



The surface hydration of soda-lime glass and its potential for historic glass dating



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ARTICLE INFO

Article history:

Received 17 June 2014

Received in revised form

27 August 2014

Accepted 31 August 2014

Available online 6 September 2014

Keywords:

Soda-lime glass

Infrared spectroscopy

Hydration

SIMS

Historic archeology

Dating

ABSTRACT

More than three decades ago the idea of using ambient water diffusion on manufactured glasses as an archeological dating method was proposed for historic period artifacts. In this study, we use infrared spectroscopy (FTIR) and secondary ion mass spectrometry (SIMS) to model water diffusion into the surface of two soda-lime glasses that differ principally in the alumina and magnesium content. Lower temperature hydration experiments (60–140 °C) were conducted and the surface diffused water was measured by infrared absorption, transmittance, and reflectance spectroscopy to establish the diffusion coefficients and activation energies, and to investigate the change in glass surface structure with time at a constant temperature. SIMS was also used to document water diffusion within a sample recovered from a 19th century archeological slave quarters at Thomas Jefferson's Monticello plantation in Virginia, USA.

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1. Introduction

Archeological chronology is central to the understanding of changing human behavior and in large part relies upon dated organics and unique forms of cultural material to estimate the time and duration of human activities. In the field of historic archeology ceramics are frequently used to provide age estimates for cultural deposits of the recent past and may provide a dating resolution of just a few decades for 18th and 19th century archeological contexts. In many other situations ceramics are only very general age estimators because of their generic appearance and lengthy period of manufacture. In addition, a temporal lag between the actual age and the disposal period (Adams, 2003) can further remove the dated event, the manufacturing period, from the target event, the disposal of the artifact (Dean, 1978). Thus, any new chronometric technique that can provide an age for the disposal event in a more direct manner has a distinct advantage. For many non-heirloom glass artifacts, it is reasonable to assume that the breakage event is very close in time to the discard of the broken glass. Therefore, determining an age of fracture (breakage) would establish the time of entry into the archeological record and provide dates for human use of structures and landscapes.

We initiated a series of preliminary experiments to look at the potential of using the hydrated surfaces of historic period glasses as chronological indicators. Similar to the method of obsidian hydration dating (Friedman and Long, 1976; Stevenson and Novak, 2011), the rate of water diffusion into the glass surface is experimentally established and used to estimate the age of an artifact based upon the total diffused water under certain environmental parameters that include ground temperature (Rogers, 2007, 2008) and soil relative humidity.

American archeological glasses beginning in the 17th century originated primarily from Great Britain which capitalized on the talents of French glassmakers. One of the most notable developments of this century was a remarkable increase in the production of containers, mostly bottles, promoted by the switch from wood to coal furnace fuel that resulted in a significant cost savings (Crossley, 1998). At this time, there was no profession-wide recipe that was circulated amongst the independent glass houses. As advances in glass processing continued, so the variety of glass compositions increased. As a result, glass compositions became highly variable as producers experimented to find combinations of silica and fluxes (e.g., calcium, potassium) that resulted in a suitable product. In this preliminary study, we are not able to address all of the complex issues surrounding compositional variability and have chosen to restrict our investigations to the soda-lime-silicate glasses that were used for containers and window panes.

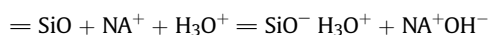
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2. Previous research

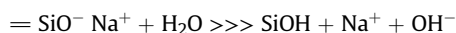
The idea of using the hydrated surface of soda-lime-silicate glass as a potential dating method was initially proposed by Lanford (1977, 1978) who used ^{15}N nuclear resonance reaction of the glass surface to record a hydrogen profile that represented the depth of water (hydrogen) diffusion. He found that water diffused into the surface of glass in a regular manner where the depth of diffusion followed the square root of time. Further investigations from an archeological dating perspective did not emerge and we are not aware of any applications of hydration dating on historic soda-lime glass artifacts, but accelerated hydration experiments with high calcium glasses (Stevenson et al., 2007) and the dating of 19th century historic contexts have given some encouraging results.

A considerable number of investigations have looked at the basic process of soda-lime-silicate glass hydration. Doremus (1975) originally proposed an ion exchange model where hydronium ions enter the glass surface and reacted with the glass network:



The model specified that H_3O^+ was the mobile water species and this was supported by the observation that the ratio of sodium to diffused hydrogen was approximately 1:3 (Lanford et al., 1979; Smets and Lommen, 1983) meaning that three hydrogen atoms replaced a single sodium atom.

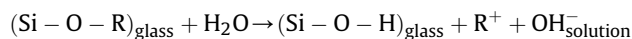
While the basic exchange process has remained accepted until the present, another exchange mechanism has been proposed by Smets and Lommen (1983) who argued that H_2O is responsible for glass leaching for conditions in the pH range of 4–7:



In this model, molecular water enters the glass network, dissociates, and bonds with non-bridging oxygen sites to form silanol groups. As a result of charge compensation, the sodium ions become mobile and migrate to the surface of the glass along with hydroxyl co-ions (OH^-) (Hamilton and Pantano, 1997). There is only a one-to-one replacement of sodium with hydrogen atoms. However, the ratio of the two will always be greater than one since inflation of the ratio can occur as a result of subsequent water diffusion as the glass structure becomes less rigid.

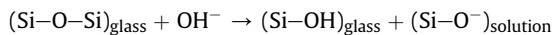
In the model of Smets and Lommen (1983) the exchange process for molecular water is determined by the number of available non-bridging oxygen sites (NBOs). Increasing the proportion of sodium (Na) to silica, for example, would accelerate the rate of molecular water diffusion by creating additional NBOs that open up the network and reduce glass connectivity. The impact of other network modifiers (e.g., CaO, MgO, K_2O , Li, Rb, Cs) depends on the strength of the cation charge and the size, or ionic radius. As a guiding rule, the lower the charge to ionic radius ratio, the more reactive the glass will be with water (Bunker, 1994).

In more complex soda-lime glasses where the number of network modifiers is greater the effect of each modifier on the rate of exchange OH^- with the alkali atom has not been fully quantified. However, Sinton and LaCourse (2001) indicate that the mechanism of exchange is still a two-stage process when in direct contact with aqueous media. In the first stage, there is an exchange at the surface between hydrogen and an alkali atom (R) that follows the reaction:



In a closed system as time proceeds, the depletion of alkalis and their transfer to solution, coupled with the increase in the

concentration of OH^- , raises the pH and breaks the Si–O–Si bonds of the glass matrix and causes the glass to dissolve:



In an open system where the moisture is water vapor, dissolution may be delayed or avoided over long exposure periods.

Developing a predictive model of glass durability involves an identification of the network modifiers that either accelerate or retard the first stage exchange process. Sinton and LaCourse (2001) have developed such a model to predict the rate of alkali exchange in a closed system for a fixed time at uniform temperature. Using the ISO static solution procedure (ISO 1985), crushed samples from twenty manufactured glasses were reacted with deionized water at 98 °C for 1 h. The leachate was analyzed by atomic absorption spectroscopy and step-wise regression analysis was used to quantify the relative effects of glass network modifiers on the exchange rate. The statistical analysis of the data set revealed that more durable glasses are those with low alkali content and a higher quantity of alumina. The addition of Na and K to the glass results in greater alkali exchange with Na^+ being preferentially leached out over the larger and slower moving K^+ . The presence of alkaline earths such as CaO and MgO were not statistically significant in terms of enhancing or reducing durability.

The work of Sinton and LaCourse (2001) indicates that the leaching of soda-lime-silicate glasses behaves in a predictable manner when exposed to solution and supports the goal of developing quantitative models to predict the leach rates for glasses of known composition. Archeological samples however, reside in open systems with a changing moisture environment and normally in vapor conditions where the relative humidity is less than 100 percent. Therefore, in this research we approach the problem of archeological glass hydration from the perspective of quantifying how much water (H_2O) enters the glass structure rather than attempting to quantify the amount of alkali removed from the glass matrix.

Research by Cummings et al. (1998) completed a series of vapor hydration experiments on a soda-lime-silicate glass containing network modifiers of CaO, K_2O , MgO, and Na_2O . In all exposures to water vapor at temperatures below 100 °C, nuclear reaction analysis of the hydrated surface layer indicated that the depth of hydration proceeded at the square root of time. Fern et al. (2006) provided additional evidence for the suitability of the $t^{1/2}$ rate model for water diffusion with depth in soda-lime glasses hydrated at room temperature. Interestingly enough, the fluctuations in the upper concentrations levels of their hydrogen profiles with time are suggestive of a dynamic period in the very early stages of hydration that is possibly indicative of a diffusion-glass relaxation process. This phenomena has been noted in hydrated silica glasses (Tomozawa et al., 2001) and obsidian (Liritzis and Diakastamatiou, 2002; Brodkey and Liritzis, 2004; Stevenson and Novak, 2011) and is indicative of water diffusion complexity of in all forms of glass.

With this understanding, we have conducted a series of low temperature hydration experiments (<150 °C). We use secondary ion mass spectrometry (SIMS) and Fourier transform infrared spectroscopy (FTIR) to monitor the water diffusion and to determine if the water diffusion coefficients parallel the compositional effects on durability as determined from leaching experiments.

3. Glass composition

Two soda-lime glass fragments were selected from the fill deposits of an archeological site known as the Golden Ball Tavern (44PG439), Petersburg, Virginia. Constructed in the middle 18th century, and used as a tavern in the 1770s, the structure later

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