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Water vapor interaction with borosilicate glass

Yuriy Kudriavtsev^{a,*}, Miguel Avendano^a, Georgina Ramirez^a, Rene Asomoza-Palacio^a, Linda Manzanilla-Naim^b

^a Departamento Ingeniería Eléctrica – SEES, CINVESTAV-IPN, México, DF 07360, Mexico
 ^b Instituto de Investigaciones Antropológicos, Universidad Nacional Autónoma de Mexico, Mexico

ARTICLE INFO	A B S T R A C T
Keywords: Borosilicate glass Hydration TOF-SIMS ¹⁸ O oxygen isotope Hydrogenation	Hydration of borosilicate glass (Corning Pyrex glass) in isotopic water $H_2^{18}O$ vapor was performed at different temperatures. The depth distributions of ¹ H and ¹⁸ O in the borosilicate glass measured by the Time-of-Flight Secondary Ion Mass-Spectrometry (TOF-SIMS) were found to be drastically different. The activation energies for the ¹⁸ O diffusion and for the glass hydrogenation were measured experimentally. The depth distribution of the ¹⁸ O isotope was described well by the complementary error function, whereas the depth distribution of hydrogen represented the so-called "S-curve". A similar hydrogen distribution was observed earlier in hydrated natural aluminosilicate glasses (obsidians). This led us to the conclusion that the hydrogenated layer was formed due to a solid state chemical reaction between the absorbed water molecules and glass network occurring in a top surface layer (< 30 nm)

1. Introduction

Borosilicate and aluminosilicate glasses are material of chose for radiative waste storage in the geological repository. Since corrosion of the glass containing nuclear waste by groundwater or meteoric water can occur during a long-term storage, scientists have conducted numerous experiments to identify the mechanism underlying the glass modification and dissolution in water [1-7]. Please note, that the most experiments in these studies were performed with glass samples in water. But we agree with Mazer et al. [3] who supposes that water vapor - glass interaction looks a more reasonable model for the "natural" hydration process occurring in the geological repository. The interaction between water vapors and aluminosilicate glass (obsidian) surface has been investigated during last 57 years [3,8] to improve the Obsidian Hydration Dating archaeological method: still there is no theoretical model, which explain all experimental data. We demonstrated in our previous studies [9,10] that aluminosilicate and borosilicate glasses show a similar behavior in the hydration process, i.e., the formation of a hydrogenated layer. This result differs from other models discussed in the literature and describing the water - glass interaction as the diffusion of water into the glass.

2. Material and methods

We performed hydrations of the commercial borosilicate glass (BSG) in vapors of isotopic water ${}^{1}\text{H}_{2}{}^{18}\text{O}$ with 97% of the ${}^{18}\text{O}$ isotope at different temperatures and during various periods. The experimental samples about $3\times5\times2$ mm in size were cut from a Pyrex dish (Corning). We did not touch the surface of the samples to avoid any surface damage. The chemical composition of the glass was found in literature (weight %): 80.6% SiO2, 12.6% B2O3, 4.2% Na2O, 2.2% Al₂O₃, 4.6% K₂O. Hydration of the samples was carried out in the pipes of a high-vacuum flange of Conflat CF 1.33" type with a copper gasket. The top flange was drilled, the hole was threaded, and BSG samples were suspended with the help of a stainless-steel screw to which a Teflon wire was attached. This prevented any contact of the samples with water and with the nipple wall. Before tightening the screws and fixing the top flange with the samples, approximately 500 mg of isotope water with 97% of the ¹⁸O isotope from Sigma Aldrich (p/n 329878-1G) was poured into the lower part of the flange. We suggested a 100% humidity with this portion of water for all experiments performed. Then the nipple with the BSG sample was loaded vertically into the oven with a digital temperature controller that was preheated to achieve the desired temperature. Our experimental temperature range was from 90 °C to 210 °C; the hydration time varied from 1 day to 2 months (depending on the hydration temperature). The hydration temperatures we used

* Corresponding author. E-mail address: yuriyk@cinvestav.mx (Y. Kudriavtsev).

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were high enough to accelerate the hydration process and get an adequate time of the experiment. On the other hand, these temperatures were far from the glass transition temperature of about 560 °C. This is very important, because the water – glass interaction at the temperatures above the transition point has another mechanism [11]. After hydration the sample was withdrawn from the nipple, cleaned in alcohol in an ultrasonic bath for 3 min, and dried in a flux of dry nitrogen. Then the sample was fixed in a special sample holder and loaded into an airlock camera of a SIMS instrument for > 8 h. The camera was pumped down to 10^{-6} Pa.

The depth profiling analysis of the hydrated BSG was carried out with a TOF-SIMS V instrument from Ion-TOF GmbH. The measurements were carried out in a double ion beam irradiation regime. The ion sputtering of the sample surface was performed by a 2 keV cesium ion beam at 45° with respect to the surface normal. The ion current reached 150-170 nA. SIMS analysis was performed with a pulsed Bi+ ion beam with an ion energy of 30 keV and an angle of incidence of 45° with respect to the normal incidence. The bismuth ion current was varied from 0.2 to 1.2 pA. The cesium beam sputtered a raster of 300×300 microns; whereas the bismuth beam scanned a 100×100 micron raster in the center of the cesium sputter crater. The secondary negative ions ${}^{1}\text{H}^{-}$, ${}^{18}\text{O}^{-}$, ${}^{11}\text{B}^{-}$, ${}^{23}\text{Na}^{-}$, ${}^{28}\text{Si}^{-}$ etc. emitted from this 100×100 -micron area were mass-separated during their flight in a reflectron-type mass analyzer. An ion irradiation of glass (as well as any dielectric) results in the surface charging effect, and, consequently, the analysis cannot be continued. To neutralize the surface charge effect, we used in this work a low-energy (20 eV) electron source with a beam current of up to 18 µA in the direction of the etching crater. All measurements were performed under ultrahigh vacuum of 1×10^{-7} Pa. The sputtering time was recalculated to the depth after the experimental crater depth measurements. The hydrogen concentration was recalculated by using the implanted standard; the implantation energy was 30 keV, and the hydrogen ion fluence was 10^{17} ions/cm². The oxygen-18 isotope concentration was determined by using the standard oxygen isotope ratio that considered the total oxygen concentration in the borosilicate glass.

After the SIMS experiments, we measured the experimental craters by a surface Dektak-XT stylus profiler from Bruker with an experimental error of 4%.

3. Experimental result and discussion



Fig. 1 shows depth distribution secondary ion intensities of main

Fig. 1. Experimental SIMS depth distribution (intensity vs depth) of main elements in the BSG sample hydrated at 90 $^\circ$ C for 20 days.

elements for the BSG sample hydrated at 90 °C for 20 days. The main result is a radical difference in ¹⁸O and ¹H distributions. Another important result is to maintain the glass composition excepting for a very thin surface layer of thickness of 20 nm, where boron and sodium concentrations decrease is observed.

Fig. 2a,b shows depth distributions (concentration vs. depth) for 1 H and 18 O in two borosilicate samples hydrated under different temperatures (and during different time periods). All the samples measured in our study demonstrated similar features. First, attention should be paid to the existence of two different layers in the glass arising after the treatment. There is a top surface layer with a thickness of up to 30 nm with high oxygen 18 and hydrogen concentrations. We also observed a slight leaching and escape of boron in this top surface layer.

The other layer is much thicker (by more than two orders of magnitude) and is characterized by radically different distributions of hydrogen and oxygen 18. The hydrogen distribution referred to as the Scurve is similar to that measured in our earlier studies and by other authors for laboratory hydrated natural aluminosilicate samples [8–12]. The ¹⁸O distribution is fitted well by the complementary error function presented in Fig. 2 a,b by the dashed line which is a wellknown solution for isotopic exchange reactions in solids [13]. This function is the solution of the Fick equation for a semi-infinite volume in the case of diffusion from a thin layer with a constant diffusion coefficient [13]

$$C(t) = \frac{C_1}{2} \cdot erfc\left(\frac{x}{2 \cdot \sqrt{(D \cdot t)}}\right) + C_0,$$
(1)

where C_1 is the ¹⁸O isotope concentration in the top surface layer loaded with the isotopic water; and C_0 is the ¹⁸O concentration in the glass volume.

Thus, we observe radically different distributions for hydrogen and oxygen-18 isotope that resulted from two different physicochemical processes. The experimental SIMS data can be interpreted if we assume that water molecules penetrate the top surface layer alone, then hydrogen ions (most probably) are formed due to a catalytic chemical reaction, and after this the atomic hydrogen (proton) and ¹⁸O isotope penetrate the BSG independently. In our previous study, we obtained different activation energies for the hydrogen and oxygen-18 penetration processes for aluminosilicate glass [9]. The same is true for the borosilicate glass.

We analyzed the kinetics of the ¹⁸O isotope exchange reaction in the borosilicate glass. Diffusion coefficients for different temperatures were defined by approximating the experimental ¹⁸O distribution with Eq. (1). Fig. 3a shows experimental diffusion coefficients of ¹⁸O and a linear fit of these data obtained by using the Arrhenius equation in the logarithmic form

$$\log(D) = \log(D_o) - \frac{E_{act}}{2.303 \cdot R \cdot T},$$
(2)

where *T* is the temperature, E_{act} is the activation energy; D_o is the preexponential coefficient (the diffusion constant at infinite temperature); and *R* is the gas constant. We estimated the activation energy for the ¹⁸O diffusion to be 80.2 kJ/mol, and the pre-exponential coefficient was found to be $D_0 = 4.9 \times 10^{-3}$ cm²/s.

A more complex procedure was used to describe the hydrogen penetration. First, we obtained experimental values for hydrogen "diffusion coefficients" at different experimental temperatures from the SIMS data. To do this, we assumed that the linear-parabolic equation describing the hydrogenated layer growth in the borosilicate glass was identical to that we used in the case of aluminosilicate glasses [9,10]. During the initial period of the hydrogenated layer growth, the reaction rate should strongly depend on the water splitting reaction and atomic hydrogen (proton) formation in the top hydrated layer of the borosilicate glass. In this case, the hydrogenated layer thickness L should be linearly proportional to the time of the treatment. However, if the Download English Version:

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