



Transient and equilibrium solubility of water in rhyolitic glass: implications for hydration rate development at elevated temperature



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ABSTRACT

Hydration rate development on obsidians within the laboratory has become the preferred calibration procedure for the obsidian dating method. A fundamental assumption of this calibration procedure has been that water concentration within the hydration layer is at equilibrium with regard to the experimental partial pressure. Our analysis of hydration layers from short-term low temperature (110–150 °C) experiments reveal that water densities decrease with higher temperature and have not reached equilibrium. This may result in non-representative activation energies for archaeological samples. Longer experimental periods will be required to obtain hydration layers that can be used for a correct calibration.

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1. Introduction

Obsidian hydration in its most basic aspect describes the diffusion process by which water is incorporated into an obsidian surface. This process involves both physical and chemical changes in the glass that may include volume expansion, surface relaxation, and molecular inter-conversion ($\text{H}_2\text{O} \rightarrow \text{OH}$) at higher temperatures (>600 °C) (Doremus, 2002; Anovitz et al., 2008). There have been numerous attempts to simulate hydration layer formation under controlled laboratory conditions at above ambient temperatures in order to investigate the mechanisms and controlling parameters of the process (Anovitz et al., 1999, 2004, 2008; Riciputi et al., 2002; Michels et al., 1983; Stevenson et al., 1998; Stevenson and Novak, 2011) and clarifying insights have resulted. Simulated hydration layers have also been successfully used to estimate the Arrhenius constants that have been used to calculate hydration rates for prehistoric archaeological samples (Ambrose and Novak, 2012; Rogers and Duke, 2011).

Three general classes of methods have been proposed for measuring the depth of simulated or archaeologically hydrated surface layers: 1) measurement of water (e.g., % H_2O) mass uptake

with time by infrared spectroscopy (FTIR) (Ebert et al., 1991; Stevenson and Novak, 2011; 2) direct measurement of water (e.g., hydrogen) depth profiles by secondary ion mass spectroscopy (SIMS) (Ambrose and Novak, 2012; Anovitz et al., 1999, 2004, 2008; Riciputi et al., 2002; Stevenson et al., 2004); and 3) micrometer measurements on the leading edge of the hydrated stress zone by optical microscopy (OM) (Friedman and Smith, 1960; Friedman and Long, 1976). When using FTIR water determinations, coupled with OM or SIMS depth determinations, the density of water in the hydration profile may also be estimated.

This paper addresses an apparent contradiction in water absorption data measured on low temperature (<160 °C) laboratory hydrated specimens of obsidian from the West Sugarloaf obsidian source in the Coso volcanic field, Inyo County, California. The measurements were made by two methods that included water mass uptake measured by infrared photoacoustic spectroscopy (IR-PAS), and classical measurement of hydration rim width by OM. The cross-sectional density (CSD) of water in the hydrated layer was then estimated by the parameter $\text{CSD} = w/r$, where w is the water mass gain (% H_2O as indicated by the IR-PAS response) and r is the thickness of the hydration rim in micrometers (μm). The experimental results indicated that the CSD decreases with temperature, which is both counter-intuitive and seemingly contrary to Henry's Law of solubility. In this paper we look at this outcome from both an empirical and theoretical perspective to discover the reason for this trend.

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2. Water solubility in obsidian

That water molecules dissolve in glasses is well known (Doremus, 1994, 2002). The extent to which they dissolve at equilibrium is defined by Henry's Law as

$$C_d = KP_w \quad (1)$$

where: C_d is the number of dissolved molecules of water per unit volume and P_w is the partial pressure of water in the gas surrounding the glass (Levine, 2002:273, Eq. 9.65). The factor K , the solubility, is not a function of temperature at partial pressures below about 100 atm (Doremus, 2002:78–79, and references cited therein). Thus, the concentration of dissolved water in obsidian at equilibrium is a function of the external water vapor partial pressure. Imperfections within the obsidian such as impact micro-fissures and the frequency and distribution of crystallites may add interferences to this predicted relationship (Liritzis, 2006), and can lead to an anomalously high water concentration at the surface. This phenomenon is often observed in SIMS profiles of hydrogen concentration with depth.

The natural hydration of obsidian at ambient temperature yields a curve of water concentration as a function of depth as shown notionally in Fig. 1A. According to Henry's Law, the water concentration near the surface is at the saturation level for the local partial pressure of water vapor. A measurement of hydrogen concentration versus depth by SIMS, for example, would yield such a curve. Fig. 1B shows the expected result if a succession of curves is measured over

time (t), with temperature and partial pressure held constant, and where $t_3 > t_2 > t_1$. The Henry's Law limit does not change, and the surface concentration is at that limit for all curves. In such a case, the hydration is proceeding slowly enough so that essentially equilibrium conditions prevail near the surface for all times.

An important conclusion can be drawn from Fig. 1B. Assuming the maximum height of the curve is constant, and that the morphology of the leading edge is the same over time, the position of a given point on the curve and the water mass uptake increase at the same rate. Furthermore, since this applies at any temperature, it follows that the activation energy for the two processes is the same. However, the data discussed in the next section of this paper suggest the concentration growth curves for accelerated laboratory hydration above ambient temperature differ. Fig. 1C shows the probable growth curves under induced hydration conducted at a stable temperature. Again, $t_3 > t_2 > t_1$, but the water concentration increases with time.

3. Experimental methods

Laboratory hydration was conducted on a geological hand sample of volcanic glass from the Coso Volcanic Field that originated from the West Sugarloaf Mountain flow (UTM 424979E, 3988466N, North American Datum 1983). Individual obsidian coupons ($8 \times 8 \times 2$ mm) were prepared by cutting on a slow speed trim saw and then dry polished to a reflective finish (1200 grit or $5 \mu\text{m}$). Each sample was cleaned with acetone and rinsed with water, allowed to air dry, and placed on a stainless steel mesh rack within a 25 ml stainless steel reaction canister. Two milliliters of distilled water was added to the canister which was then sealed under high torque with a copper gasket. Five canisters were prepared and placed in convection ovens at 110, 120, 130, 140, and 150 °C for predetermined intervals (Table 1). The specimens were immersed in saturated water vapor, but were not in contact with liquid water.

At the end of the reaction period, the samples were removed and allowed to air dry. Infrared photoacoustic spectroscopy (IR-PAS) (Stevenson et al., 2013) was then conducted to determine the accumulated mass gain of molecular water, as reflected by the intensity of the IR-PAS response (Table 1). This result was achieved by subtracting the pre-hydration IR-PAS response from the post-hydration response value of the infrared water peak at 1630 cm^{-1} . The samples were then mailed to a second laboratory where thin sections were prepared. Optical measurements of the hydration layer thickness were made on a petrographic microscope at $800\times$. All measurements have an associated error of $\pm 0.1 \mu\text{m}$.

4. Experimental results

Table 1 presents the data as measured on a specimen of West Sugarloaf obsidian from the Coso volcanic field. Hydration rim thickness is shown in microns, and the water content in the hydrated layer is reflected by the amplitude value of the 1630 cm^{-1} band measured by IR-PAS (Newman et al., 1986). The relatively

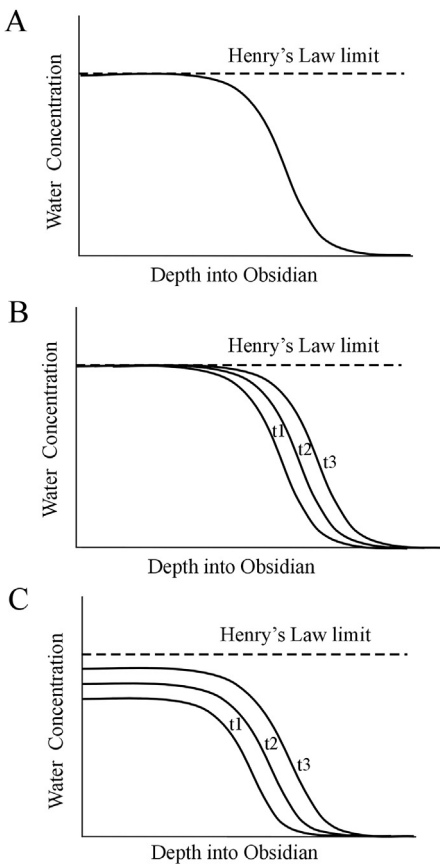


Fig. 1. A) Hydrogen profile with water concentration following Henry's Law; B) A series of hydrogen profiles at sequential times with water concentrations following Henry's Law with temperature held constant; C) Expected water concentration profiles for short term laboratory accelerated hydration that is below the Henry's law limit.

Table 1
Induced hydration results for Coso volcanic field, West Sugarloaf Mountain obsidian.

Temperature (°C)	Hot-soak time (Days)	Hydration rim (μm)	IR-PAS response
110	30	1.7	0.1633
120	25	2.5	0.1887
130	20	3.0	0.2013
140	15	3.7	0.2045
150	10	3.7	0.1819

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