Interaction of Water Vapor with Silicate Glass Surfaces: Mass-Spectrometric Investigations

Yu. Kudriavtsev[a]*, R. Asomoza-Palacio[a], and L. Manzanilla-Naim[b]

[a] *Electrical Engineering Department, CINVESTAV-IPN, 07360 Mexico*
[b] *Institute for Anthropological Research, UNAM, Mexico*
*e-mail: yuriyk@cinvestav.mx
Received September 28, 2016

Abstract—The secondary ion mass-spectroscopy technique was used to study the results of hydration of borosilicate, aluminosilicate, and soda-lime silicate glasses in $^{1}H_2^{18}O$ water vapor containing 97% of the isotope ^{18}O. It is shown that hydration of the surface of the soda-lime silicate glass occurs as a result of the ion-exchange reaction with alkali metals. In the case of borosilicate and aluminosilicate glasses, water molecules decompose on the glass surface, with the observed formation of hydrogenated layer in the glass being the result of a solid-state chemical reaction—presumably, with the formation of hydroxides from aluminum and boron oxides.

Interaction of glasses with water is quite important for applications and has been investigated actively during the last 50 years. One of the most important issues that can be noted is the nuclear-waste disposal in special containers made of borosilicate (BS) and aluminosilicate (AS) glasses with the purpose of containing waste in repositories over long periods of time [1, 2]. Another issue that deserves attention is the protection of the glass surfaces of exhibits in the museums from interaction with water vapor [3]. Mention must also be made of a method of dating archeological artifacts made of volcanic glass (obsidian). Obsidian is a natural aluminosilicate glass containing 10−14 wt % aluminum oxide, depending on deposit location. The obsidian-dating technique is based on the assumption that water molecules from air deposited on a freshly cleaved obsidian surface gradually diffuse into the glass, forming a modified or hydrated layer [4, 5]. Thickness d of the "hydrated" layer, determined by an optical microscope or secondary ion mass spectroscopy (SIMS), can be used to determine the age of the an artifact from the empirical relation [4]

$$d = \sqrt{Dt}, \tag{1}$$

where D is the diffusion coefficient, which depends on the local temperature and chemical composition of glass, and t is the time from the instant of formation of glass or the age of the given artifact.

In this letter, we report experimental verification of the idea that diffusion takes place of water molecules into silicate glasses. Experimental samples of Pyrex BS glass and soda-lime silicate (SLS) glass were cut from workpieces of appropriate size for preparing samples with an approximate size of $3 \times 5 \times 2$ mm. For AS glass, obsidian samples with an approximate size of $3 \times 5 \times 2$ mm were cut from a large obsidian workpiece with a diamond disk. The obsidian-sample surface subjected to investigation was preliminarily polished. 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. A hole was drilled through the upper sealing flange, and a stainless-steel bolt was screwed into it. The sample was suspended from this bolt on a Teflon thread. This ensured that there was no contact between the sample, water, and the walls, as well as between different samples. About 500 mg of water $^{1}H_2^{18}O$ with 97% of isotope ^{18}O was poured into the lower part of the flange (Sigma-Aldrich 329878) before tightening the bolts. The flanges with the samples were kept for 30 days in a furnace heated to 90°C. After extraction from the furnace and before SIMS analysis, the samples were cleaned by ultrasound in an alcohol bath for 3 min, dried in a dry-nitrogen jet, and then placed on a special holder in the prechamber of the mass spectrometer, which was evacuated to 10^{-8} Torr for at least 8 h, before being transferred to the experimental chamber.

Layer-by-layer analysis of the samples was carried out by the SIMS technique using a TOF-SIMS-V time-of-flight mass spectrometer manufactured by Ion-TOF, Germany. The instrument was used for analysis with a dual beam: the surface was etched by cesium ions with an energy of 2 keV incident at an angle of 45°. Analysis was performed using a liquid-metal source of bismuth ions with an energy of 30 keV incident at an angle of 45°. Analysis of secondary neg-
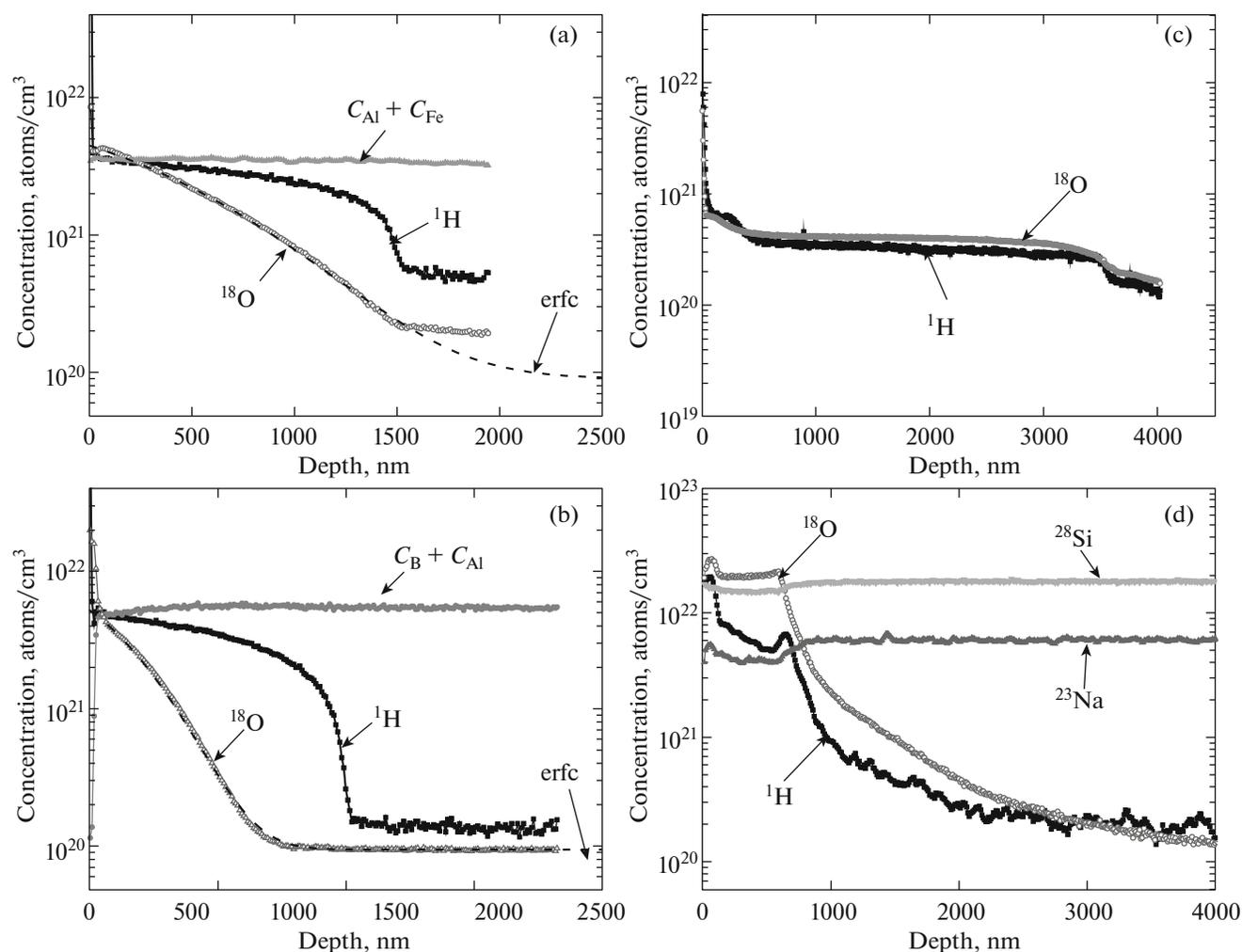
Fig. 1. Distribution of hydrogen and oxygen isotope ^{18}O in (a) aluminosilicate (obsidian), (b) borosilicate, and (c, d) soda-lime silicate glasses after hydration in vapor of water ^{1}H$_2$^{18}O at a temperature of 90°C over a period of 1 month. The dashed curve shows the approximation of ^{18}O isotope distribution by a complementary error function (Eq. (2)).

ative ions was carried out from the central region (100×100 µm) of a 300×300-µm crater etched by the cesium source to minimize the etching crater boundary effect. Secondary negative ions ^{1}H^{-}, ^{18}O^{-}, ^{23}Na^{-}, ^{28}Si^{-}, etc., were analyzed. The signal from silicon ions ^{28}Si^{-} was used for normalizing all other signals. Bombardment of the glass surface by positive ions resulted in the formation of a positive surface charge that prevented further analysis. 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. The residual pressure in the test chamber during SIMS analysis was maintained at a level not exceeding 1×10^{-9} Torr. The depth of the experimental etching craters was determined by a Dektak-XT profilograph (Bruker) for recalculating the time of etching into the sample. The concentration of hydrogen (as well as water in the bulk of obsidian) was calculated with the help of an

implanted standard. The concentration of isotope ^{18}O was determined by taking into account oxygen concentration in all oxides measured by X-ray-fluorescence analysis (XFA) taking into account the natural abundance of oxygen isotopes. The chemical composition of obsidian and SLS glass was determined independently by the XFA method in a commercial laboratory. The composition of the BS glass was taken from the certificate of the article. The table shows the chemical composition of the glasses used in the present work.

The profiles of distribution of hydrogen ^{1}H and the oxygen isotope ^{18}O are depicted in Figs. 1a–1d for three different glasses. The SLS glass surface was found to be modified strongly as a result of hydration. Hence, measurements for this sample were carried out in (c) the most modified region and (d) the least modified region. Both profiles are characterized by a synchronous variation of hydrogen and oxygen (^{18}O) con-

Chemical composition (in wt %) of glasses used in this research, determined by XFA technique and taken from the certificate of the article (Pyrex). Only the main impurities are considered

Glass	Na_2O	Al_2O_3	B_2O_3	SiO_2	K_2O	CaO	Fe_2O_3	MgO
Borosilicate	4.2	2.2	12.6	80.6	4.6	–	–	–
Aluminosilicate (obsidian)	4.5	10.0	–	76.6	4.8	0.2	3.2	–
Soda-lime silicate	~12.7	1.9	–	72.4	0.6	6.9	0.1	4.2

centrations, which confirms the earlier results concerning the ion-exchange reaction between molecules of water and alkali metal oxides (Na_2O and K_2O). As a result, a hydrated layer is formed on the glass surface, while sodium and potassium leave the glass. This effect is known as "dealkalization" [6].

It should be observed that two different layers are formed in BS and AS glasses, i.e., a very thin (about 10 nm thick) surface layer with a high concentration of hydrogen, oxygen ^{18}O (and, most probably, water), and a much thicker (more than a micrometer) layer with a drastically different distribution of hydrogen and isotope ^{18}O concentrations. In this layer, we observe the so-called "S-distribution" for hydrogen as in the case of other measurements of concentration of hydrogen in obsidians [7, 8]. The distribution of ^{18}O in these two samples is described by a complimentary error function characteristic of the isotope exchange reaction in a solid [9]:

$$C(t) = \frac{C_1}{2}\operatorname{erfc}\left(\frac{-x}{2\sqrt{Dt}}\right) - C_O. \qquad (2)$$

Here, C_1 is the concentration of oxygen ^{18}O isotope at the boundary of the surface layer, which is saturated with isotopic water and serves as a source of the diffusant, and C_O is the concentration of oxygen ^{18}O isotope in the bulk of the glass.

Thus, in borosilicate and aluminosilicate glasses, we observe the results of two different physicochemical processes of "penetration" of hydrogen and oxygen ^{18}O isotope atoms into glass rather than diffusion of water as was assumed earlier. Obviously, water molecules are decomposed in the surface layer (about 10 nm thick) of these glasses, after which hydrogen and oxygen ^{18}O independently "penetrate" into AS and BS glasses. This conclusion is in conformity with our earlier result based on analysis of obsidians hydrated under "natural conditions" [8]. The typical shape of the hydrogen profile allows us to exclude diffusion with a constant coefficient from further analysis [9]. For the working hypothesis, we considered the solid-state chemical reaction between hydrogen and the oxides constituting the glass, with the most promising result seeming to be the formation of hydroxides from modifier oxides like aluminum oxide, boron oxide, and iron oxide (in obsidian), i.e., oxides of trivalent metals. This conclusion follows from a comparison of the experimental results shown in Fig. 1 and

the chemical composition of the glasses. Indeed, the limiting concentration of hydrogen in the hydrogenated layer nearly coincides with (or is restricted from above by) the concentration of boron and aluminum oxides, as well as iron oxide in BS and AS glasses, respectively (in at %). In the case of SLS glasses containing oxides of bivalent metals (calcium and magnesium oxides) as modifiers instead of oxides of trivalent metals, the glass is indeed hydrated, as has been mentioned above. A conclusive answer to the question of hydrogenated layer formation in BS and AS glasses can be obtained only from further investigations, which are being carried out at present.

Finally, the decomposition of water molecules into hydrogen and oxygen in the thin surface layer of BS and AS glasses at low temperatures (beginning with room temperature), as well as the accumulation of hydrogen with a concentration of up to about 10 at % in these glasses, are extremely interesting phenomena from the point of view of further studies to explore the possible applications of these glasses in hydrogen fuel cells due to their low cost in comparison with the less-common metals and rare-earth oxides that are used at present.

REFERENCES

1. S. Gin, Proc. Mater. Sci. **7**, 163 (2014).
2. T. Geisler, T. Nagel, M. R. Kilburn, et al., Geochim. Cosmochim. Acta **158**, 112 (2015).
3. S. Fearn, D. S. McPhail, and V. Oakley, Appl. Surf. Sci. **231−232**, 510 (2004).
4. I. Friedman and R. Smith, Am. Antiquity **25**, 476 (1960).
5. Io. Liritzis and N. Laskaris, J. Non-Cryst. Solids **357**, 2011 (2011).
6. W. A. Lanford, K. Davis, P. Lamarche, et al., J. Non-Cryst. Solids **33**, 249 (1979).
7. L. M. Anovitz, J. M. Elam, L. R. Riciputi, and D. R. Cole, J. Arc. Sci. **26**, 735 (1999).
8. Yu. Kudriavtsev, S. Gallardo, A. Villegas, et al., Rev. Mex. Fis. **56**, 204 (2010).
9. J. Crank, *The Mathematics of Diffusion* (Oxford Univ. Press, Oxford, 1975), p. 414.

Translated by R. Wadhwa