

A NEW AND SIMPLE LABORATORY METHOD FOR ESTIMATING HYDRATION RATE OF OBSIDIAN

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Obsidian hydration rate is frequently estimated by radiocarbon association, temporally-sensitive artifacts, or induced hydration in the laboratory. We describe a simpler method. The hydration rate is determined primarily by temperature and intrinsic water content of the obsidian. Intrinsic water content, in turn, can be determined from a simple measurement of density. We describe the method of measuring density, and provide the equation (previously published) to compute intrinsic water. We further describe the equation (also previously published) relating intrinsic water and temperature to hydration rate, and show examples of the goodness of the resulting fit.

Obsidian hydration dating (OHD) is a widely-used technique in the desert west, complementary to projectile point typology and radiocarbon (Thomas 2013:134). The standard method is to group specimens by geochemical source, obtain a hydration rate for that source, make appropriate temperature corrections, measure the hydration rims, and perform the analysis.

A recurrent issue in OHD is determination of an appropriate hydration rate. Methods often used include obsidian-radiocarbon association (Rogers and Yohe 2011), association with temporally-sensitive artifacts (Rogers 2014), and induced hydration (Rogers and Duke 2011; Stevenson et al. 1998). All these methods work to some degree, but have the drawback that they assign a rate to a geochemical source, and thus do not account for intra-source variations in hydration rate. The method we describe here is simple, inexpensive, and non-destructive, and can assign a rate to a specific artifact.

A major caveat is that although this method provides a hydration rate, it does not solve the problem of determining effective hydration temperature (EHT), which must still be computed by other means.

HYDRATION RATE AND WATER CONTENT

The relationship between hydration rate, intrinsic water content, and temperature has been studied for years, and the form of the equation is well known (e.g., Rogers 2015; Stevenson et al. 1998, 2000; Stevenson and Novak 2011; Zhang et al. 1991; Zhang and Behrens 2000). The general form of the equation is:

$$k = \exp(A_1 + B_1*w + C_1/T + D_1*w/T) \quad (1)$$

where k is the hydration rate, w is intrinsic water concentration in wt%, T is temperature in °K, and A_1 – D_1 are numerical constants, the values of which depend on the temperature and pressure regime. Intrinsic water can be either total water or hydroxyl, although the parameter values differ slightly, and T corresponds to the EHT of the specimen.

Parameter values were developed by Zhang et al. (1991) and Zhang and Behrens (2000) for geological cases (temperature 400 - 1200°C, pressure 0.1 – 810 mPa); however, these values do not yield realistic hydration rates for archaeological conditions. Rogers (2015) proposed values for archaeological conditions (temperature 10-30°C, pressure 1 atmosphere) based on data in Stevenson and Novak (2011), augmented by data from Stevenson et al. (1993) and Rogers (2013). Table 1 presents the current best estimate of the parameter values.

Table 1. Best-Fit Parameters for Equation.

PARAMETER	%H ₂ O _T	%OH	UNITS
A1	37.979	37.941	none
B1	-2.289	-2.289	/wt%
C1	-10,443	-10,443	°K
D1	955	1,066	°K/wt%

Table 2. Density Calibration Parameters.

PARAMETER	%OH	%H ₂ O _T
A2	35.21	61.56
B2	-14.95	-26.19
C2	14.59	25.59
D2	2.348	2.346

To make archaeological use of equation (1), the intrinsic water content of the obsidian specimen must be known. Intrinsic water in obsidian occurs as two species, molecular water (H₂O_m) and hydroxyl (OH); the sum of the two is the total water, H₂O_t. Molecular water occupies voids in the glass matrix, while hydroxyl is chemically bound to the matrix atoms. Measuring intrinsic water has typically been done by infrared spectrometry, either Fourier Transform Infrared Spectrometry (FTIR) (Newman et al. 1986) or Infrared Photo-Acoustic Spectrometry (IR-PAS) (Stevenson and Novak 2011), or by manometry (Newman et al. 1986). Unfortunately, these methods are destructive to the archaeological specimen.

An alternative method of measuring water content was proposed by Ambrose and Stevenson (2004). They demonstrated that the intrinsic water content is strongly correlated with the density of the obsidian, so that measuring the density permits calculation of the water content; the higher the density, the lower the water content. They used FTIR methods to measure water content of obsidian specimens from 31 sources, and computed a best-fit equation between density and water content. They showed that both the hydroxyl content and total water content (molecular water plus hydroxyl) can be predicted from obsidian density measurement by the equation:

$$w = A_2 + B_2 * d + (\rho - D_2) * C_2 * (\rho - D_2) \quad (2)$$

where w is either %H₂O_t or %OH in wt% and ρ is density in gm/ml. The concentration of water species was measured by FTIR: the concentration of OH was measured by absorbance at the 4500 cm⁻¹ band, and the concentration of total H₂O (%H₂O_t) computed from data in Newman et al. (1986). The parameters A₂ – D₂ in equation (2) are given in Table 2 (Ambrose and Stevenson 2004:12).

The rms error of the fit between the data set and equation (2) is 0.103 wt%, with $R^2 = 0.8998$.

Density Measurement

The density of the specimen can be determined by gravimetry (Archimedes' principle). The specimen is first weighed in the air, and then weighed when immersed in a heavy liquid. The density is then computed by:

$$\rho_s = \rho_l * w_a / (w_a - w_l) \quad (3)$$

where ρ_s is the density of the specimen, ρ_l is the density of the liquid, w_a is the specimen weight in air, and w_l is specimen weight when immersed in liquid. The commercially available Unigrav 1.6 is a useful immersion fluid, as it is non-toxic and 1.6 times as dense as water.

During the density determination process, the temperature of the liquid will increase as specimens of slightly higher temperature are repeatedly placed into the beaker containing the liquid. The impact of this is an increase in fluid volume which results in a decrease in density of the immersion liquid. To compensate for this effect, a calibration was developed that quantified the relationship between the density of the immersion liquid and temperature. A simple linear regression line was fit to the paired data values that resulted in the calibration:

$$\rho_l = 1.8797 - 0.0007 * T \quad (4)$$

where ρ_l is density of the liquid and T is temperature in °C. Note that equation (4) only applies to Unigrav 1.6.

The density of an archaeological specimen must be determined to within 0.1 milligrams. We used a shielded Ohaus Adventurer Pro analytical balance with a precision of ± 0.0001 gm using the manufacturer supplied density kit. A Vernier thermal probe and data logger was used to monitor the temperature of the immersion liquid. Three trials of 10 repeat measurements on different coupons from a single obsidian source indicated that the precision of density determinations ranged between 0.0009 and 0.0016 g/cm³. A separate analysis of error effects showed that an accuracy of better than 0.003 gm/cm³ is required for good results.

EXAMPLES

Once density has been measured, intrinsic water concentration (%H₂O_t and %OH) can be computed from equation (2), and the resulting values used to compute hydration rate from equation (1). Alternatively, if water content is known from spectrometry or manometry, those values can be used instead. The temperature T in equation (1) corresponds to the expected EHT of the specimen.

Here we present examples for five obsidian sources whose density was measured, combined with four other sources whose water content was determined by FTIR. The sources include seven from California (Casa Diablo [CD], Napa Glass Mountain [NGM], Mono Glass Mountain [MGM], Coso West Sugarloaf [WSL], Coso Sugarloaf Mountain [SLM], Coso West Cactus Peak [WCP], and Coso Joshua Ridge [JR]) and two from Nevada (Queen, Mt. Hicks). Table 3 summarizes the water data set.

Corresponding hydration rates for comparison are summarized in Table 4.

Hydration Rate Prediction

Based on these values, Table 5 presents the rate predictions, compared to the input data set of Table 4. Results are shown graphically in Figures 1 and 2.

Notice that the prediction by total water gives better results than the prediction by hydroxyl. This is borne out by the error statistics: for rate prediction by %H₂O_t the error standard deviation is 1.03 $\mu^2/1000$ years, and $R^2 = 0.9753$; for prediction by %OH the error standard deviation is 1.33 $\mu^2/1000$ years and $R^2 = 0.9613$. It is not clear why prediction based on %H₂O_t is more accurate than based on %OH, but it may be a quirk of the small data set.

DISCUSSION AND CONCLUSIONS

This paper presents a method for predicting obsidian hydration rate based on intrinsic water content for typical archaeological conditions of temperature and pressure. The form of the equation is well-attested geochemically, and the parameter values used here give archaeologically reasonable hydration rates. Effective hydration temperature must still be computed by other methods.

This method of estimating hydration rate has many benefits over previous methods. It is simple and non-destructive, and it avoids the problems of non-equilibrium conditions that often arise in induced hydration (Rogers and Duke 2011; Stevenson and Rogers 2014). It is inexpensive, and does not require

Table 3. Intrinsic Water Content Data.

SOURCE	METHOD	DENSITY, GM/ML	%OH	%H ₂ O _T	REFERENCE
CD	Density	2.3973	0.09	0.09	Stevenson p.c.*
NGM	Density	2.3774	0.18	0.18	Stevenson p.c.
MGM	Density	2.3659	0.10	0.11	Stevenson p.c.
Queen	Density	2.3553	0.10	0.11	Stevenson p.c.
Mt. Hicks	Density	2.3332	0.54	0.78	Stevenson p.c.
WSL	FTIR		0.48	0.62	Stevenson et al. 1993; Rogers 2008
JR	FTIR		0.81	0.62	Stevenson et al. 1993; Rogers 2008
WCP	FTIR		1.01	0.71	Stevenson et al. 1993; Rogers 2008
SLM	FTIR		1.02	0.80	Stevenson et al. 1993; Rogers 2008

Notes: * p.c. = personal communication.

Table 4. Hydration Rate Data, in $\mu^2/1000$ years at 20°C.

SOURCE	RATE	METHOD	REFERENCE
CD	12.10	Archaeological	Rogers 2016, 2017
NGM	11.70	Induced Hydration	Rogers 2016, 2010
MGM	12.55	Archaeological	Rogers 2016
Queen	12.55	Archaeological	Rogers 2016
Mt. Hicks	24.10	Archaeological	Rogers 2016
WSL	18.10	Induced Hydration, Archaeological	Rogers 2013, 2016
JR	22.30	Induced Hydration, Archaeological	Rogers 2013, 2016
WCP	27.30	Induced Hydration, Archaeological	Rogers 2013, 2016
SLM	29.90	Induced Hydration, Archaeological	Rogers 2013, 2016

Table 5. Rate Prediction, in $\mu^2/1000$ Years at 20°C.

SOURCE	BASILINE RATE DATA (TABLE 3)	RATE PREDICTION BY %H ₂ O _T	RATE PREDICTION BY %OH	% DELTA, %H ₂ O _T	% DELTA, OH
CD	12.10	11.48	11.46	-5.30%	-5.48%
NGM	11.70	12.55	12.94	7.03%	10.06%
MGM	12.55	11.69	11.63	-7.12%	-7.60%
Queen	12.55	11.76	11.69	-6.51%	-7.09%
Mt. Hicks	24.10	22.47	21.16	-6.98%	-13.00%
WSL	18.10	19.23	19.39	6.04%	6.90%
JR	22.30	23.11	23.42	3.59%	4.92%
WCP	27.30	28.06	26.45	2.74%	-3.17%
SLM	29.90	28.33	29.86	-5.39%	-0.13%

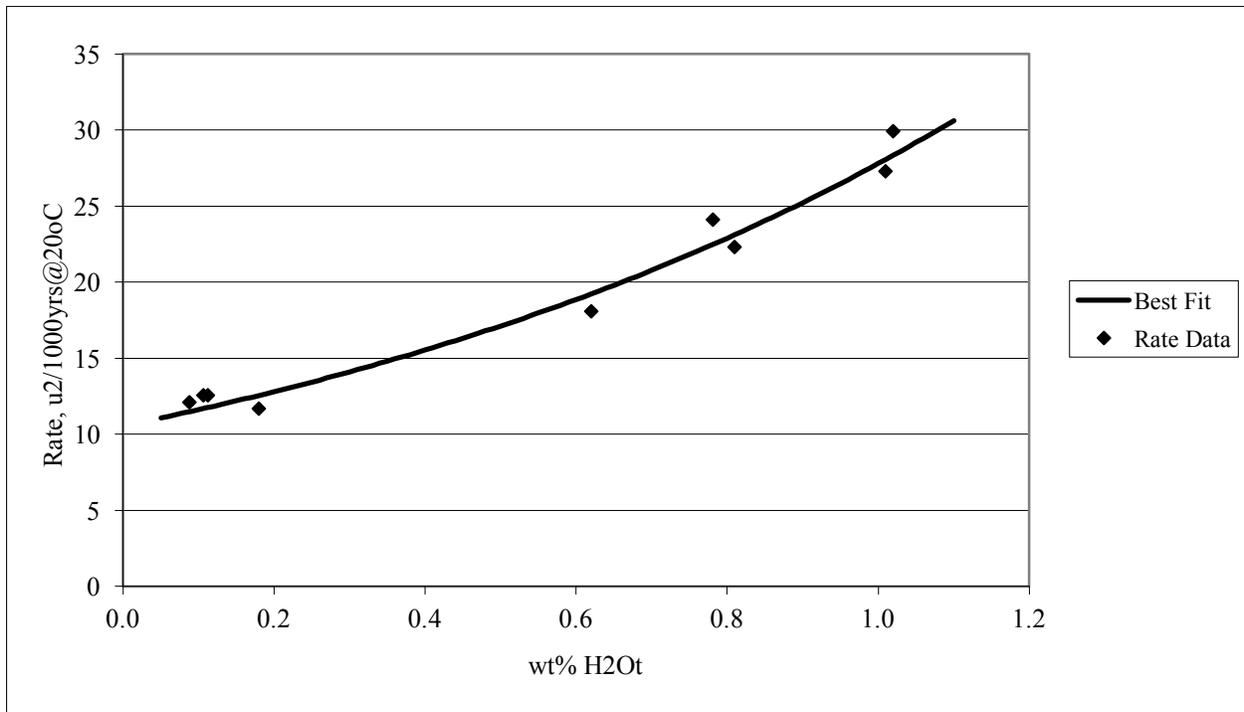


Figure 1. Rate Prediction Based on %H₂O_t.

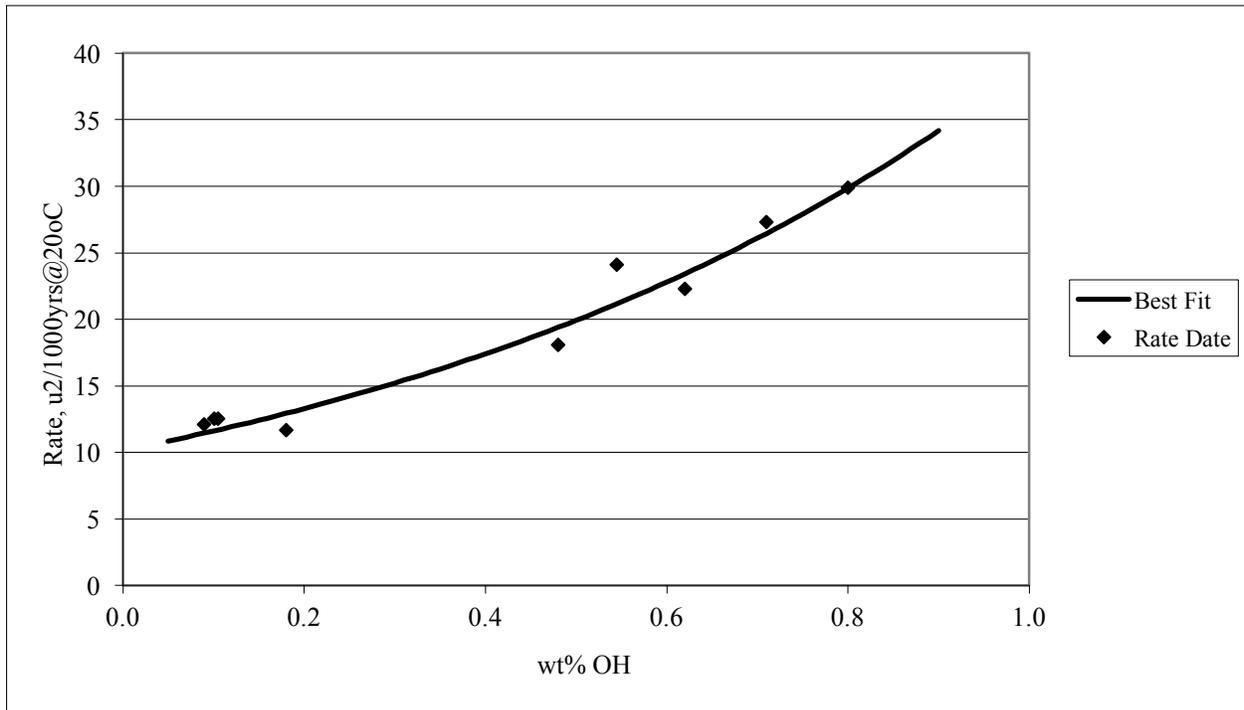


Figure 2. Rate Prediction Based on %OH.

time-consuming laboratory work as induced hydration does. It also avoids the ambiguities that arise from associating obsidian hydration with radiocarbon or temporally sensitive artifacts. On a positive side, it allows determining a hydration rate for a particular specimen of obsidian, rather than using a rate ascribed to a geochemical source, and thus holds the potential for overcoming uncertainties arising from intra-

source variations. It is worth recalling that obsidian hydration dating is one of the few dating methods that holds promise for directly dating an artifact.

A refinement of the equation relating density to water content is in process, including a larger data set and more convenient best fit. A caveat is that parameters for the rate equation are based on a rather small data set, and will be refined as additional high-quality data points become available. Rates determined by this method should be used with caution, and cross-checked against those derived by other methods. No chronometric technique should ever be treated as a black box!

A further caveat, based on data which came to light in July 2017, is that some obsidian specimens do not seem to follow the density-water content equation (equation 2) very well. Obsidian with high water content, such as Coso, seem to be particularly prone to this. The cause of this anomaly is still under investigation. Thus, the method should be used with caution and continually cross-checked against archaeological data.

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