical solutions (Greiner-Wronowa and Stoch, 1996, Morgenstein *et al.*, 1999, Vilarigues and da Silva, 2006, Tournié *et al.*, 2008) or in simulated sea water (Carmona *et al.*, 2005). Two experiments have been carried out in the United Kingdom with glasses buried in natural conditions. Nine glasses different in composition were buried in an acid soil in Wareham (Evans and Limbrey, 1974) and in a basic soil in Ballidon (McLoughlin *et al.*, 2006). The results of these experiments pointed out that glass samples buried in the basic soil presented a higher corrosion degree than those buried in the acid one.

The main goal of this research was to study for the first time the behaviour and corrosion mechanisms of different historical model glasses under simulated burial conditions. Weathering pathologies were observed and analyzed to determine degradation mechanisms and corrosion rates. The results of the experiments carried out have been useful to understand the different pathologies observed in original archaeological glasses and to know how the nearby environment can affect the preservation of buried glasses.

Methodology

Four model glasses were melted in the laboratory following the composition of the main representative historical glass types (Table 1):

1) Roman glass: Soda lime silicate glass containing a low percentage of Fe_2O_3 that reproduces the impurities of raw materials and a low concentration of MnO to compensate the colour of iron ions.

2) Medieval glass: Potash lime silicate glass with the common composition of Medieval stained glasses.

3) Modern glass: Soda lime silicate glass with the composition of the modern conventional window glasses. Note the higher percentage of SiO_2 compared with the Roman model glass (Glass 1).

4) Crystal glass: Silicate glass with high content of PbO (approximately 24 wt %) (UNE 43-603-79, 1979).

The model glasses obtained were cut in slices of 10x10x2 mm and then polished using an aqueous suspension of cerium oxide to obtain optical quality surfaces. These glass slices were buried into three natural soils with acid, neutral and basic characteristics. They were first irrigated with 12.5 ml of distilled water to moisten them and later introduced in a stove at 60 °C. With the aim to maintain wet conditions, the soils were further irrigated with 5.0 ml of distilled water every 5 days during 105 days. Medieval glass samples were taken out after 30 days of experiment, while crystal glass samples maintained in neutral and basic soils were taken out after 70 days of treatment.

Table 1. Model glass compositions analyzed by EDS (wt %). The results were normalized to 100 wt %.

	Type of glass			
	Roman	Medieval	Modern	Crystal
Na_2O	23.4	1.5	18.1	5.4
MgO	1.4	3.2	1.6	--
Al_2O_3	4.0	3.3	3.2	--
SiO_2	57.5	37.6	65.4	60.6
P_2O_5	--	3.0	--	--
K_2O	2.2	24.7	1.5	8.4
CaO	9.3	26.9	10.2	--
MnO	0.8	--	--	--
Fe_2O_3	1.4	--	--	--
BaO	--	--	--	2.4
PbO	--	--	--	23.2

Abbreviations: -- (not detected).

The surface of glasses after weathering was observed by optical microscopy (OM) with a reflected light microscope Leica model DM-LM, equipped with a digital camera Leica DFC 480. Scanning electron microscope (SEM) observations were carried out with a Hitachi microscope model S-3400-N (CCHS-CSIC) using acceleration voltages of 15 kV. The samples were observed on their surface without carbon coating and on their resin inlayed polished cross-section with a thin carbon coating to make it conductive. The EDS microanalyses were accomplished with an energy dispersive X-ray spectrometer Bruker AXS (133 eV) attached to the electron microscope. The analyses of OM images were made using the Motic Image Plus 2.0 program.

Results and discussion

The general evolution of the experiment demonstrated that main degradation pathologies were related with the composition of the glasses. The Medieval model glass presented a multiple layer on its surface, while the other three glasses presented cracks and pits on their surfaces.

The Medieval model glass showed a very fast degradation rate. In the 5th day of the experiment, interconnected cracks appeared on the surface. During the next days, corrosion advanced and dealkalinization layers were formed. Finally, the samples were taken out in the 30th day. Physical tensions caused several cracks in the dealkalinization layers, which showed poor adherence with the bulk glass, which in turns produce iridescent colours (Figure 1a).

The six surface layers observed in the cross-section of Figure 1b could be connected with the six irrigation times. However, these layers were not continuous, since poor adherence between them caused the entrance of small grains of the soil into the cracks, thereby detaching the outermost layers.

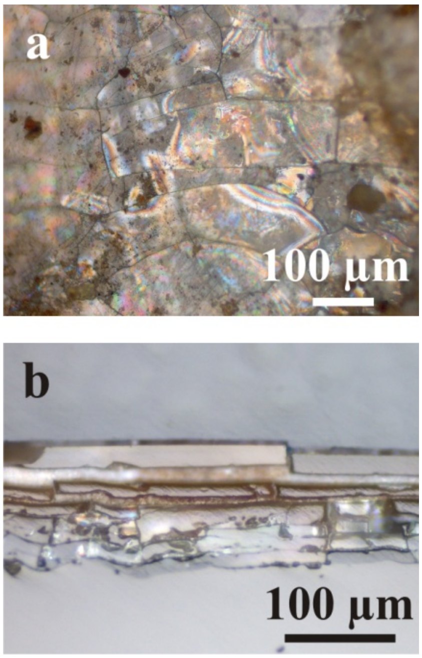

Figure 1. Medieval model glass buried in an acid soil after 30 days of treatment. OM images from a) surface and b) cross-section of the surface.

The other three model glasses (Roman, Modern and Crystal glass) showed another different corrosion mechanism. Firstly, some cracks appeared on the surface of the glasses which later grew into pits of ellipsoidal shape. Pits became interconnected as the corrosion advanced and finally an attacked surface appeared.

To compare the different corrosion mechanisms, some images of the crystal model glass buried during 70 days in different soils were analyzed (Figure 2). In the acid soil (Figure 2a), the surface presented isolated and shallow cracks, which showed a width less than 0.3 µm and over 7.0 µm of length.

The crystal glasses weathered in neutral and basic soils were almost totally corroded. In these samples the cracks grew to form pits, even though they presented different size and interconnection degree. In the neutral soil

(Figure 2b), the pits showed 13.2 μm in length and 7.0 μm in width on average (Table 2). They formed an interconnected net in which every pit was connected with other three (± 1). All of them presented a rough aspect since they were filled with soil deposits. In the basic soil (Figure 2c), the pits were two times larger. They presented 21.8 μm in length and 13.4 μm in width on average (Table 2).

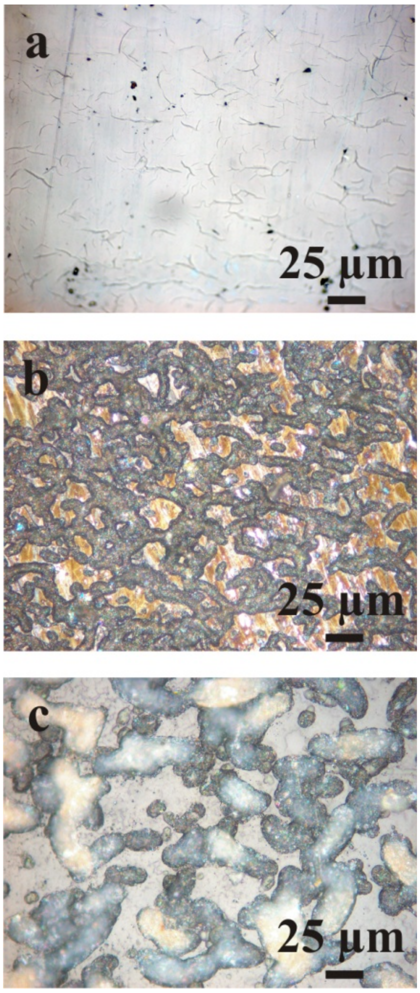

Figure 2. OM images of the crystal model glass after 70 cycles buried in a) acid soil, b) neutral soil, c) basic soil.

Table 2. Average length / width of pits from model glass samples after 70 cycles for crystal glass samples in neutral and basic soils and after 105 cycles in the other glasses (distances in μm).

	Soil		
	Acid	**Neutral**	**Basic**
Roman	28.4 / 0.2	7.5 / 1.4	11.5 / 5.5
Modern	34.9 / 0.2	10.1 / 3.3	14.1 / 6.6
Crystal	8.3 / 0.2	13.2 / 7.0	21.8/ 13.4

The samples of model glasses showed different corrosion degree according to their composition. After 70 days, the Roman and modern glasses showed isolated cracks (Figure 3a, 3b). In both cases the cracks showed over 8 μm in length, even though they presented different widths. The Roman glass exhibited ~0.5 μm in width, while the modern glass showed ~2.5 μm. In contrast, the crystal glass presented a more advanced corrosion degree (Figure 3c). In the crystal glass, the cracks length was slightly longer, but the width was two times higher than in modern glass and five times higher than in Roman glass (Table 2). This behaviour is similar in both acid and basic soils in which the crystal glass presented larger and wider pits (Table 2).

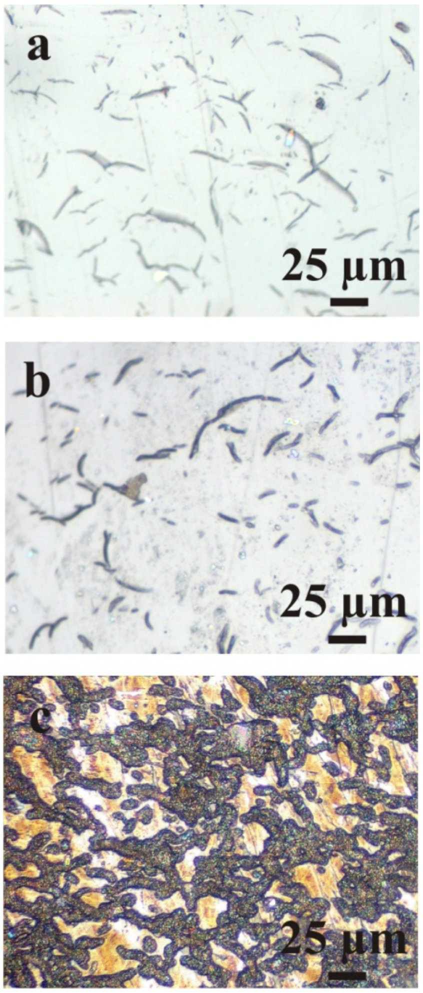

Figure 3. OM images after 70 cycles buried in neutral soil of model glasses a) Roman, b) modern, c) crystal.

The pit size depends on the corrosion rate. The plots of Figure 4 demonstrate that the crystal glass samples experienced the fastest corrosion rate. Therefore, such a glass is the most sensitive against external conditions. Roman and modern glasses showed a similar corrosion rate in the three types of soil.

The results indicated that the acid soil is the least corrosive. After 105 days, the samples presented less than 2.5 % of attacked area (Figure 4). The Roman and the modern glasses resulted unaltered until the 105th day. The crystal glass samples showed fast degradation rate during the first days, but after 59 days, the corrosion was slower. The basic soil was the most aggressive environment, and enhances the corrosion of the model samples, which were corroded faster than in the other two types of soil. In the neutral soil, the corrosion rate was fast, but not as fast as in the basic soil.

Comparison of the corrosion rate of all the samples confirmed, on the one hand, that the crystal glass samples were the most sensitive to the external conditions, and on the other hand that the basic soil was the most aggressive medium (Figure 4).

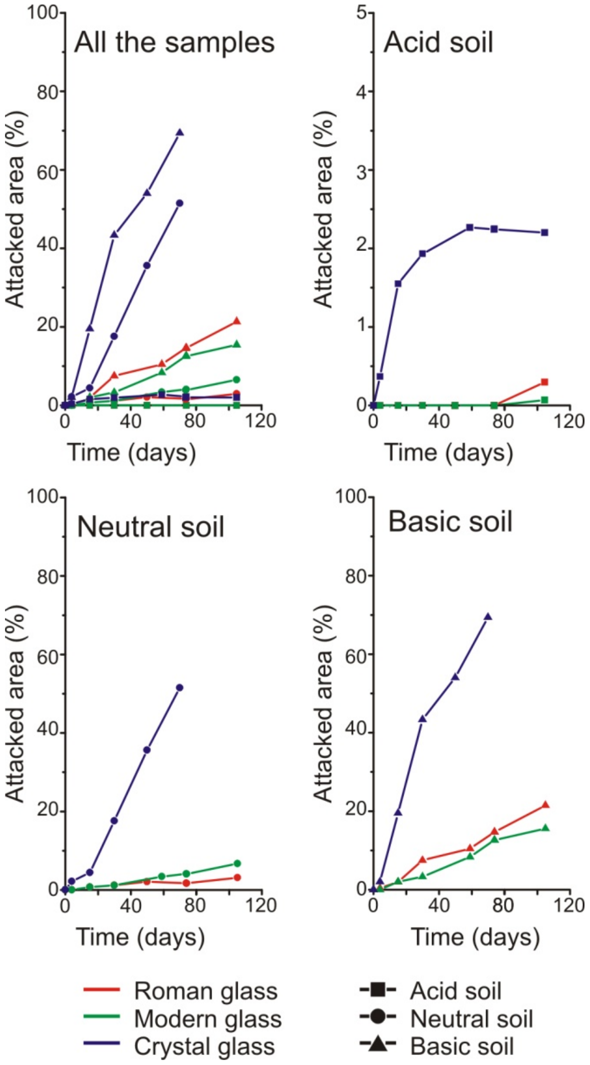

Figure 4. Plots of corrosion evolution, A) all the samples, b) samples in acid soil, c) samples in neutral soil, d) samples in basic soil.

Conclusions

The experiments with the main types of historical glasses buried in soils with different acidity during 30, 70 and 105 days showed that degradation mechanisms depend on the glass composition. Medieval model glass presented a multilayer of corroded surface, instead of the cracks and pits observed commonly in Roman, modern and crystal glasses. The most corrosive medium was the basic soil and the least one was the acid soil.

The experiments carried out demonstrate that potash lime silicate glass was the most sensitive against external conditions. However, this kind of glass is not frequent among the archaeological findings, probably because they are easily corroded during burial. Lead silicate glasses were strongly corroded in neutral and basic soils. On the contrary, soda lime silicate glasses were the most stable, since after 105 days of accelerated attack in the more severe conditions, they presented a corrosion extent less than 25 % of their surface. This fact confirms the exceptional well conservation state that can be observed in most of Roman glasses after two thousand years of burial.

Burial simulation tests with model glasses have proved to be useful to understand patterns of degradation of archaeological counterparts. The resulting data of the present study may thus contribute to better know to what extent the surrounding environment have affected the conservation of archaeological glass items.

Acknowledgments

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PORTABLE SPECTROSCOPIC INSTRUMENTATION AT THE SERVICE OF ARCHAEOLOGISTS AND CONSERVATORS FOR NON-INVASIVE IN SITU ANALYSIS: THE CASE OF POMPEII

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Introduction

Archaeological sites are parts of the cultural heritage and attract millions of people that want to learn the past and from the past. Archaeologists and historians primarily are shouldered with the duty of revealing the secrets of the ancient times. Furthermore, a plethora of scientists, such as chemists, biologists, engineers and more are responsible to answer questions concerning the physical and chemical nature of the materials, the manufacturing method of objects like ceramics and alloys, etc.

This identification of the materials from which the archaeological objects were made from is usually complicated, since the objects have suffered alterations during their burial and after their exposure to the atmospheric factors and pollutants. In the first case, the result can be the formation of a patina on the surface of the object, the transformation of the original material to another compound (like happens with the shell of an oyster) or the transfer on the surface of new elements present in the soil, wall, etc., in contact with the object coming from infiltration.

By atmospheric factors are meant the physical phenomena, like rain and other sources of water, heat, humidity, salt crystallization, etc. For example, water infiltrations from the rain, stagnant waters or ground and underground natural water sources, as well as humidity could influence a wall by changing its aesthetic appearance. In cases that the building materials are porous, the continuous cycle of reception of water and then the drying/evaporating can lead to salt crystallization on the surface or inside the pores that fatigue the material and can cause cracks. Furthermore, when water is present, it can provide the adequate conditions for the formation of biological attack (micro-organisms). Nevertheless, the presence of water without the contribution of pollutants is not the main responsible for the loss of material and the subsequent collapse of it.

Moreover, the ultraviolet radiation of the sun can fade possible colors that are present. This process is called photodegradation and is explained by the ability of radiation of certain wavelength to break the chemical bonds from which a pigment is composed. Nevertheless, in the case of wall paintings from the antiquity and the Roman times, the pigments are inorganic and therefore stable against photodegradation.

The most prejudicial factor for the archaeological sites and their constituents is the atmospheric pollution that causes deterioration. In the majority of the cases, the burial environment has protected the archaeological remains for ages. Their exposure to the atmosphere has begun a continuous deterioration process that has formed new materials on the surface of the objects and their identification is essential in order to reveal the mechanisms of their formation. In this way, these mechanisms could be stopped, slowed down or even reversed.

In order to identify the different kinds of materials, various analytical techniques are used. In each case, the proper analytical technique is applied, depending if molecular or elemental analysis is required, how low detection limits are proper, which will be the precision and accuracy, etc. But especially in the case of the cultural heritage objects there is an extra requirement: the minimum intervention. Due to the high value of the archaeological objects, in the majority of the cases, archaeologists prohibit sampling and there is strict legislation concerning the