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Protocols for laboratory hydration of obsidian, and their effect on hydration rate accuracy: A Monte Carlo simulation study

Alexander K. Rogers[a,*], Christopher M. Stevenson[b]

[a] Maturango Museum, Ridgecrest, CA, USA
[b] School of World Studies, Virginia Commonwealth University, Richmond, VA, USA

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ABSTRACT

Laboratory hydration of obsidian is based on the principle that the measurement of water penetration at high temperatures allows computation of hydration rates at archaeological temperatures. Accuracy of the laboratory hydration method is sensitive to the details of the laboratory and analysis protocols employed. We present the results of a simulation study showing that accuracy of the standard protocol is poor, but is improved by longer hot-soak times, more accurate hydration rim measurements, and use of statistical weighting factors in the analysis. A revised protocol is proposed which permits hydration rate development with accuracies of 10–15%. However, inherent limitations of optical microscopy make further improvements difficult and the measurement of hydration layers using alternate technologies is recommended.

1. Introduction

Accelerated laboratory hydration at temperatures > 90 °C is a frequently-used method of determining experimental hydration rates for application to the archaeological record. It is based on the principle that the temperature dependence of hydration rate can be established using rapidly formed surface hydration layers. Quantification of the temperature dependence then allows the computation of a hydration rate at lower archaeological temperature. A major advantage of the method is that hydration rate accuracy is not influenced by the poor integrity of archaeological contexts; a situation which can plague hydration rate estimates based on association of radiocarbon samples, or temporally-sensitive artifacts, with hydrated artifacts (Rogers, 2008).

Despite this clear advantage, the accuracy of the accelerated hydration rate determinations has been found to be very sensitive to the detail of laboratory protocols and statistical methods of analysis (Rogers and Duke, 2014). The former was initially noted early in the development of accelerated hydration methods by Stevenson et al. (1998), who showed that obsidian exposed to high temperature distilled water is rapidly eroded within the reaction canister water bath, leading to an incomplete final hydration history and incorrect hydration rates (see also Rogers and Duke, 2011). Current laboratory methods add silica gel to the distilled water as a buffering agent (Stevenson et al., 1989a), or use vapor-phase methods in which the specimen is not in contact with the water (Ambrose, 1976; Anovitz et al., 2004; Mazer et al., 1991; Stevenson et al., 1998; Stevenson et al., 2000). In addition, recent research has shown that the diffusion coefficient of water goes through an initial transient phase before reaching a steady state, and thus the use of abbreviated hot-soak times can lead to hydration rates which are too high (Rogers and Duke, 2014; Stevenson and Rogers, 2014). Furthermore, analysis of the data derived from elevated temperatures requires use of linear least-squares methods, and statistical theory suggests that the least-squares process should include weighting factors for the data points (Cvetanovic et al., 1979). Unfortunately, the weighting factors significantly complicate the analysis, and so most researchers do not use them. Finally, the accuracy of the resulting obsidian parameters is dependent on the measurement accuracy of the hydration rim thickness (Rogers, 2006).

This paper reports the results of a simulation study which quantifies the effects on the accuracy of the obsidian parameters and computed hydration rates using hydration layers measured by optical microscopy. The study addresses hydration rim measurement errors, length of hot-soak times, and the mathematical form of the weighting factors in the least-squares best fit. Previous studies of laboratory hydration methods by Rogers (2006) addressed only the issue of measurement accuracy and its effects on age estimates. To integrate the effects of all these parameters, our analysis is based on a Monte Carlo simulation of the laboratory hydration process and of the least-squares analysis method. The obsidian hydration process itself is based on the model of Rogers (2015), discussed further below. Experimental errors are introduced by a Gaussian random number generator with appropriate standard deviation, the obsidian parameters and rate are computed for each

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[*] Corresponding author at: Maturango Museum, 100 E. Las Flores Ave., Ridgecrest, CA 93555, USA.
E-mail address: sandy@maturango.org (A.K. Rogers).

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iteration, and statistics are collected after $N = 10{,}000$ iterations. The hydration rate of obsidian is a strong function of intrinsic water content of the obsidian (Stevenson et al., 1998, 2000), and total intrinsic water content of obsidian typically lies between 0.1 wt% and 1.5 wt%. For this analysis, two nominal values of 0.1 wt% and 0.6 wt% were chosen for modeling. In archaeological terms, these correspond to Napa Glass Mountain (C. M. Stevenson, personal communication) and Coso West Sugarloaf obsidian (Stevenson et al., 1993), both from California.

This study of experimental protocol examines three case examples: the typical protocol employed today, which features relatively short hydration times, of 10 to 30 days; an example with hot-soak times that are roughly twice the standard protocol; and a case with greatly extended hot-soak times based on the transient phenomena described in Rogers and Duke (2014). Hot-soak temperatures are limited to 110–150 °C, since earlier studies have shown that higher temperatures can lead to hydration layers with optically diffuse hydration fronts that cannot be reliably defined (Stevenson et al., 1998). Experimental errors associated with hydration rim measurement are modeled by a random number generator and the least-squares analysis process is modeled mathematically.

The study of the analysis procedure also examines two cases of weighting of the data points: uniform weighting, which is commonly used today in laboratory hydration studies; and weighting based on estimated experimental measurement uncertainties as recommended by Cvetanovic et al. (1979).

2. The obsidian hydration process

"Obsidian hydration", in its most basic aspect, simply describes the process by which water diffuses into the obsidian and creates physical and chemical changes within the glass (Doremus, 2002; Anovitz et al., 2008). When a fresh surface of obsidian is exposed to air, water molecules adsorb onto the surface. Since any unannealed obsidian surface exhibits cracks at the nano-scale, the amount of surface area available for adsorption is much greater than the macro-level surface area would suggest, creating a large surface concentration. Some of the adsorbed water molecules diffuse into the glass matrix. The diffusion seems to be due to chemical dissociation of molecular water (Kudriatsev et al., 2017), followed by chemical reactions between H^+ ions and oxygen atoms in the glass matrix (see also Behrens and Nowak, 1997 for a discussion of a possible interconversion process). The diffusion process, driven by the water concentration gradient, causes an increase in the openness of the glass matrix itself, possibly due to chemical reactions in which the H^+ ions combine with bridging oxygen atoms, facilitating further diffusion of water. Since the hydrated region is volumetrically expanded and the non-hydrated region is not, a stress region exists between the two. As time passes, the region of increased water concentration progresses into the glass, its rate being a function of the initial openness of the glass, the temperature, and the dynamics of the process itself. When the hydrated layer becomes thick enough, typically around ~20 μ, the accumulated stresses may cause the layer to spall off as perlite (Friedman et al., 1966; Morgenstein et al., 1999), although the current authors have occasionally observed thicker hydrated layers.

The classical field of obsidian hydration dating (OHD) is based on measuring the thickness of the stress zone caused by the diffusion process. The interface between the hydrated and unhydrated volumes is a zone of optical contrast when seen in thin-section under polarized light, due to the phenomenon of "stress birefringence" (Born and Wolf, 1980, 703–705; Haller, 1963:220). Both theory (Doremus, 2002) and laboratory measurements (e.g. Friedman and Long, 1976; Stevenson et al., 1998) indicate that the hydration of obsidian proceeds with the square root of time:

$$r^2 = k * t \tag{1}$$

where: r is the depth of the stress region (hydration rim), t is time, and k is the hydration rate. The hydration rate also varies with temperature as described by the Arrhenius equation:

$$k = A * \exp(-E/(R^* T)) \tag{2}$$

where: E is the activation energy, A is the pre-exponential, R is the universal gas constant (8.314 J/mol), and T is temperature in °K (Doremus, 2002). Over typical ranges of archaeological interest, the activation energy and pre-exponential are independent of temperature but dependent upon glass composition.

3. Current laboratory hydration protocol

To perform laboratory hydration, a set of specimens with fresh surfaces is first prepared. This involves removing a number of flakes (in this case five) by percussion from the same piece of obsidian. Each flake is placed in a stainless steel pressure vessel with distilled water, to which silica gel is added to create a saturated solution; the amount required varies from 21.99 mg/100 ml at 110 °C to 36.51 mg/100 ml at 150 °C (Fournier and Rowe 1977:1055, Eq. (2)). The purpose of the gel is to saturate the solution in the hot-soak bath with silica, to prevent dissolution of the surface of the obsidian. Alternatively, the specimens can be suspended in a 100%RH vapor bath created by the addition of minor amounts of water, although care must be taken to avoid condensate coming into contact with the specimen (Stevenson et al., 2000). The pressure vessel is then placed in a pre-heated mechanical convection oven with a laboratory-grade controller, and quickly raised to the specified hot-soak temperature. After the length of time prescribed by the experimental protocol, the pressure vessel is removed from the oven, quickly quenched under running water, the specimen removed, and the hydration rim measured. This measurement set (time, temperature, and hydration rim thickness) constitutes one data point. The process is repeated with the other specimens at different temperatures and times. A detailed description of the protocol can be found in Stevenson et al. (1998).

The analytical process determines the activation energy (E) and pre-exponential factor (A), from which hydration rate can be computed for any desired temperature using the Arrhenius equation. Eqs. (1) and (2) can be combined to give:

$$r^2/t = A * \exp(-E/(R^* T)) \tag{3}$$

Taking the natural logarithm of both sides gives the logarithmic Arrhenius equation:

$$\ln(r^2/t) = \ln(A) - (E/R) * (1/T) \tag{4}$$

If we define:

$$Y = \ln(r^2/t) \tag{5}$$

and

$$X = 1/T \tag{6}$$

then Eq. (4) is a linear equation of the form:

$$Y = I + S * X \tag{7}$$

with the intercept $I = \ln(A)$ and slope $S = -E/R$.

With five data points the equation is over-defined, and must be solved by least-squares methods. A linear least-squares solution for I and S is defined by Cvetanovic et al. (1979):

$$I = \{\sum w_i x_i^2 \sum w_i y_i - \sum w_i x_i \sum w_i x_i y_i\}/D \tag{8a}$$

$$S = \{\sum w_i \sum w_i x_i y_i - \sum w_i x_i \sum w_i y_i\}/D \tag{8b}$$

where:

$$D = \sum w_i \sum w_i x_i^2 - \left(\sum w_i x_i\right)^2 \tag{8c}$$

Thus, given five data points $\{r_i, t_i, T_i\}$ a least-squares best fit can be computed for I and S. From them, A and E can be computed, which allows computation of the hydration rate at any desired temperature.

The parameters w_i in Eqs. (8a), (8b) and (8c) are weighting factors