

**LABORATORY MEASUREMENT OF HYDRATION RATE FOR  
NAPA VALLEY OBSIDIAN**

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Abstract:

This paper reports the computation of hydration rate for Napa Valley obsidian from laboratory data. Napa Valley obsidian, from northern California, is found to be a slow-hydrating obsidian, with a rate of  $0.0912 \pm 0.051 \mu/\text{yr}^{1/2}$  at an effective hydration temperature of  $17.0^\circ\text{C}$ . An equation to scale the rate with effective hydration temperature is provided. Activation energy of Napa Valley obsidian is  $10014 \pm 956^\circ\text{K}$ , and its diffusion constant, or pre-exponential factor, is  $8.012 \times 10^{12} \mu^2/\text{yr}$ , both of which are independent of temperature. Its intra-source variability in hydration rate is very low (CV  $\approx 0.014$ ), implying a low variability in intrinsic water. The sample size is very small (N = 2) so further measurements are desirable.

## Introduction

Quantitative measurement of hydration rate by laboratory methods (sometimes known as “induced hydration”) has an equivocal history in archaeology. The temperature dependence of hydration rate is well known, as are attempts to measure hydration rate in the laboratory (e.g. Friedman and Long 1976; Stevenson et al. 1998). However, rates measured in the laboratory often have not agreed well with archaeological data (see, for example, the pointed observations in Hall and Jackson 1989:32), and are generally not used by practicing archaeologists today.

This paper reports a protocol to compute the hydration rate for Napa Valley obsidian from laboratory data, based on recent successful application to Topaz Mountain obsidian, which agreed closely with archaeological data (Rogers and Duke, in press). Laboratory hydration data for this investigation were provided by Origer’s Obsidian Laboratory (Origer 2010), and the laboratory methodology was as described in Stevenson et al. (1998) and Rogers (2006). The obsidian hydration parameters (activation energy and diffusion constant) were determined from laboratory hydration data, after which the hydration rate was computed at an effective hydration temperature (EHT) of 17.0°C, typical of northern California sites.

The standard deviation of the laboratory rate was estimated by a Monte Carlo simulation using measured parameters and accuracies, and intra-source variability of Napa Valley obsidian was calculated.

## Theory and Notation

The basic equation from diffusion theory is

$$r^2 = DT \tag{1}$$

where  $r$  is the hydration rim,  $D$  is the diffusion coefficient, and  $t$  is time; units of  $D$  are  $\mu^2/\text{yr}$  (Crank 1975). An equivalent form is

$$r = k_e \sqrt{t} \text{ (or } k_e t^{1/2} \text{)} \tag{2}$$

where now  $k_e$  is in units of  $\mu/\text{yr}^{1/2}$ . A convenient expression for age in terms of hydration rim is

$$t = K_a r^2 \tag{3}$$

where the age coefficient  $K_a$  is the reciprocal of  $D$ , and is in  $\text{yrs}/\mu^2$ .

The diffusion coefficient  $D$  is a function of temperature by the Arrhenius equation

$$D = A \exp(-E/T) \tag{4}$$

where A is the diffusion constant or “pre-exponential”, E is activation energy in °K and T is temperature in °K (Doremus 2002; Rogers 2007). Note that D is a function of temperature, but E and A are not.

Finally, the diffusion equation (1) can be combined with the Arrhenius equation (4) to yield

$$r^2/t = A \exp(-E/T) \quad (5)$$

This is the equation used for computing E and A, and hence D, from laboratory data.

### Linear Best-Fit Technique

Equation (5) can be expressed in logarithmic form as

$$\ln(r^2/t) = \ln(A) - E/T \quad (6)$$

If we define  $y = \ln(r^2/t)$  and  $x = 1/T$ , equation (5) becomes a linear equation of the form

$$y = I + Sx \quad (7)$$

with  $I = \ln(A)$  and  $S = -E$ . Given data for r, t, and T for two or more points, equations (6) and (7) can be solved as a linear best fit (Cvetanovic et al. 1979; Meyer 1975):

$$S = \{N\sum x_i y_i - \sum x_i \sum y_i\}/D \quad (8a)$$

$$I = \{\sum x_i^2 \sum y_i - \sum x_i \sum y_i\}/D \quad (8b)$$

and

$$D = N\sum x_i^2 - (\sum x_i)^2 \quad (8c)$$

Here weighting for all points is assumed equal. The slope value S is the activation energy, and A, the diffusion constant, is given by

$$A = \exp(I) \quad (9)$$

The laboratory data set provides three points: one at 110°C for 29 days, one at 150°C for 29 days, and one in which the samples were soaked at a variable temperature. The last case involves 29 days at 110°C and 29 days at 150°C; one sample of eight specimens underwent the hot soak first, followed by the cool, while the process was reversed for the other sample of eight. Since the rim values were the same regardless of sequence, as predicted by theory (Crank 1975; Rogers 2007), these two samples can be combined. A computation of effective hydration temperature (EHT) for this situation (per Rogers 2007) gives a value of 139.39°C. Six readings of the hydration rim were made on each specimen. The data are summarized in Table 1.

Table 1. Origer data for Napa Valley obsidian.

T, °C	t, days	mean r, μ	σ <sub>r</sub> , μ	N
110	29	1.72500	0.04523	12
139.39	58	5.97917	0.07211	24
150	29	5.84167	0.05149	12

Using these values in equation (8a) - (8c), and assuming a site EHT of 16.0°C, typical of northern California sites, gives results as in Table 2.

Table 2. Napa Valley obsidian hydration parameters

Parameter	Value	Units
Activation energy	10014	°K
Diffusion constant	$8.0123 \times 10^{-12}$	μ <sup>2</sup> /yr
Hydration rate k <sub>e</sub> at 17.0°C	0.0912	μ/yr <sup>1/2</sup>
Hydration rate D at 17.0°C	8.32	μ <sup>2</sup> /1000yr
Age coefficient K <sub>a</sub> at 17.0°C	120.2	yr/μ <sup>2</sup>

Napa Valley obsidian is thus relatively slow in hydration; the hydration rate for the Coso volcanic field is about a factor of three greater.

The accuracy of the rate computed above was estimated by a Monte Carlo simulation of the experimental errors. The technique is to introduce random errors into the r values, based on the standard deviations in Table 1, compute values of E, A, and k<sub>e</sub>, and accumulate statistics. Results are in Table 3.

Table 3. Napa Valley obsidian parameter accuracies.

Parameter	Value	Units
Std. dev of activation energy	956	°K
St. dev of diffusion constant	$6.89 \times 10^{-14}$	μ/yr <sup>1/2</sup>
St. dev. of hydration rate	0.051	μ/yr <sup>1/2</sup> .

Note that the standard deviation of the diffusion constant is greater than its mean. This occurs because errors in y-intercept (I in equation 8b) are being raised to an exponential per equation (9), and is unavoidable.

The hydration rate standard deviation corresponds to a  $CV_{k_e} \approx 0.49$ . This rather poor accuracy is due to the small number of data points, and again to the relatively large error in A caused by the exponentiation process in equation (9). It should be emphasized that σ<sub>k<sub>e</sub></sub> affects the accuracy of the age estimate, but does not affect the spread of ages as long as all age computations for a site use the same rate.

### Variability of Napa Valley Hydration Rates

It has been shown (Rogers 2010b) that the coefficient of variance of intra-source variations in hydration rate ( $CV_{ks}$ ) is given by

$$CV_{ks}^2 = 4[CV_r^2 - (\sigma_r/r)^2 - (0.06\sigma_{EHT})^2] \quad (10)$$

where  $CV_r$  is the CV of the aggregated rim values, σ<sub>r</sub> is the standard deviation of the rim measurement process, r is the mean rim value for the aggregate, and σ<sub>EHT</sub> is the standard

deviation of the EHT uncertainty. For laboratory measurements,  $\sigma_{\text{EHT}} \approx 0$ ; a best-fit procedure as described in Rogers 2010 using the data in Table 1 then yields

$$\sigma_r = 0.044\mu \quad (11)$$

and

$$\text{CV}_{k_s} = 0.014 \quad (12)$$

Two observations can be made here. First, the rim readings are very accurate, and fully validate Origer's claim of an accuracy of  $< 0.1\mu$ . Second, the obsidian has very little variability; in contrast, the corresponding values of  $\text{CV}_{k_s}$  for the Coso sources range as high as 0.25 (Stevenson et al. 1993; Rogers 2008). Since the hydration rate is small, it is likely that intrinsic water content of Napa Valley obsidian is also small; further, it is likely that the water variability is low. Thus, variations in rim thickness in field data are more likely due to differing ages or differing EHT than to rate variations for this obsidian.

### Conclusions

Napa Valley obsidian is a slow-hydrating obsidian, with a rate ( $0.0859 \pm 0.048 \mu/\text{yr}^{1/2}$ ) at  $16.0^\circ\text{C}$ , about one-third that of Coso obsidians. The rate can be adjusted to other values of effective hydration temperature by the equation

$$k_s = 0.0912 \exp[0.06(T_s - 16)] \mu/\text{yr}^{1/2} \quad (13)$$

where  $k_s$  is the hydration rate at the site of interest and  $T_s$  is the EHT at that site, in  $^\circ\text{C}$ . Alternatively, the age factor  $K_a$  can be scaled by

$$K_{as} = 120.2 \exp(0.12(16 - T_s)) \text{ yrs}/\mu^2 \quad (14)$$

where  $K_{as}$  is the age factor for the site of interest.

The intra-source variability in hydration rate for this sample of Napa Valley obsidian is very low ( $\text{CV} \approx 0.014$ ), approximately an order of magnitude less than Coso obsidian, which suggests its intrinsic water variability is also very low. As a consequence, the contribution of rate variations to the spread of hydration rims in field data is probably negligible. Finally, the measurement of hydration rims by optical microscopy is giving very good results for Napa Valley obsidians, with a measurement standard deviation of  $0.04\mu$ .

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