

FLOW-SPECIFIC HYDRATION RATES FOR COSO OBSIDIAN

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Four principal flows have been geochemically identified within the Coso volcanic field, with significantly varying hydration rates. Effective use of obsidian hydration dating requires the specific flows be taken into account. A hydration rate for the Sugarloaf Mountain flow determined by induced hydration in the laboratory is $29.87 \mu^2 / 1,000$ years at 20°C . Rates for the other flows at 20°C computed from relative values of intrinsic water are: West Sugarloaf, $18.14 \mu^2 / 1,000$ years; West Cactus Peak, $27.28 \mu^2 / 1,000$ years; and Joshua Ridge, $22.27 \mu^2 / 1,000$ years. These rates yield archaeologically reasonable ages when the correct compensation for effective hydration temperature is made, and they are used with the equation: $\text{age} = \text{rim squared} / \text{rate}$. The rates are consistent with the composite hydration rate of $23.42 \mu^2 / 1,000$ years computed from archaeological obsidian-radiocarbon data (Rogers and Yohe 2011).

The Coso volcanic field, located in southern Inyo County, California, is the source of much of the obsidian recovered from archaeological sites in the southern part of the state. Because of this ubiquity, Coso obsidians are frequently used for chronological sequence construction, and hence a reliable determination of hydration rate is essential. Previous estimates of Coso hydration rate (e.g. Basgall 1990; Basgall and Hall 2000; Pearson 1995; Rogers 2009a; Rogers and Yohe 2011) were based on obsidian-radiocarbon association and did not take account of the differing characteristics of specific obsidian flows within the Coso volcanic field. Four such flows are geochemically recognized under the general rubric of Coso: West Sugarloaf (WSL), Sugarloaf Mountain (SLM), West Cactus Peak (WCP), and Joshua Ridge (JRR) (Hughes 1988). It is well-established that hydration rate is strongly dependent on intrinsic water content of the obsidian (Stevenson et al. 2000; Zhang and Behrens 2000; Zhang et al. 1991); it is also well-established that the intrinsic water content of Coso obsidian exhibits significant variation from flow to flow (Stevenson et al. 1993). Thus, previously published rates for “Coso,” which did not distinguish between flows, are composites and may be significantly in error for any specific flow.

This paper develops hydration rates for the four Coso flows by a combination of induced hydration in the laboratory and computations based on intrinsic water content. The standard deviation of the rate is estimated based on water content data and compared with archaeological data. A case study shows the benefit of using flow-specific rates.

The resulting rates yield archaeologically reasonable ages when the correct compensation for effective hydration temperature is made, and when they are used with the equation: $\text{age} = \text{rim}^2 / \text{rate}$. They also are consistent with the hydration rate computed from archaeological obsidian-radiocarbon data.

OBSIDIAN MINERALOGY

Obsidian is an aluminosilicate, or rhyolitic, glass, formed by rapid cooling of magma under the proper geologic conditions. Like any other glass, it is not a crystal, and thus it lacks the lattice structure typical of crystals at the atomic level. Glasses do, however, possess a matrix-like structure exhibiting some degree of spatial order (Doremus 1994:27, Fig. 2, 2002:59-73). Obsidians are typically about 75 percent SiO_2 and about 20 percent Al_2O_3 by weight, the remainder being trace elements, some of which are source-specific (Doremus 2002:109, Table 8.1; Hughes 1988; Stevenson et al. 1998; Zhang et al. 1997). The anhydrous composition of obsidians from a wide variety of sources has been shown to be remarkably consistent (within a few tenths of a weight percent) (Zhang et al. 1997). The minute

interstices within the glass matrix, on the order of 0.1-0.2 nanometer in diameter, are where water penetration takes place.

All obsidians also contain small amounts of natural water, known as intrinsic water or structural water, resulting from the magma formation process; the amount is generally < 2 percent by weight in natural obsidians, although cases of somewhat higher concentration are occasionally encountered. Some of the absorbing water molecules react with atoms of the glass matrix to form hydroxyl (OH⁻) groups (Doremus 2002; Silver et al. 1990), although reaction does not appear to be significant below the glass transition temperature, ~ 400°C (Anovitz et al. 2008).

Obsidian anhydrous chemistry, or chemical composition independent of water, has traditionally been regarded as a major influence on hydration rate (see attempts to determine a chemical index to hydration, e.g. in Friedman and Long 1976 or Stevenson and Scheetz 1989). In archaeological analyses, anhydrous chemistry is controlled by grouping and analyzing the obsidian by geochemical source, based on trace element composition as determined by X-ray fluorescence (XRF) or neutron activation analysis. However, Stevenson et al. (1998, 2000) found no consistent influence of anhydrous chemistry on hydration rate. Zhang and Behrens (2000) and Behrens and Nowak (1997) found the effect of anhydrous chemistry to be negligibly small, although Karsten et al. (1982) reported that Ca²⁺ concentration may influence hydration rate to a very slight extent. It now appears that anhydrous chemistry has negligible effect on hydration rate.

Intrinsic water, on the other hand, has a profound affect on hydration rate (Behrens and Nowak 1997; Delaney and Karsten 1981; Karsten et al. 1982; Lapham et al. 1984; Stevenson et al. 1998, 2000; Zhang and Behrens 2000; Zhang et al. 1991). Four methods are currently used for measuring intrinsic water in obsidian: micro-densitometry (Ambrose and Stevenson 2004); mass loss when obsidian powder is baked (usually called “loss-on-ignition,” or LOI) (Newman et al. 1986; Steffen 2005); infrared (IR) transmission spectrometry (Newman et al. 1986); and IR photo-acoustic spectrometry (Stevenson and Novak 2011). Because all these techniques are costly and currently are destructive to the artifact, intrinsic water measurement is not conducted for most practical archaeological investigations in the United States today. The resulting intra-source rate variations increase the uncertainty (statistical error) in age analysis. Operationally, it is likely that controlling for source actually functions as a proxy for controlling for intrinsic water (Stevenson et al. 2000), albeit rather poorly (Rogers 2008a; Stevenson et al. 1993).

HYDRATION THEORY

The Hydration Process

“Obsidian hydration,” in its most basic aspect, simply describes the process by which water is absorbed by obsidian, and involves both physical and chemical changes in the glass (Anovitz et al. 2008; Doremus 2002). Five steps may be distinguished in the process:

1. When a fresh surface of obsidian is exposed to air, water molecules adsorb on 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.

2. Some of the adsorbed water molecules, plus other water molecules impinging directly from the atmosphere, are absorbed into the glass and diffuse into the interstices in the glass matrix. The diffusion process seems to be driven by three phenomena: a water concentration gradient (Doremus 2002), intra-matrix capillary action, and surface tension between the water molecules and the matrix (Vesely 2001, 2008). Although it has been suggested that chemical reactions play a role (Doremus 2002:108), it is unlikely that they are a major factor below the glass transition temperature (Anovitz et al. 2008), and thus the “diffusion-reaction” nomenclature of Doremus is likely inappropriate for

archaeological temperatures. (The glass transition temperature is the temperature at which the glass starts to exhibit fluid-like properties; Ochs and Lange 1999).

3. The molecules entering the glass by diffusion and by capillary action stretch the glass matrix, causing an increase in volume and openness of the hydrated region. Since the hydrated region is expanded and the non-hydrated region is not, a stress region exists between the two.

4. 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, temperature, and the dynamics of the process itself.

5. When the hydrated layer becomes thick enough, typically greater than 20 microns, the accumulated stresses cause the layer to spall off as perlite.

Methods

Three general classes of methods have been proposed for measuring obsidian hydration: measurement of water mass uptake or loss vs. time (Ebert et al. 1991; Stevenson and Novak 2011); direct measurement of water profiles vs. depth (Anovitz et al. 1999, 2004, 2008; Riciputi et al. 2002; Stevenson et al. 2004); and observation of the leading edge of the stress zone by optical microscopy (many papers, e.g., Friedman and Smith 1960; Friedman and Long 1979).

Measurement of the mass of water absorbed or lost by an obsidian sample, per unit obsidian mass, is the most physically fundamental method of measuring hydration, and has a long history. Methods employed for such measurements have been mass loss on heating (e.g. Ebert et al. 1991), IR transmission spectrometry (e.g. Newman et al. 1986), and IR photo-acoustic spectrometry (e.g. Stevenson and Novak 2011). It has been shown that mass gain or loss proceeds proportional to t^n where t is time and n is an exponent lying between approximately 0.5 and 0.6 (Stevenson and Novak 2011).

Water profile measurement is generally performed by Secondary Ion Mass Spectrometry (SIMS) or the electron microprobe. The principle is to measure the concentration of H^+ ions, as a proxy for water, as a function of depth. The depth of the half-amplitude point is found to be proportional to t^n , where t is time and n is an exponent lying between approximately 0.6 and 0.7 (Anovitz et al. 1999, 2004; Stevenson and Novak 2011; Stevenson et al. 2004).

The classical field of obsidian hydration dating is based on measuring the position of the stress zone caused by the diffusion process. The stress arises because the volume behind the optical hydration front has enlarged due to penetration of the glass matrix by water molecules, while the matrix of the unhydrated glass has not (Vesely 2001). The stress zone is visible under a polarized microscope due to stress birefringence (Born and Wolf 1980:703-705). Laboratory data (Rogers and Duke 2011; Stevenson and Scheetz 1989; Stevenson et al. 1998) indicate that the position of this stress zone, or hydration front, progresses into the obsidian proportional to t^n , where n is approximately 0.5 within limits of experimental error. The agreement with classical diffusion theory, in particular Fick's formulations and the Boltzmann transformation (Crank 1975:105; Rogers 2007, 2012), may be a coincidence or may be due to an as-yet-undiscovered property of the hydration process itself.

The present analysis is based on optical measurement of the hydration rim, so the hydration dynamic model employed is

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

where t is age in calendar years, r is rim thickness in microns, and k is the hydration rate (see e.g. Doremus 1968, 1994, 1999, 2002; Ebert et al. 1991; Rogers 2009b, 2010a; Stevenson et al. 1989, 1998, 2004; Zhang et al. 1991).

The hydration rate varies with effective hydration temperature (EHT; see e.g. Hull 2001; Onken 2006; Rogers 2007; Stevenson et al. 1989, 1998, 2004), with relative humidity (Friedman et al. 1994;

Mazer et al. 1991; Onken 2006), and with intrinsic water concentration in the obsidian (Ambrose and Stevenson 2004; Friedman et al. 1966; Karsten and Delaney 1981; Karsten et al. 1982; Rogers 2008a; Stevenson et al. 1998, 2000; Zhang and Behrens 2000; Zhang et al. 1991). Relative humidity has a small effect in a practical sense, because the interstitial water content of even the driest sand is very high (Friedman et al. 1994), so the effect is generally ignored in practical analyses.

Induced Hydration Theory

The hydration rate of obsidian is strongly temperature-dependent, so that if hydration is allowed to proceed at elevated temperatures, measurable hydration rims develop in days rather than years. The principle of laboratory hydration is to hydrate a set of obsidian samples at elevated temperatures, determine the activation energy and diffusion constant, and then compute the hydration rate for temperatures of archaeological interest (e.g., Rogers 2006; Rogers and Duke 2011; Stevenson and Scheetz 1989; Stevenson et al. 1998, 2004).

The temperature dependence of hydration rate is described approximately by the Arrhenius equation

$$k = k_0 \exp(-E/T) \quad (2)$$

where k is hydration rate, k_0 is the diffusion constant or pre-exponential factor, E is activation energy expressed in $^{\circ}\text{K}$, T is temperature in $^{\circ}\text{K}$. (Many authors express activation energy in $\text{J}\cdot^{\circ}\text{K} / \text{mole}$; this value can be obtained by multiplying E by the universal gas constant, $8.314 \text{ J} / \text{mole}$).

Substituting for k from equation (1) results in

$$r^2/t = k_0 \exp(-E/T) \quad (3)$$

Equation (3) can be expressed in logarithmic form as

$$\ln(r^2/t) = \ln(A) - E/T, \quad (4)$$

known as the logarithmic Arrhenius equation. If we define $y = \ln(r^2/t)$ and $x = 1/T$, equation (4) becomes a linear equation of the form

$$y = I + Sx. \quad (5)$$

Given data for r , t , and T for three or more points, equation (5) can be solved as a linear best fit. The solution is (Cvetanovic et al. 1979:52; Meyer 1975):

$$S = \{\sum w_i \sum w_i x_i y_i - \sum w_i x_i \sum w_i y_i\} / D \quad (6a)$$

$$I = \{\sum w_i x_i^2 \sum w_i y_i - \sum w_i x_i \sum w_i y_i\} / D \quad (6b)$$

and

$$D = \sum w_i \sum w_i x_i^2 - (\sum w_i x_i)^2 \quad (6c)$$

The activation energy E is equal to $-S$, and the diffusion constant A is equal to $\exp(I)$.

The parameter w_i in equations (6a - c) is the weight factor for each data point (Cvetanovic et al. 1979:52-53). Assuming that all $w_i = 1$ minimizes the least-square error in y , and is implemented in the SLOPE and INTERCEPT functions in MS Excel. In the present case, however, the dependent variable $y_i = \ln(r_i^2/t_i)$, while we want to minimize mean-square errors in r_i^2/t_i . To do this, the weighting factor $w_i = r_i^2/t_i$ must be used (Cvetanovic et al. 1979:54).

The values of E and A as computed are mean values; the accuracy, defined by the standard deviation, is given by (Cvetanovic et al. 1979:52)

$$\sigma_E = \sigma_y \sqrt{(\sum w_i / D)} \quad (7)$$

Table 1. Induced hydration results, Sugarloaf Mountain obsidian.

TEMPERATURE (°C)	HYDRATION TIME (DAYS)	HYDRATION RIM (μ)
120	25	2.5
130	20	2.9
140	15	3.6
150	10	3.6

$$\sigma_I = \sigma_y \sqrt{(\sum w_i x_i^2 / D)} \quad (8)$$

where

$$\sigma_y = \{ \sum w_i (y_i - y_i^*)^2 / (N - 2) \}^{1/2} \quad (9)$$

and

$$y_i^* = I + S x_i \quad (10)$$

It can be shown further that

$$\sigma_A = A \sigma_I \quad (11)$$

Equations (9) and (11) give the standard deviations for activation energy and diffusion constant, respectively, but estimating the error in hydration rate, σ_k , is more complicated. It cannot be determined from σ_E and σ_A by a simple square-root-of-sum-of-squares procedure, because the two errors are strongly correlated. Instead the value of σ_k is computed here by a simple Monte Carlo simulation of the hydration process. The algorithm is described in Rogers 2006 and Rogers and Duke 2011. Parameters used in the simulation are: standard deviation of rim readings = 0.1 μ; standard deviation of hydration time = 30 minutes; effective hydration temperature error arising from the oven temperature controller = 0.06° C (the computation of this EHT correction is given in Rogers and Duke 2011).

COSO HYDRATION RATES

Hydration Rate for Sugarloaf Mountain

A hydration rate for SLM obsidian was computed by the method above based on two data sets, the first by the present author and the second by Stevenson and Scheetz (1989:25, Table 1). In each case, the identity of the source flow was determined by X-ray fluorescence.

For the first data set, the obsidian specimens were hot-soaked in vapor phase to prevent erosion of the surface. After the required soak time, the specimens were quenched and hydration rims read optically. Table 1 presents the results. Since the data of Stevenson and Scheetz (1989) have been published, they are not reproduced here.

Stevenson and Scheetz (1989) also reported data for West Sugarloaf obsidian. However, the fit of the data to equation (4) is so poor that they are not used here, and the West Sugarloaf hydration rate is computed by a different method (see below).

Computation of obsidian parameters and hydration rates yields the results of Table 2. Note that k_{20} is the hydration rate at an EHT of 20°C.

Scaling of Rates for Other Coso Flows

The hydration rates for WSL, WCP, and JRR were computed by a different technique: scaling from the SLM rate based on intrinsic water content. Both theory and experimental results suggest that the hydration rate of obsidian should be directly proportional to the intrinsic water concentration (Karsten and

Table 2. Sugarloaf Mountain obsidian parameters.

PARAMETER	UNITS	1989 DATA	2012 DATA	COMPOSITE
Mean E	°K	9858	9229	9548
Std. dev. E	°K	334	537	546
Mean E	J °K / mole	81962	76734	79348
Std. dev. E	J °K / mole	2775	4458	4541
Mean A	$\mu^2 / 1000$ yrs.	1.15×10^{13}	1.44×10^{12}	6.46×10^{12}
Std. dev. A	$\mu^2 / 1000$ yrs.	8.84×10^{12}	1.86×10^{12}	5.02×10^{12}
Mean k_{20}	$\mu^2 / 1000$ yrs.	28.86	30.87	29.87
Std. dev. k_{20}	$\mu^2 / 1000$ yrs.	2.27	4.46	3.68

Table 3. Mean intrinsic water concentration in Coso obsidians, weight percent.

FLOW	SLM	WSL	WCP	JRR
Mean H ₂ O, wt. %	1.02	0.62	1.01	0.81
Std. dev. H ₂ O, wt. %	0.18	0.16	0.54	0.30
Computed CV H ₂ O	0.18	0.26	0.53	0.37
Adjusted CV H ₂ O	0.13	0.20	0.37	0.26
N	21	22	20	63

Delaney 1981; Karsten et al. 1982; Rogers 2008a; Zhang and Behrens 2000; Zhang et al. 1991). Thus, if the hydration rate and water concentration are known for one obsidian source, the rates for other sources can be inferred if their corresponding concentrations are known.

The only source of laboratory data on Coso intrinsic water content is Stevenson et al. 1993, which provides data based on transmission IR spectrometry measurements of 126 specimens. Three readings were eliminated by Chauvenet's criterion prior to analysis, leaving a data set of 123. The data clearly show variations in mean water content of the various flows, and agree with archaeological observations. Stevenson et al. (1993) suggested the dominant factor affecting rate is the hydroxyl ion (OH⁻) concentration rather than the H₂O concentration; however, since the two are roughly proportional (Ambrose and Stevenson 2004; Silver et al. 1990; Zhang et al. 1991), the effect is the same. To complicate matters further, Zhang and Behrens (2000) developed a relationship which scales rate based on total water concentration. For the present study, scaling is performed based on total water. The data used for scaling here are those of Stevenson et al. (1993) as refined by Rogers (2008a), presented in Table 3.

The mean values presented in Table 3 yield archaeologically reasonable results when used to analyze obsidian sets from multiple flows, but the standard deviations (line 4, Table 3) have been found to be too large, due to the analytical method employed (Stevenson and Novak 2011). The water content was computed from IR absorbance by an algorithm developed by Newman et al. (1986) (Stevenson et al. 1993). Subsequently, Zhang et al. (1997) developed an improved algorithm and compared it with the algorithm of Newman et al., and found that the improved algorithm yields similar mean values but standard deviations which are reduced by over 15 percent (Zhang et al. 1997:3096-3097).

Simulation and archaeological data also suggest a need to reduce the estimates of standard deviation and of coefficient of variation. A standard deviation value of 3.68 $\mu^2 / 1,000$ years for hydration rate for Sugarloaf Mountain was computed by a Monte Carlo simulation from the laboratory data (Rogers 2006; Rogers and Duke 2011); see Table 2 above. This corresponds to a coefficient of variation of 0.12, a reduction of 33 percent from the computed CV value in Table 3.

Archaeological data provide a means to check the estimate for West Sugarloaf obsidian. Gilreath et al. (2011) reported data on the Hay Ranch biface cache, a collection of 58 obsidian bifaces recovered in Rose Valley, southern Inyo County, California, in 2010. The bifaces were clearly a cache, and recovered

in a single backhoe scoop from a depth of 1.8 m. Of the bifaces, 53 were manufactured from West Sugarloaf obsidian, and exhibited a mean hydration rim of 5.9 μ with a standard deviation of 0.59 μ , yielding a coefficient of variation of 0.10. The bifaces were dated to the Newberry period by obsidian hydration dating and by technological analysis. Since they were composed of the same source flow, were probably of the same age, and had probably experienced the same temperature history, the variation in hydration rims is almost certainly due to variations in hydration rate due to intrinsic water variability. A coefficient of variation of 0.10 for hydration rims implies a coefficient of variation of 0.20 in hydration rate, or a reduction of 23 percent from the computed CV value in Table 3.

Data for West Cactus Peak obsidian are less certain. The Hay Ranch biface cache contained only two bifaces manufactured from West Cactus Peak obsidian, which yielded a mean rim value of 7.00 μ and a standard deviation of 1.34 μ . The coefficient of variation is approximately 0.19, which would correspond to a coefficient of variation of hydration rate of 0.38. This value must be treated with caution due to the small sample size, but represents a reduction of 28 percent from the computed CV value in Table 3. An analysis of the statistical distribution of the West Cactus Peak intrinsic water data from Stevenson et al. 1993 suggests the presence of at least two sources with differing water distribution within the general West Cactus Peak geochemical category. This would account for the large coefficient of variation of water content for West Cactus Peak.

Since no comparison data for Joshua Ridge obsidian are available, the data for WSL, SLM, and WCP were used to make an adjustment to the computed CV values of Table 3. A reduction of 30 percent was judgmentally chosen as the adjustment for all Coso flows, and the computed CV values were multiplied by 0.7 to yield the adjusted CV values in Table 3. These adjusted values are the current best estimate, and are recommended for use in obsidian hydration analyses.

Mean hydration rate is directly proportional to concentration (Zhang et al. 1991), so the rate of an unmeasured source can be inferred from that of a known source by

$$k_u = k_{SLM} \times [u] / [SLM] \quad (12)$$

where k_u be the rate for a source whose rate is unknown, $[u]$ is the water concentration (OH^- , H_2O , or total) for that source, k_{SLM} is the rate for the SLM source, and $[SLM]$ is the corresponding concentration for SLM.

If this calculation is performed using the concentration data of Table 3 and a rate for SLM of 29.87 $\mu^2 / 1,000$ years from Table 1, the resulting hydration rates are 18.14 $\mu^2 / 1,000$ years for WSL, 27.28 $\mu^2 / 1,000$ years for WCP, and 22.27 $\mu^2 / 1,000$ years for JRR, at an effective hydration temperature (EHT) of 20°C.

West Sugarloaf obsidian is the most abundant of the Coso obsidians in archaeological sites. Overall, typical abundances are approximately WSL = 50 percent, SLM = 25 percent, WCP = 15 percent, and JRR = 10 percent. Averaging the flow-specific rates based on these ratios yields a composite rate of 22.86 $\mu^2 / 1,000$ years, which agrees reasonably well with previously published data for the Coso volcanic field based on obsidian-radiocarbon association (23.42 $\mu^2 / 1,000$ years; Rogers and Yohe 2011). The coefficient of variation values for water content translates directly into coefficient of variation of hydration rates.

Temperature Variation of Rate

As indicated by equation (2), hydration rate is temperature-dependent, with the activation energy E being the critical parameter. Stevenson and Novak (2011) have shown that the activation energy decreases with increasing intrinsic water content, and derived an equation to quantify the dependence (Stevenson and Novak 2011:1724, Fig. 12); for the mean water contents in Table 3, values of activation energy computed from their equation range from 7,508°K to 8,657°K. However, their activation energy is

Table 4. Hydration rim values for GBCB points, Rose Valley, California.

SPEC. NO.	MEAN RIM (μ)	FLOW	REMARKS
1	3.2	WSL	Exclude by Chauvenet's criterion
1	15.3	WSL	
3	18.5	WSL	
4	14.6	WSL	
4	14.8	WSL	
4	14.9	WSL	
5	13.0	WSL	
5	13.0	WSL	
2	15.7	SLM	
2	24.6	SLM	
7	22.1	SLM	
6	16.0	WCP	
6	17.0	WCP	
14	21.0	WCP	

Table 5. Hydration rim statistics for GBCB points, Rose Valley, California.

FLOW	MEAN RIM (μ)	STD. DEV. (μ)	CV	N
WSL	14.9	1.85	0.12	7
SLM	20.8	4.59	0.22	3
WCP	18.0	2.65	0.15	3
SLM + WCP	19.4	3.69	0.19	6
Aggregate	17.0	3.59	0.21	13

measured from water mass uptake, not by optical microscopy, and it is not certain that the activation energies are the same for the two processes.

Therefore, the safest procedure is to use the activation energy from Table 2 ($9,548 \pm 546^\circ\text{K}$) for all four Coso flows, recognizing that there is a potential source of error involved. This is very close to the aggregate value of $8,918.8^\circ\text{K}$, independent of flow, given by Stevens (2005), based on archaeological data, although no standard deviation was given by Stevens.

Archaeological Case Study

A case study is presented here, based on hydration measurements of a set of Great Basin Concave Based (GBCB) points from Rose Valley, in southern Inyo County, California. The data set contains points which were manufactured from WSL, SLM, and WCP obsidians. Source and hydration rim data are presented in Table 4. In some cases, more than one measurement was made on a given point, leading to 14 individual rim measurements. The Coso data points in Table 4 are grouped by obsidian flow; one data point was excluded from the WSL data set by Chauvenet's criterion (seq. no. 1 at 3.2μ).

Hydration rim means and standard deviations of the resulting data sets were computed (Table 5), which shows that the mean value of the hydration rims for WSL artifacts ($14.9 \pm 1.85 \mu$) is noticeably smaller than those from SLM ($20.8 \pm 4.59 \mu$) or WCP ($18.0 \pm 2.65 \mu$). Applying Student's t-test shows that WSL specimens can be statistically distinguished from other Coso sources at the 95 percent confidence level.

This difference in mean rim value could be due to any of three factors: differing hydration rates of the obsidian flows, a different temperature history (EHT), or different ages. Since the points are similar in typology and manufacture, and are from the same provenience, there is no reason to suspect different

ages or different EHT. The hypothesis is therefore adopted that the artifacts actually represent the same age and temperature history but hydrated at different rates.

Hydration rim data from the WCP and SLM sources cannot be distinguished from each other at the 95 percent level, so for further analysis they are combined into a single data set ($19.4 \pm 3.69 \mu$); the last line in Table 5, labeled “Aggregate,” treats the entire data set as an entity ($17.0 \pm 3.59 \mu$).

Ages (t) for the points were computed from

$$t = (r \times \text{RCF})^2 / k, \quad (13)$$

where r is the mean hydration rim from Table 5, k is the rate, t is age in calibrated years before 2000 (cyb2k), RCF is the rim correction factor to correct for the EHT difference between the site and the reference EHT (Rogers 2007). For the case of SLM + WCP obsidians, the rate employed is the mean of the individual rates for the two sources ($28.57 \mu^2 / 1,000$ years, $CV = 0.32$).

Temperature parameters for the site are computed by regional temperature scaling, based on a site altitude of 3,420 ft. amsl, yielding an EHT of 20.56°C (Rogers 2008b). The reference EHT is 20°C, so the rim correction factor to control for the EHT difference is 0.967. Surface conditions are assumed for the finds. For clarity, the age computation omits the correction for paleotemperature change (Rogers 2010b).

The standard deviation of age σ_t is

$$\sigma_t = CV_w \times t \quad (14)$$

where CV_w is the coefficient of variation of the water concentration from Table 3 and t is age from equation (13).

For the WSL points, the age computation yields $11,398 \pm 2,846$ cyb2k, while the age for the SLM + WCP data set is $12,269 \pm 4,741$ cyb2k. Applying Student’s t-test shows that the ages cannot be distinguished at the 95 percent confidence level, which supports the hypothesis that differences in hydration rate can account for the difference in hydration rim values. Combining the two dates into a single date yields $11,334 \pm 3,911$ cyb2k.

The usual way to compute the age would be to use a single rate for the Coso volcanic field, and hydration rim data for the Aggregated case (Table 5). Using the prior best available hydration rate for Coso ($23.46 \mu^2 / 1,000$ years at 20°C; Rogers and Yohe 2011), this procedure yields an age of $11,492 \pm 4,889$ cyb2k; using the composite rate from this study ($22.86 \mu^2 / 1,000$ years), the age is $11,774 \pm 5,028$ cyb2k. These two ages are statistically indistinguishable.

Another very likely analytical scenario would be to partition the data set, treat the WSL and SLM + WCP samples as independent, and compute ages for each using the aggregate rate value for the Coso volcanic field. This is fully justifiable statistically, since the WSL and SLM + WCP data sets are distinguishable by Student’s t-test. If this is done the age computed for the WSL sample is $9,045 \pm 3,140$ cyb2k, and the age of the SLM + WCP sample is $15,333 \pm 6,221$ cyb2k.

SUMMARY AND DISCUSSION

The analysis above has argued that (a) hydration rate is dependent on intrinsic water concentration of the obsidian, (b) that intrinsic water content varies significantly between geochemically identified flows within the Coso volcanic field, and (c) that flow-specific rates are required and give better results than a single rate. The analysis above derives a mean hydration rate for each flow based on laboratory measurements and on scaling from intrinsic water content data; standard deviations are computed from intrinsic water data. Table 6 and Figure 1 summarize the findings.

Table 6. Hydration Rates for Coso Obsidians, by Source Flow (in $\mu^2 / 1000$ yrs, at EHT = 20°C)

FLOW	MEAN	STD. DEV.	CV
Sugarloaf Mountain (SLM)	29.87	3.88	0.13
West Sugarloaf (WSL)	18.14	3.63	0.20
West Cactus Peak (WCP)	27.28	10.09	0.37
Joshua Ridge (JRR)	22.27	5.79	0.26
Composite (Coso Volcanic Field, typical archaeological abundances)	22.86	7.44	0.33

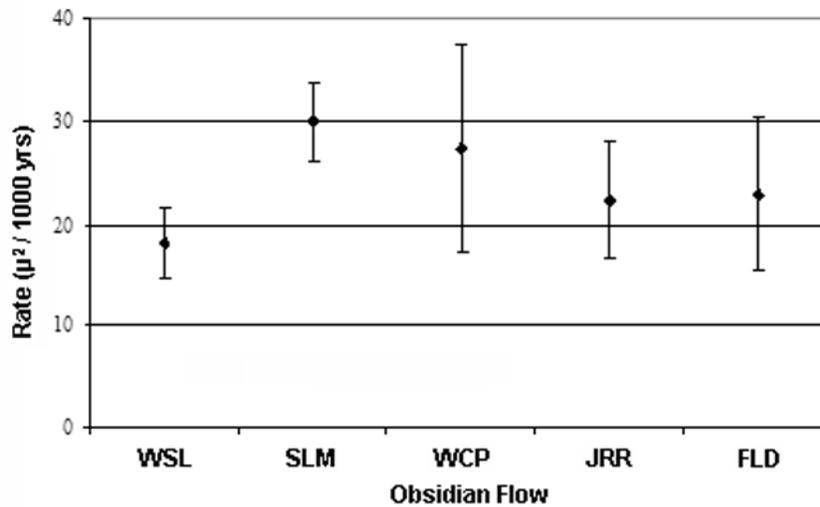


Figure 1. Coso flow-specific hydration rates, in $\mu^2 / 1,000$ years, at an EHT of 20°C.

A case study based on a set of GBCB points, manufactured from WSL, SLM, and WCP obsidians, shows the benefits of using flow-specific rates. The hydration rim values for the WSL sample are significantly different from those from the SLM + WCP sample. However, the computed ages using flow-specific hydration rates are not statistically distinguishable. It is thus reasonable to conclude that the difference in flow-specific hydration rates accounts for the difference in hydration rim values. Furthermore, since the ages are statistically indistinguishable, they can be combined to a single best estimate.

In comparison, if the WSL and SLM + WCP samples had been analyzed separately but using a single aggregated hydration rate, the analysis would have erroneously indicated two separate episodes of manufacture. In addition, the computed ages of the two episodes would both be unrealistic for this point type.

If the aggregated sample had been analyzed with a single aggregated rate based on Rogers and Yohe (2011), the computed age would have been statistically indistinguishable from the ages computed by flow-specific rates. In both cases, the analyst would reach the conclusion that the points were manufactured during a single period. This is largely fortuitous, however, since the aggregated method is sensitive to the relative sizes of the two samples, and the fraction of WSL and SLM + WCP obsidians is essentially the same in this case (7/13 vs. 6/13); if the proportions were more skewed, the age computed from the aggregate data set would also be more skewed, toward the flow with the larger proportion. The age computed with flow-specific rates would not be affected by such a change in proportions, and hence is more robust.

In conclusion, the rates derived here, when used with a quadratic law for age (equation [13]) and appropriate temperature correction (per Rogers 2008b and not Lee 1969), yield archaeologically reasonable ages, even for artifacts of Paleoindian age.

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