Effect of varying the K2O/Na2O ratio on the chemical durability of Culture Heritage model glasses in a humid atmosphere

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Abstract

The glass recipe has changed since the 2nd millennium BC by using different raw flux materials (mineral carbonates, plant ashes). Throughout history, different types of glasses were created and were predominant in different periods: soda-lime glass for Antiquity, potassium glass for the Middle Ages in occidental Europe and a mixed sodium-potassium composition has existed at different times (1).

Depending on the glass composition (relative ratio in alkalis (Na2O, K2O) and alkaline earths (CaO, MgO), and content in SiO2 and Al2O3), the glass network can be more or less reactive in contact with liquid or vapour water and altered more or less rapidly according to two reactions: the acid-base reaction (reaction of the non-bridging oxygens with water), and the hydrolysis which leads to silicate network depolymerisation. Glass alteration is less studied in the unsaturated atmosphere (Relative humidity, RH< 100%) even though it is an

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issue for museum curators and industry (glazing, containment of nuclear waste...)

Depending on the glass composition, altered glass in humid atmosphere presents visible degradation signs at different levels of progress: salts, crizzling... In the field of Cultural Heritage, curators estimate that it concerns 15-30% of glass objects, even with good preservation conditions in North European museums (2). In this paper, our study aims to understand the effect of K2O in glass: can it deteriorate the chemical durability by itself? In response, three compositions were prepared and studied: an alkali mixed composition representative of chemically degraded Limoges enamels made in 1480-1530 (Na, K-glass) and the same composition with K2O only (K-glass) or Na2O only (Na-glass).

To conduct this study, we work with two types of samples: powders and polished plates to be able to use different characterization techniques. These glasses are artificially aged at different temperatures (35∘C or 80∘C), fixed humidity (80%RH) and different duration (between a few days to a few months) in a climatic chamber before being characterized. The surface state, including the existence and distribution of carbonate salts and the phenomenon of crizzling, is described using optical microscopy, SEM, Raman and XRD. The thickness of the hydrated layer and its profile composition is evaluated by SEM-EDX and ToF-SIMS. The water content of the hydrated layer is also assessed by DTA-TGA and its structure by solid-state NMR of the altered powders. At last, to compare with the chemical durability in liquid water, the measurement of the dissolution kinetics of these three compositions is underway.

In this paper, we will focus on the first results concerning the alteration of the mixed Na, K-glass and the Na-glass, at 35∘C and 80∘C. In both atmospheric and liquid conditions, the chemical durability of the Na-glass is equivalent to that of the Na K-glass, revealing that K2O only is not the origin of the low durability of this composition. Moreover, atmospheric conditions seem to be more aggressive than the immersed ones, because the hydrated layer is thicker. The retroactive action of salts and the probable difficulty of the hydrated layer to densify and become passivating are possible hypotheses of explanation.

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