# COMPUTATION OF A HYDRATION RATE FOR BODIE HILLS OBSIDIAN, FROM MONO COUNTY, EASTERN CALIFORNIA

Alexander K. Rogers, MA, MS Archaeology Curator Maturango Museum

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## Abstract

This paper reports a hydration rate for Bodie Hills obsidian from Mono County in Eastern California USA, based on obsidian – radiocarbon pairing data from the western slope of the Sierra Nevada, and on obsidian pairing with temporally-sensitive artifact types from the eastern Sierra. The analysis employs regional temperature scaling to determine site temperature parameters, and temperature-dependent hydration theory to compute hydration rim corrections for effective hydration temperature (EHT), including the effects artifact burial depth. The rate is based on a linear least-squares best fit between the square root of age (independent variable) and EHT-corrected rim value (dependent variable), an algorithm which minimizes errors. The rates determined for the eastern slope and the western slope are statistically indistinguishable when corrected to the same EHT, so the final rate is based on the consolidated data set. The resulting hydration rate is 14.20  $\pm$  0.74  $\mu^2/1000$  yrs at an EHT of 20°C. The rate is valid for both east and west sides of the Sierra Nevada, provided the EHT is computed by the method described herein.

#### INTRODUCTION

This paper computes a hydration rate for Bodie Hills obsidian, whose source is in Mono County in eastern California, USA. The calculations are based on two sets of data: obsidian-radiocarbon pairing data from the western slope of the Sierra Nevada, kindly provided by Jeff Rosenthal of Far Western Anthropological Research Group (Rosenthal and Waechter 2002); and obsidian pairings with temporally-sensitive artifacts from the eastern Sierra Nevada, kindly supplied by Kirk Halford (Halford 2002). The calculation explicitly takes effective hydration temperature (EHT) into account in computing the rate, using temperature parameters computed from 30-year weather data by regional temperature scaling (Cole 1970; Rogers 2007, 2008a). All EHT values are corrected for burial depth of the artifact. The output is a hydration rate applicable to archaeological sites on either the western or eastern slope of the Sierra Nevada, as long as it is corrected for EHT by the methods described here.

The tentative nature of this rate must be emphasized. The data set employed is relatively error-prone, and an attitude of skepticism is appropriate in applying the rate in chronological analyses until better data are available.

#### **OBSIDIAN MINERALOGY**

Obsidian is an alumino-silicate, 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% SiO<sub>2</sub> and about 20%  $Al_2O_3$  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% by weight in natural obsidians, although cases of somewhat higher concentration are occasionally encountered (Zhang et al. 1997). Some of the absorbing water molecules react with atoms of the glass matrix to form hydroxyl (OH<sup>-</sup>) groups (Doremus 2002; Silver at al. 1990), so water exists in the obsidian in the form of two species (molecular H<sub>2</sub>O and OH<sup>-</sup>). However, the hydroxyl 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  $Ca^{2+}$  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 et al. 1991; Zhang and Behrens 2000). 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 (Stevenson et al. 1993; Rogers 2008b).

#### 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 (Doremus 2002; Anovitz et al. 2008). (A note on terminology: "adsorption" refers to the process by which water molecules attach themselves to the surface of the glass; "absorption" refers to the transfer of water molecules into the glass matrix; "sorption" refers to the combination of these two processes.) Five steps may be distinguished in the hydration 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 others 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 (Vesely 2001), 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 2002:108ff.; Rogers 2007), 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; it is ~400°C, and decreases with increasing water content (Ochs and Lange 1999). Vesiculation tends to occur above the transition temperature (Steffen 2005).

- 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, which can be observed under a polarizing microscope (Scheetz and Stevenson 1988).
- 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 (Morgenstein et al. 1999).

## MEASUREMENT 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<sup>n</sup> 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 et al. 2004; Stevenson and Novak 2011).

The classical field of OHD 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 1908:703-705). Laboratory data (Rogers and Duke 2011; Stevenson and Scheetz 1989; Stevenson et al. 1989; Stevenson et al. 2004) indicate that the position of this stress zone, or hydration front, progresses into the obsidian proportional to t<sup>n</sup>, where n is approximately 0.5 within limits of experimental error. Put another way, the position of the square root of time; the agreement with classical diffusion theory, in particular Fick's formulations and the Boltzmann transformation (Crank 1975:105ff.; 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

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

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 2007, 2012; 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 2008b; 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.

Determining a hydration rate is a problem of parameter optimization, not a regression problem. Regression is a technique to estimate to what extent one variable depends on another. In the present case, however, the degree of dependence is fully known *a priori* from physics and chemistry, so the problem is rather of optimizing a parameter (the rate) which defines the fit between data and the physical model. Mathematically, the formalism used to compute the best fit, described below, is the same as that used in a regression analyses with no linear term and the best-fit line constrained to pass through the origin; the difference is that here the physical model, and hence the degree of dependence, is known.

It follows that, since the form of the hydration equation is known from physics, other forms must be explicitly avoided, such as linear forms or inclusion of higher-order terms or other exponent values. With virtually any archaeological data set it is possible to obtain a better fit (measured by residuals) with MS Excel by other forms of the equation. However, the apparent accuracy thus achieved is spurious, because each data point is a combination of valid data and experimental error, and so a linear or higher degree polynomial or exponent is simply a better fit to the experimental error. If a data set appears to yield a better fit with other functional forms, for example, a linear growth with time (e.g. Bettinger 1989; Meighan 1983), such data can be used to infer a "rule of thumb" correspondence between hydration rim thickness and age for that particular data set, but the resulting parameter is not the "hydration rate" in a strict sense.

Good practice in numerical analysis is to select the model equation based on the nature of the problem (Hanning 1973; Matthews 1992) and then optimize the best fit parameters. For obsidian hydration this means the physical/chemical model, which is a linear dependence of hydration rim thickness on the square root of time.

# BODIE HILLS ANALYSIS

The approach taken in this analysis is to infer a hydration rate based on association between obsidian readings and radiocarbon dates or dates inferred from temporally-sensitive artifacts. However, obsidian hydration process is well known to be extremely sensitive to temperature, so it is critical that the obsidian readings all be corrected to a common, known, effective hydration temperature (EHT). This is accomplished by correcting the measured hydration rims by the method of temperaturedependent diffusion theory (Rogers 2007). The necessary temperature parameters are computed from regional temperature scaling (Rogers 2007, 2008a). Once the hydration rim data are reduced to a common EHT they can be combined into a single data set. The radiocarbon ages are all converted to calibrated years before the year 2000 (cyb2k), using the median value of age from Calib 6.0.

The Bodie Hills analysis is based on two data sets. The data set from the western slope of the Sierra Nevada consists of 20 obsidian-radiocarbon pairs from excavations, at elevations ranging from the floor of the Central Valley to CA-CAL-114 at 3444 ft above mean sea level (amsl); see Table 1. The eastern Sierra data (Table 2) consist of temporally-sensitive obsidian projectile points; in most cases elevation is known or can be inferred.

| -    | (From Rosential and Waechter 2002) |                                 |           |       |      |           |           |
|------|------------------------------------|---------------------------------|-----------|-------|------|-----------|-----------|
|      |                                    |                                 | Elevation |       | Age  | median    |           |
| Seq. |                                    |                                 | meters    | Age,  | std. | intercept |           |
| No.  | Site                               | Context                         | amsl      | rcybp | dev. | (cal BP)  | Rim, µ    |
| 1    | CAL-991                            | Component 991A1, 0-20 cm        | 1005      | 250   | 60   | 300       | 1.31      |
| 2    | TUO-2197                           | Unit 4/5, Feature 3, 30-35 cm   | 870       | 270   | 70   | 330       | 2.2       |
| 3    | Same as #2                         |                                 | 870       | 270   | 50   | 340       | 2.2       |
|      |                                    | Unit N104/E97: Feat 6 fill, 20  |           |       |      |           |           |
| 4    | TUO-407                            | cm                              | 610       | 320   | 110  | 363       | 1.9       |
| 5    | CAL-114/H                          | Unit 7; Feature 2, 38-73 cm     | 1050      | 360   | 70   | 400       | $1.9^{2}$ |
| 6    | AMA-56                             | Feature 1B: 60-76 cm            | 65        | 1160  | 60   | 1080      | 3.1       |
| 7    | CAL-789                            | Unit S44/W30: 20-50 cm          | 450       | 1220  | 40   | 1160      | 3.6       |
| 8    | CAL-789                            | Unit S10/E20: 30-40 cm          | 450       | 1270  | 40   | 1210      | 3.4       |
| 9    | PLA-695/H                          | Unit 95Q: 130-140 cm            | 670       | 1340  | 60   | 1255      | 3.8       |
| 10   | SAC-60                             | Burial 38-11, 122 cm            | 2         | 1550  | 150  | 1465      | 4.0       |
| 11   | PLA-695/H                          | Unit 95F: 70-90 cm              | 670       | 2170  | 70   | 2175      | 4.5       |
| 12   | SJO-142                            | Burial 18, 71 cm                | 0         | 2495  | 120  | 2560      | 4.8       |
| 13   | CAL-789                            | Feature 1, 60-80 cm             | 450       | 2510  | 40   | 2580      | 3.9       |
| 14   | SJO-68                             | Burial 23, 120 cm               | 0         | 3775  | 160  | 4155      | 4.9       |
| 15   | SJO-68                             | Cremation 1, 119 cm             | 0         | 4350  | 250  | 4950      | 5.5       |
|      | CAL-                               | 90N/26E, Feat. 232, Black Clay: |           |       |      |           |           |
| 16   | 629/630                            | 203-212 cm                      | 305       | 8510  | 150  | 9050      | 7.3       |
|      | Same as #                          |                                 |           |       |      |           |           |
| 17   | 16                                 |                                 |           | 8630  | 145  | 9370      | 7.3       |
|      | CAL-                               | 96N/25E, Green Clay, : 225-235  |           |       |      |           |           |
| 18   | 629/630                            | cm                              | 305       | 9040  | 90   | 9990      | 7.3       |
|      | CAL-                               | 93N/24E, Feat 212, Black Clay:  |           |       |      |           |           |
| 19   | 629/630                            | 170-200 cm                      | 305       | 9230  | 100  | 10195     | 7.4       |
|      | CAL-                               | 86N/23E, Black Clay: 190-200    |           |       |      |           |           |
| 20   | 629/630                            | cm                              | 305       | 9240  | 150  | 10200     | 8.2       |

Table 1. Bodie Hills Obsidian-Radiocarbon Pairings, Western Sierra Nevada (From Rosenthal and Waechter 2002)

Data for the eastern slope of the Sierra Nevada are based on temporally-sensitive projectile points, since associated radiocarbon data are lacking (Halford 2002). Table 2 shows the point types reported by Halford (2002), with their hydration rim readings and

estimated elevation. The ages are based on Justice (2002), corrected from BC/AD to cyb2k; the standard deviation is the range divided by the square root of twelve.

| Туре  | Ν | Rim mean, | Rim   | Elevation, | Age range        | Mean age, | Age sd, |
|-------|---|-----------|-------|------------|------------------|-----------|---------|
|       |   | μ         | sd, μ | ft amsl    |                  | cyb2k     | yrs     |
| DSN   | 1 | 1.3       | 0.1   | 7000       | AD 1300-1900     | 400       | 173     |
| DSN   | 1 | 2.8       | 0.1   | 6500       | AD 1300-1900     | 400       | 173     |
| DSN   | 5 | 1.82      | 0.26  | 6500       | AD 1300-1900     | 400       | 173     |
| DSN   | 3 | 1.4       | 0.36  | 8200       | AD 1300-1900     | 400       | 173     |
| DSN   | 8 | 2.05      | 0.65  | 6500       | AD 1300-1900     | 400       | 173     |
| RS/EG | 1 | 3.2       | 0.1   | 7000       | AD 500 - 1300    | 1100      | 231     |
| RS/EG | 1 | 2.8       | 0.1   | 6500       | AD 500 - 1300    | 1100      | 231     |
| RS/EG | 7 | 2.26      | 0.73  | 6500       | AD 500 - 1300    | 1100      | 231     |
| RS/EG | 2 | 2.2       | 0     | 8200       | AD 500 - 1300    | 1100      | 231     |
| RS/EG | 4 | 3.45      | 0.19  | 6500       | AD 500 - 1300    | 1100      | 231     |
| ELK   | 5 | 4.5       | 1.86  | 7000       | 1400 BC – AD 650 | 2375      | 592     |
| ELK   | 1 | 4.8       | 0.1   | 6500       | 1400 BC – AD 650 | 2375      | 592     |
| ELK   | 5 | 4.84      | 0.99  | 8200       | 1400 BC – AD 650 | 2375      | 592     |
| ELK   | 2 | 3.65      | 1.34  | 6500       | 1400 BC – AD 650 | 2375      | 592     |
| ELK   | 5 | 4.28      | 1.65  | 6500       | 1400 BC – AD 650 | 2375      | 592     |
| GBS   | 1 | 6.4       | 0.1   | 8200       | 9,000 - 6,000 BC | 9500      | 866     |
| GBS   | 3 | 5.98      | 1.5   | 6500       | 9,000 – 6,000 BC | 9500      | 866     |

Table 2. Projectile point data for sites in the eastern Sierra Nevada, from Halford (2002)

Correction of the hydration rims to a common EHT requires a temperature analysis, in this case using regional temperature scaling, following the method of Rogers (2007, 2008a). Three temperature parameters are computed from meteorological records:  $T_a$ , annual average temperature;  $V_{a0}$ , annual temperature variation; and  $V_{d0}$ , mean diurnal range. Table 3 presents the temperature parameters for the eastern Sierra, computed from 30-year temperature summaries from the Western Regional Climate Center (WRCC) for seven meteorological stations.

| Station          | Alt, ft amsl | T <sub>a</sub> , °C | V <sub>a</sub> , °C | V <sub>d</sub> , °C | EHT, °C |
|------------------|--------------|---------------------|---------------------|---------------------|---------|
| Hawthorn Airport | 4220         | 12.81               | 23.42               | 15.75               | 17.74   |
| Yerington        | 4380         | 11.33               | 22.03               | 17.64               | 16.27   |
| Truckee          | 5980         | 6.61                | 18.69               | 17.81               | 10.74   |
| Tahoe Airport    | 6250         | 6.14                | 17.03               | 17.86               | 9.91    |
| Bridgeport       | 6370         | 6.39                | 19.75               | 21.19               | 11.59   |
| Mono Lake        | 6530         | 8.28                | 20.36               | 15.64               | 12.36   |
| Bodie            | 8370         | 3.28                | 17.97               | 21.03               | 8.02    |

Table 3. Temperature Parameters, East Slope of Sierra Nevada

The resulting temperature scaling equations in °C are

$$T_a = 20.99 - 0.0022h \tag{2a}$$

$$V_{a0} = 27.37 - 0.0012h \tag{2b}$$

$$V_{d0} = 12.24 + 0.001h \tag{2c}$$

Here h is site elevation in ft amsl. The equations were derived from data from 4220 ft amsl to 8370 ft amsl, and should be used with caution for elevations outside this range. Within this elevation range, the equations predict the meteorologically-derived EHT with an error standard deviation of 1.31°C.

The situation is more complex for the western slope, due to temperature inversions in the Central Valley. The inversion layer lies typically at about 1500 ft amsl, and below this there is virtually no variation of temperature parameters with elevation. Table 4 presents the temperature parameters for the western slope, based on WRCC data for twelve meteorological stations.

| Station             | Alt, ft amsl | T <sub>a</sub> , °C | V <sub>a</sub> , °C | V <sub>d</sub> , °C | EHT, °C |
|---------------------|--------------|---------------------|---------------------|---------------------|---------|
| Sacramento Airport  | 20           | 16.19               | 16.03               | 13.64               | 18.94   |
| Stockton            | 30           | 16.64               | 17.31               | 13.42               | 19.61   |
| Lodi                | 40           | 15.78               | 15.17               | 14.44               | 18.50   |
| Knights Ferry       | 320          | 15.50               | 17.97               | 14.97               | 18.89   |
| Electra Power House | 700          | 15.64               | 16.97               | 17.69               | 19.37   |
| New Melones Dam     | 780          | 15.47               | 18.28               | 16.44               | 19.22   |
| Auburn              | 1360         | 15.72               | 17.22               | 12.78               | 18.57   |
| Sonora              | 1830         | 14.36               | 17.28               | 17.17               | 18.04   |
| Placerville         | 1890         | 14.47               | 16.78               | 15.39               | 17.69   |
| Grass Valley        | 2400         | 12.92               | 15.50               | 14.89               | 15.78   |
| Nevada Cty          | 2600         | 12.64               | 16.50               | 13.56               | 15.47   |
| Deer Cr Power House | 3700         | 9.44                | 17.03               | 13.75               | 12.41   |

Table 4. Temperature Parameters, West Slope of Sierra Nevada

The resulting equations for elevations below 1500 ft amsl are

| $T_{a} = 15.85^{\circ}C$ | (3a) |
|--------------------------|------|
| $1_{a} - 15.05$ C        | (34) |

$$V_{a0} = 16.99^{\circ}C$$
 (3b)

$$V_{d0} = 14.77^{\circ}C$$
 (3c)

For elevations above 1500 ft amsl, the equations are

 $T_a = 19.44 - 0.0027h \tag{4a}$ 

$$V_{a0} = 16.84^{\circ}C$$
 (4b)

$$V_{d0} = 14.84^{\circ}C$$
 (4c)

Here again h is site elevation in ft amsl. The equations were derived from data from sea level to 3700 ft amsl, and should be used with caution for elevations outside this range. Within this elevation range, the equations predict the meteorologically-derived EHT with an error standard deviation of  $0.3^{\circ}$ C.

In computing EHT, the temperature parameters at the artifact burial depth are needed, which is related to conditions at the surface by (Carslaw and Jaeger 1959)

$$V_a = V_{a0} \exp(-0.44z) \tag{5a}$$

$$V_d = V_{d0} \exp(-8.5z) \tag{5b}$$

Note that annual average temperature is not affected by burial depth.

The temperature history of each site is modeled by a time series with a sum of three terms: a constant of magnitude  $T_a$ , representing annual average temperature; a sinusoid with period of twelve months and amplitude  $V_a$ , representing the month-to-month variation of average temperature; and a sinusoid with a period of twenty-four hours and amplitude  $V_d$ , representing diurnal temperature variation. The hydration rate is known to depend on temperature by the equation

$$\mathbf{k} = \mathbf{k}_0 \exp(-\mathbf{E}/\mathbf{T}) \tag{6}$$

where k is hydration rate,  $k_0$  is a constant, E is the activation energy in °K, and T is temperature in °K (Doremus 2002). The effective hydration temperature is computed from a numerical integration of the hydration rate over the temperature model (see Rogers 2007 for computation details). The computer code to perform the computation is written in MatLab®; copies may be obtained from the author. After determining an EHT for each artifact, based on site elevation and burial depth, a rim correction factor (RCF) is computed to correct the rim value to a consistent reference temperature (EHT<sub>R</sub>, chosen as 20°C). The rim correction factor is

$$RCF = \exp\{[-E/(EHT + 273.15)] + [E/(EHT_R + 273.15)]/2\}$$
(8)

For small differences in temperatures between EHT and  $\text{EHT}_R$ , this is roughly equivalent to 6%/°C; however, equation 6 is more accurate for large temperature differences, as in this case. In equation 7, E is the activation energy of the obsidian, typically on the order of 10,000°K (Friedman and Long 1976; Stevenson and Scheetz 1989).

The hydration rate is computed by a linear least-squares best fit between the square root of age and the corresponding hydration rim value. Data points were weighted by the inverse of the variance of the hydration rim reading (Cvetanovic et al. 1979; Meyer 1975). In each case the independent variable (x) is the square root of age, and the dependent variable (y) is the EHT-corrected hydration rim value.

The best-fit slope is computed as (e.g. Cvetanovic et al. 1979; Meyer 1975:71ff)

$$\mathbf{S} = \sum \mathbf{w}_i \mathbf{N}_i \mathbf{x}_i \mathbf{y}_i / \sum \mathbf{w}_i \mathbf{N}_i \mathbf{x}_i^2 \tag{8}$$

which is the standard best-fit equation for a line constrained to pass through the origin;  $\{x_i, y_i\}$  are the data points being fit, each consisting of Ni obsidian-radiocarbon pairs. The parameter wi is a weighting factor defined by

$$wi = 1/\sigma_{yi}^{2}$$
<sup>(9)</sup>

where  $\sigma yi$  is the standard deviation of the errors in y associated with the i<sup>th</sup> data point. Since for this case  $x = t^{1/2}$  and y = r, equation 8 becomes

$$\mathbf{S} = \sum \mathbf{w}_i \mathbf{r}_i \mathbf{t}_i^{1/2} / \sum \mathbf{w}_i \mathbf{t}_i \tag{10}$$

Using the same data set, the standard deviation of the rate estimate can be computed from

$$\sigma_{ke} = \sigma_r / \Sigma t_i \tag{11}$$

where

$$\sigma_{\rm r}^2 = \sum [r_i^2 - S \ \sqrt{t_i}]^2 \tag{12}$$

(Equation 12 from Taylor 1982:173; equation 13 derived based on Taylor 1982:261, 8.8)

Using the EHT-corrected rim values, and ages derived from either calibrated radiocarbon or temporally-sensitive artifacts, best-fit values of hydration rate were computed for the two data sets. Table 5 shows the resulting rates.

| Tuote et Boule Time ocestului nyututon tutes ut 20 et |                     |                     |  |  |  |
|-------------------------------------------------------|---------------------|---------------------|--|--|--|
| Statistic                                             | West Slope Data Set | East Slope Data Set |  |  |  |
| Mean, $\mu/yr^{0.5}$                                  | 0.1191              | 0.1258              |  |  |  |
| Standard deviation, $\mu/yr^{0.5}$                    | 0.0034              | 0.0177              |  |  |  |
| Ν                                                     | 20                  | 4                   |  |  |  |

Table 5. Bodie Hills obsidian hydration rates at 20°C.

A t-test for significance gives a t = 0.75, against a threshold value of 1.96 for distinguishability at the 95% confidence level. Thus, the two data sets are not statistically distinguishable and may be merged.

The final rate was thus computed using the merged data sets at an EHT of 20°C, typical of an elevation of 3000 ft in the southern Inyo County. Figure 1 shows the quality of the fit.

The resulting hydration rate is summarized in Table 6. It is shown in two forms for convenience.

| EHT, °C | Mean Rate                    | Rate Standard deviation     |
|---------|------------------------------|-----------------------------|
| 20      | 0.1192 μ/yr <sup>0.5</sup>   | 0.0031 µ/yr <sup>0.5</sup>  |
| 20      | $14.20 \ \mu^2 / 1000 \ yrs$ | $0.74 \ \mu^2 / 1000 \ yrs$ |

Table 6. Bodie Hills obsidian hydration rate.

Finally, the age for any set of conditions is

$$t_{cvb2k} = 70.42 \times r_{20}^{2}$$
(13)

where  $r_{20}$  is the hydration rim value corrected to an EHT of 20°C by the methods described above.

#### DISCUSSION

The hydration rate for Bodie Hills obsidian at 20°C of 14.31  $\mu^2/1000$  yrs is considerably slower than the hydration of Coso obsidians (18.14  $\mu^2/1000$  yrs for West Sugarloaf and 29.87  $\mu^2/1000$  yrs for Sugarloaf Mountain – see Rogers 2013). This slower rate, coupled with the generally lower temperatures typical of high-altitude sites, accounts for the generally small hydration rims encountered in the eastern Sierra Nevada.

To employ this rate the following procedure should be used:

- 1. Compute temperature parameters for the site from equations 2, 3 or 4, as appropriate. If the site is located in another region, modify the temperature scaling as appropriate. Do not use the Lee equation (Lee 1969).
- 2. Compute  $V_a$  and  $V_d$  for the buried artifacts (equation 5).
- 3. Compute EHT. Numerical integration as described in Rogers 2007 is preferable, but an adequate, although somewhat less accurate, algebraic approximation for EHT is

$$EHT = T_a + 0.0062 \times (V_a^2 + V_d^2).$$
(14)

- 4. Use a reference EHT of 20°C and compute rim correction factors from equation 7.
- 5. Compute age from equation 14.

The major caveat is that, to employ equation 7, EHT must be computed by the method described herein. The Lee equation (Lee 1969) and various rules of thumb will give incorrect answers.

The rate has an accuracy of approximately 5%, but overall uncertainty in the age estimate is further affected by EHT uncertainties, site formation processes such as turbation, and variability in the intrinsic water of the obsidian source (Rogers 2008b, 2010).

Equation 7 can be used to compute the ages of the specimens from the west side in Table 1, for comparison with the calibrated radiocarbon ages (Figure 2). When this is done, the mean relative error between the model and the radiocarbon data is approximately 5%, showing that the least-squares best fit is eliminating bias quite well. The standard deviation of the percent error is relatively large, 23%; approximately half this error is due to EHT uncertainties, while the remainder probably reflects the poorlyunderstood chemistry and water content variability of Bodie Hills obsidian (Rogers 2008b).

When applied to the temporally-sensitive point types from the eastern Sierra region, the ages computed for Desert Side-Notched, Rose Spring/Eastgate, and Elko point types generally too large (Figure 2), although the predicted age for Great Basin Stemmed points is 10% too small. The large errors represent the expected uncertainties that arise when trying to estimate a rate based on temporally-sensitive artifacts, since there is no way of knowing when the artifacts were manufactured within long span of time.

Overall, in performing chronometric analyses, it would be unwise to expect an accuracy better than about 20%, given the current state of knowledge of Bodie Hills obsidian.

# CONCLUSIONS

The analysis here presents a hydration rate for Bodie Hills obsidian based on obsidian-radiocarbon pairing and on obsidian pairing with temporally-sensitive artifacts. The rate equation as presented in equation 7 is equally valid for east or west sides of the Sierra Nevada, and for surface or buried artifacts, provided the EHT is computed by the method described herein. Accuracy of the age estimate is approximately 20%.

Refinement of hydration rates will require laboratory work to quantify intrinsic water variability, and to develop a lab rate.

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Figure 1. Linear best fit between the square root of calibrated age and EHT-corrected hydration rim values.



Figure 2. Fit between model and data from sites on the western and eastern slopes of the Sierra Nevada.

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