Analytical study of the obsidian hydration process

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Depth profiling analysis of some elements in a set of naturally hydrated obsidian samples was performed by using Secondary Ion Mass Spectrometry. We have investigated the mechanism of water penetration into obsidian and have revealed that water penetrates into the top surface layer alone. From this layer atomic hydrogen penetrates into the obsidian bulk through a still unknown mechanism; the penetration cannot be described by Fick's law with a constant diffusion coefficient.

Keywords: Obsidian hydration dating; SIMS.

Reportamos los resultados de análisis por SIMS (Secondary Ion Mass Spectrometry) de concentración en profundidad de algunos elementos en un grupo de muestras de obsidiana hidratadas naturalmente. Se ha estudiado el mecanismo de penetración del agua en obsidiana y se ha observado que sólo existe penetración en la capa superficial. Sin embargo, el hidrogeno penetra en el sólido a través de un mecanismo aún desconocido; esta penetración no puede ser descrita por la ley de Fick con un coeficiente constante de difusión.

Descriptores: Datación por hidratación de obsidiana; SIMS.

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1. Introduction

In 1960 Friedman and Smith [1] suggested a new method of dating of both archaeological and geological obsidian materials based on water diffusion into obsidian, the so-called Obsidian Hydration Dating (OHD). The method is based on the solution of the Fick's diffusion equation and the "square-root-of-time" law is used to obtain chronometric information:

$$x = (D \cdot t)^{0.5}, \tag{1}$$

where x is the water penetration depth, D is the diffusion coefficient, and is t the "exposure" time. It was found that the hydration rim reaches microns for typical archaeological samples and can be seen in an optical microscope after a special sample preparation procedure. Optical analysis of the hydration rim was a very cheap and simple technique and excited a great interest in the archaeological community in the 1970s. However, it was soon realized that there were considerable discrepancies between the dating obtained by the new hydration method and that obtained using alternative techniques [2]. Moreover, hydration dating of the obsidian collected in different areas (having different chemical compositions) demonstrated a strong scatter.

Starting from the 1990s, the depth distribution of hydrogen in obsidian artifacts has been analyzed by Secondary Ion Mass Spectrometry (SIMS) [3-6]. It has been found that the hydration rim thicknesses observed in an optical microscope differ from the hydrogen enriched layer defined by SIMS [3]. Moreover, different research teams have revealed a complex character of water diffusion into obsidian: a diffusion coefficient depending on the "exposure" time or on the difusante concentration has been suggested [3,6].

This paper reports on depth profiling analysis of a set of obsidian samples with hydrated layers. In order to understand the hydration mechanism, which still remains unclear, we compared the depth distributions of atomic hydrogen and hydrogen-containing cluster ions with each other and also with distributions of other elements in a hydrated layer.

2. Experimental

All experimental measurements were carried out with a Cameca ims-6f ion microprobe. A primary focused negative oxygen ($^{16}O^-$) ion beam scanned a raster with dimensions in the range 50-250 μm on the surface being examined. The secondary ions emitted from the central area of the raster 30-60 μm in diameter were analyzed with a double-focusing magnetic sector mass-spectrometer and monitored by a Faraday Cup or by an Electron Multiplier, depending on the secondary ion current. The depth analyzed was recalculated from the time of sputtering after additional experimental crater depth measurements performed with a stylus profiler. Craters for the samples with minimal surface roughness were measured, and then the experimental sputtering rate was used to recalculate the depth scale for other samples. SIMS is a semi-quantitative method, and the atomic concentration of the elements of interest can be recalculated from experimental data only by using special standards. In this study we recalculated experimental ion intensities as concentrations by using Relative Sensitivity Factors (RSFs) defined for implanted SiO_2 standards [7]. This seems to give quite a good approximation because SiO_2 constitutes about 75-77 weight % of a typical obsidian. We did not aim at precise quantification, which was not necessary for our study.
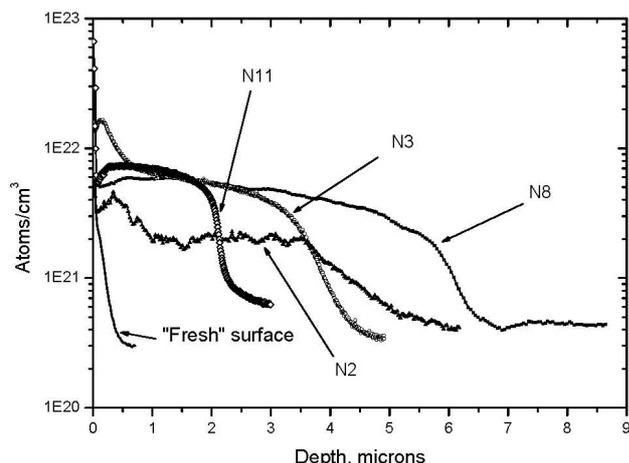
FIGURE 1. Hydrogen distribution in a near-surface layer of "antique" obsidian samples.

A set of naturally hydrated obsidian samples was collected; obsidian commonly encountered in the central part of Mexico was selected. The goal of our study was to gain insight into the problem of hydration dating and to develop an appropriate experimental SIMS technique for dating archaeological obsidian samples. We chose the samples with flat smooth surfaces and with limited sizes to fix them in our standard sample holder. The smooth surface was necessary to prevent any electron optics effects arising due to a sample surface curvature and affecting the secondary ion collection efficiency. Obsidian represents a natural glass, which is a strong dielectric. Ion bombardment of any dielectric sample results in a surface charging effect, which makes any analysis impossible. To avoid the charging effect, we used a negative oxygen ion beam and deposited a gold film to obtain good electrical contact. A "fresh" obsidian surface was assumed to be free of diffused water and was used for comparison with the "antique" samples. We prepared special reference samples with fresh surfaces from a large obsidian rock broken into small pieces and chose the pieces having the smoothest surfaces. Experimental samples were cleaned in an ultrasonic bath in alcohol for 15-25 minutes in order to remove possible contamination. After 20-30-min drying in the ambient atmosphere, the samples were placed into a thermal evaporator and were covered with a 50-nm gold film under vacuum.

3. Experimental results and discussion

Following other investigators [3-6] we performed the Obsidian Hydration Dating by a depth profiling analysis of H distribution by monitoring H^+ secondary ions. Figure 1 shows experimental data for several "antique" obsidian samples and for a "fresh" obsidian surface. It can be seen that the maximum concentration of incorporated H and the original concentration of H (water) vary only slightly for different obsidians samples; this is a typical situation [3,6]. The experimentally measured H profiles have quite a distinctive shape which is evidently far from the exponent or Error function predicted

by Fick's law with a constant diffusion coefficient. Following the authors of [3,6], we are inclined to believe that the diffusion is complex, with a time- or concentration-dependent coefficient.

The experimental H distributions presented in Fig. 1 exhibit surface "peaks" that correspond to thin surface layers; they are rather wide for some samples (samples N2, N3 in Fig. 1). We suggested that the composition of the top surface layers differs from that of the sample bulk. The surface roughness and the top surface layer width have been found to correlate strongly: the samples with the highest roughness have the widest "peaks". This effect has an evident explanation: any mono-atomic layer is transformed into a wider one in an experimental depth profile due to a convolution of the original element distribution and the surface roughness distribution occurring during SIMS measurement [8]. So, an increase in the surface roughness results in a broader experimental surface peak. We used this effect to study the depth
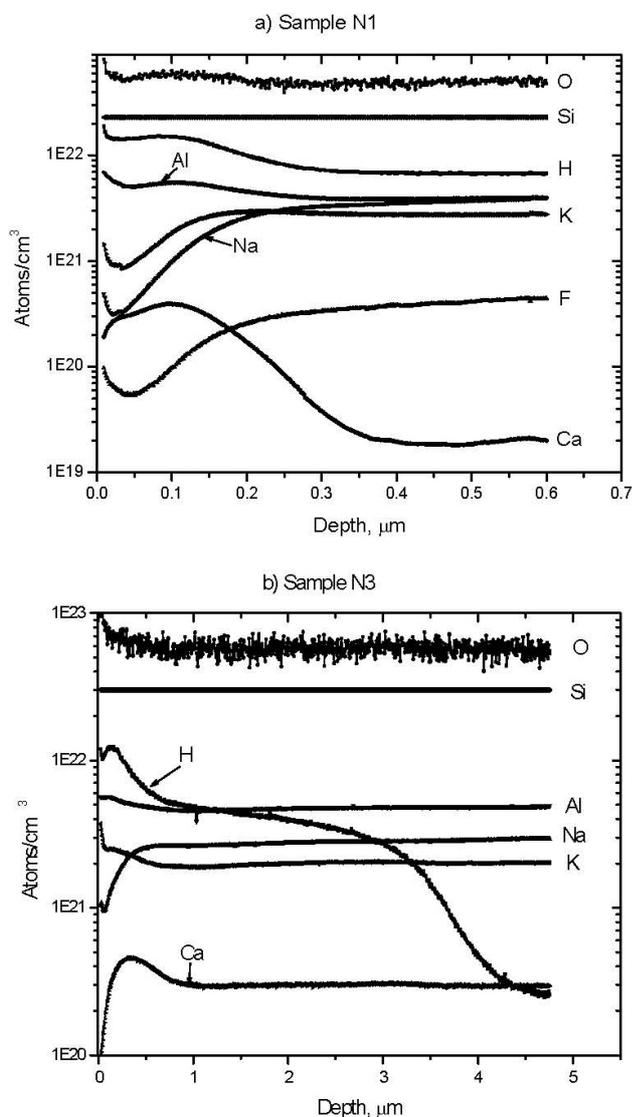

FIGURE 2. Depth distributions of some elements of interests in a near-surface layer of two obsidian samples.

distribution of the elements with relatively high concentrations in the top surface layer in order to clarify the mechanism of water penetration into obsidian. Depth profiling of the elements of interest was performed for rough samples by applying the so-called High Resolution Mode in order to remove their interferences with cluster ions.

Figures 2a and 2b shows typical depth distributions of some elements in a near surface layer. First of all let us consider the oxygen depth distribution. It is important to say a few words about the experimental technique used here. We performed ion sputtering of experimental samples by a $^{16}O^-$ ion beam and monitored oxygen $^{18}O^+$ secondary ions in order to avoid the influence of implanted primary ions on the experimental signal. Figures 2a and 2b shows the depth distribution of oxygen in samples N1 and N3 in comparison with the distributions of hydrogen and other elements. A constant oxygen level across both the hydrated layer and the non-hydrated layer is evident, whereas the oxygen concentration increases slightly in the top surface layer discussed above (please take into account the logarithmic scale used). This contradicts the ideas of Friedman and Smith on water diffusion [1]. We arrived at the conclusion that there is a diffusion of atomic hydrogen, but not water.

Another important experimental result shown in Fig. 2 is a strong leaching of the top surface layer: all alkali metals, *i.e.*, Na, K, Li, Cs, Rb (the last three elements are not presented in Fig. 2), leave the layer: their concentrations decrease by almost one order of magnitude in Fig. 2b. On the other hand, the hydrogen and the oxygen concentrations increase in this layer as compared with the deeper "hydrated" layer. Both these effects lead to our conclusion that the water concentration in the top surface layer increases. Most probably, a direct ion exchange reaction between alkali elements (Alk) and hydrogen occurs in this layer:

$$\text{Alk}_2\text{O} + 2\text{H}^+ - > \text{H}_2\text{O} + 2\text{Alk}^+ \qquad (2)$$

Then, the water-enriched surface layer acts as a hydrogen source for atomic hydrogen diffusion into the obsidian bulk.

SIMS is the method of elemental analysis of surface and near-surface layers, but in some cases information on the chemical (molecular) composition of samples can be obtained by this technique. In this study we used the emission of secondary cluster ions to get information on the chemical state of H (and of O in an indirect way) in a hydrated layer. We compared the ion yields of the secondary cluster ions containing one H atom (OH^+, NaH^+, $NaOH^+$, SiH^+, KH^+) and two H atoms (H_2^+, H_2O^+) with the ion yield of H^+ secondary ions (see Fig. 3a and 3b). A radical difference between them is evident. H^+, OH^+, $NaOH^+$, and SiH^+ cluster ion yields demonstrate very similar behaviors. Some deviations can be explained by a very complicated experimental regime used: we applied the High Resolution mode with a mass resolution power of M/DM $\approx$ 7500 to separate all the arising interferences. The high resolution, together with a residual surface charging (occurring due to incomplete charge compensation) results in experimental errors for cluster ions be-

cause of their narrow energy distributions. NaH^+ and KH^+ cluster ion yields behave in the opposite manner to the H^+ in the "hydrated" layer. This becomes clear if we build the normalized yields (with respect to H^+) of these clusters (see Fig. 3a). Note that there is a constant level of K and Na in the "hydrated" layer (but not in the top surface layer). It is known that any obsidian contains about 0.2 weight % of water [1-6]. As is shown above, hydrated obsidian also has a water-enriched top surface layer. We have found that H_2^+, H_2O^+ and H^+ distributions are similar in the top surface layer and in the bulk, but radically differ in the "hydrated" layer (see Fig. 3b). This suggests that there are no water molecules in the hydrated layer and hydrogenation of the obsidian actually takes place. We obtained the same results for all analyzed samples and for different experimental regimes (different Mass Resolution Powers). Unfortunately, the exact
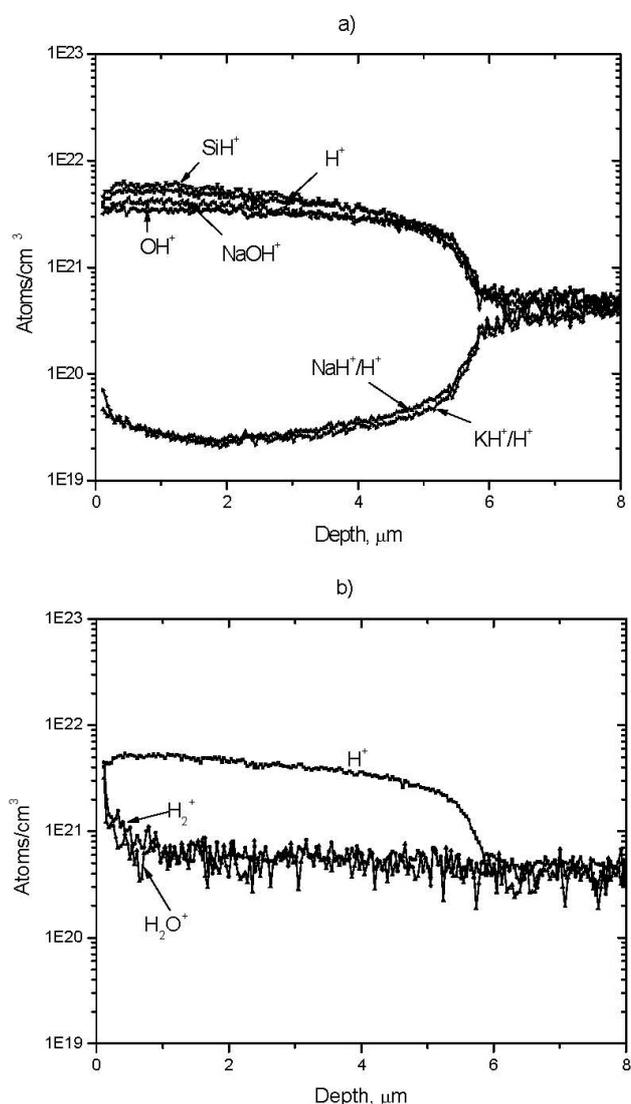

FIGURE 3. Distribution of hydrogen-containing cluster ions in a near-surface layer of obsidian sample N8. Yields of cluster ions with one H atom (a) and two H atoms (b) are compared with the H^+ ion yield.

chemical hydrogen state cannot be found from SIMS data. But we need this information in order to explain the H penetration into obsidian and use this effect for dating antique obsidian.

4. Conclusion

SIMS depth profiling analysis of hydrated obsidian samples has demonstrated that H penetration into obsidian occurs in two steps:

(i) water molecules are absorbed from the ambient air by a fresh obsidian surface, dissolve into H and OH, and participate in an ion-exchange reaction with alkali metal oxides. This leads to the leaching of a top surface layer and its hydration.

(ii) The thin surface layer becomes a source of H diffusion (penetration) into the obsidian volume through the yet undefined complex mechanism. There is no diffusion of water molecules into the obsidian.

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