

UC Berkeley

International Association of Obsidian Studies Bulletin

Title

IAOS Bulletin 71

Permalink

<https://escholarship.org/uc/item/8vj420s5>

Author

Dillian, Carolyn D.

Publication Date

2023

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IAOS

International Association for Obsidian Studies

Bulletin

ISSN: 2310-5097

Number 71

Winter 2023

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NEWS AND INFORMATION

IAOS Annual Meeting in New Orleans

Please join us for the IAOS meeting to be held during the Society for American Archaeology meeting in New Orleans, Louisiana, USA, on Saturday, April 20 at noon. See your SAA conference program for location.

CONSIDER PUBLISHING IN THE IAOS BULLETIN

The *Bulletin* is a twice-yearly publication that reaches a wide audience in the obsidian community. Please review your research notes and consider submitting an article, research update, news, or lab report for publication in the *IAOS Bulletin*. Articles and inquiries can be sent to IAOS.Editor@gmail.com. Thank you for your help and support!

LOOK FOR IAOS AT REGIONAL AND INTERNATIONAL CONFERENCES!

The International Association for Obsidian Studies works to have a presence at regional and international conferences, as well as the annual Society for American Archaeology conference, where we typically hold our annual business meeting. If you are an IAOS member and plan to attend an international or regional conference and would like to help advertise the organization, please reach out to our Executive Board for information and materials.

If you're attending a conference and see the IAOS there, please stop by and say hello!

NOTES FROM THE *BULLETIN* EDITOR

Twenty years ago (twenty!!), I assumed the role of Editor and published my first issue of the *IAOS Bulletin*. In an introductory column in that issue (No. 31, 2004), I wrote “I recognize that many of you were perhaps wondering whether the IAOS has folded, and I assure you, we are beginning a new effort to resurrect our organization.” Now, forty (forty!!!) issues of the *IAOS Bulletin* later, I am pleased to report that we have a robust twice-yearly publication, a close-knit community of scholars, and interest and enthusiasm for obsidian research around the world.

During my tenure in this role over the past twenty years, we have benefitted from the leadership of a series of IAOS Presidents, including Phil LeTourneau, Ana Steffen, Tristan Carter, Ellery Frahm, Jeff Ferguson, Rob Tykot, Kyle Freund, Sean Dolan, and our current IAOS President, Theodora Moutsiou. Our Secretary-Treasurers have kept us organized (and legal), through the service of Janine Loyd, Colby Phillips, Kyle Freund, Matt Boulanger, and our current Secretary-Treasurer, Lucas Martindale-Johnson. And finally, and most importantly, Craig Skinner has served as our IAOS Webmaster since the beginning of the Web (for a great historical reflection from 1995, please see Chapter 3 of the IAOS edited volume entitled *Twenty-Five Years on the Cutting Edge of Obsidian Studies: Selected Readings from the IAOS Bulletin*, in which he tells us “I can guarantee that you’ll be hearing much more about the WWW in the near future.” To order:

https://www.deschutesmeridian.com/IAOS/iaos_publications.html). These people, and many more, who have contributed time, *IAOS Bulletin* articles, skills, resources, and support, are the reason why the IAOS continues as a valuable network for all of us with an interest in obsidian studies, and they all deserve our sincere gratitude.

When I first joined the IAOS, as a young graduate student more than 25 years ago, I was

welcomed in to a supportive and friendly community, with members who answered my (probably ridiculous) questions, pointed me towards articles, data, and resources that helped me in my research, and were happy to talk with me and explain their work over a beer during endless conversations at conferences and workshops. I’m glad to know we continue to offer that kind of welcome and support for our younger members.

I treat you to a picture of me from the summer of 2000, during my dissertation research on Glass Mountain, in the Medicine Lake Highlands of northern California (photo credit: Steve Shackley):



I didn’t really start writing this as a sentimental retrospective, but that’s where this column ended up. Thanks to all of you for your membership, service, and support to the IAOS. I hope to not still be serving as the *IAOS Bulletin* Editor in another 20 years, but we’ll see where life takes me. In the meantime, please send articles for publication!

Sincerely,

Carolyn Dillian, Ph.D., RPA
Professor and Associate Dean
Department of Anthropology and Geography
Coastal Carolina University
Conway, South Carolina, USA
cdillian@coastal.edu

WORKSHOP ANNOUNCEMENT!

The Archaeometry Laboratory at the University of Missouri Research Reactor (MURR) will be hosting a workshop at the 89th annual meeting of the Society for American Archaeology in New Orleans on April 17th, 2024. Please see below, the SAA's website (<https://saa.org/annual-meeting/workshops>). We look forward to seeing you there!

Everything You Wanted to Know about Archaeometry but Were Afraid to Ask: Tips and Guidelines for Collaborating with the Archaeometry Lab at MURR

- Sponsored by the Archaeometry Laboratory at the University of Missouri Research Reactor (MURR)
- Wednesday, April 17, 12:00 p.m. - 4:00 p.m.
- 40 maximum
- Free to participants
- Instructors: Brandi L. MacDonald, Whitney Goodwin, James A. Davenport, Wesley Stoner, Virginie Renson, Jay Stephens, and Alejandro J. Figueroa

Do you have questions about provenance research? Have you ever considered undertaking chemical analysis but not sure where to start? Are you curious about what techniques and training opportunities are available to students and early career researchers or to those looking to broaden their use of archaeological science? Come join the team of experts from the Archaeometry Laboratory at MURR for a workshop that will cover a wide range of provenance topics and collaborative research opportunities. We will discuss the use of methods including neutron activation analysis (NAA), X-ray fluorescence (XRF), and elemental and isotopic analysis by mass spectrometry (LA-ICP-MS, MC-ICP-MS) and how these can be applied to varied archaeological materials—from ceramics and obsidian, to glasses, glazes, metals, pigments, and bone. We will also discuss aspects of our legacy NAA databases and the Lab's data management policies, our NSF-funded opportunities for education and training, and our NSF subsidy program for researchers in academic and nonprofit organizations. A pre-workshop survey will be circulated to all registered participants in advance of the workshop to inform the organizers of specific questions, topics, and issues for discussion. Workshop organizers will use this information to help guide the content. The topics will either be covered in the main content of the workshop or through a Q&A session.

Learning Objectives:

- Gain an understanding of the fundamental concepts and methods involved in provenance studies and the scientific methods available at the Archaeometry Lab
- Advantages and disadvantages of different techniques
- The range of materials that can be analyzed by varied techniques
- Best practices for sample selection and preparation
- Basic analytical procedures and statistical routines for elemental data
- Knowledge of existing regional databases for comparative materials
- Education and training opportunities at MURR

WILL THE REAL OBSIDIAN HYDRATION RATE PLEASE STAND UP?

Alexander K. Rogers

Maturango Museum, Ridgecrest, California, USA

This is a short paper to clarify what a hydration rate is and is not, prompted by questions I have received over the years from archaeologists. To begin with, for any given geochemical source, there is no such thing as simply a “hydration rate”; it is always a “hydration rate at a specific temperature”. When I publish rates I am always careful to state that they are for a reference temperature of 20°C, typical of the high desert. Tom Origer, by contrast, generally uses 16.6°C as his reference temperature, and here in Oregon it is customary to use 12°C. It is important to specify what the reference temperature is when publishing rates.

This brings us to the effective hydration temperature (EHT). When I state a reference temperature of 20°C, it is the effective hydration temperature. The EHT is a single, constant, temperature which would yield the same hydration rim as the actual, fluctuating temperature over the same length of time. Methods to compute EHT have been published (summarized in Rogers and Stevenson 2020). The EHT is important because a published hydration rate cannot be simply used as is, unless it happens to be for a site whose EHT corresponds to the reference temperature of the published rate. To apply a rate in a chronometric analysis you have to start by determining the EHT for the specimen, which generally means computing it for the site and then adjusting for the burial depth of the specimen (or else measuring the temperature). Again, ways to do this have been published. Then you have to adjust the published hydration rate to the EHT of the specimen (or adjust the specimen’s hydration rim to the EHT of the rate), and the method has, again, been published. Only then are you

in a position to compute age and age standard deviation and do your archaeological analysis. For example, the hydration rate for the Bodie Hills source in eastern California is $10.36 \pm 0.72 \mu^2/1000 \text{ yrs. at } 20^\circ\text{C}$ (Stevenson et al. 2021), but if you are applying it to a site in, say, the High Sierra, where the EHT is more like 9°C, you need to adjust the rate accordingly (to $6.25 \pm 0.43 \mu^2/1000 \text{ yrs. at } 9^\circ\text{C}$.)

I realize it has been customary in some archaeological circles to use terms like “upland Bodie Hills rate” or “lower desert Coso rate”. This is an attempt to make a rough adjustment for local EHT, and originated back before the physics of hydration was understood, but it doesn’t really work very well. In my OHD workshop I always urge attendees not to use such terms, but to know the rate and apply the EHT quantitatively and explicitly.

To summarize, when stating a hydration rate, always include the temperature.

References Cited

- Rogers, A.K., and C.M. Stevenson (2020) Archaeological Age Computation Based on Obsidian Hydration: A Summary and Current State of the Art. *International Association for Obsidian Studies Bulletin* 63: 2-44.
- Stevenson, C.M., A.K. Rogers, and G. Haverstock (2021) A Brief Note on Hydration Rates for the Bodie Hills Obsidian Source, Eastern California, Based on Infrared Spectroscopy and Optical Measurement. *International Association for Obsidian Studies Bulletin* 67: 30-35.

CAN OBSIDIAN-RADIOCARBON PAIRING DATA BE USED TO DETERMINE THE OBSIDIAN HYDRATION AGE MODEL?

Alexander K. Rogers^a and Christopher M. Stevenson^b

^a Maturango Museum, Ridgecrest, California, USA

^b Virginia Commonwealth University, Richmond, Virginia, USA

Abstract

Obsidian hydration dating (OHD) is a method for estimating age of an obsidian artifact from the amount of water it has absorbed since it was manufactured. Typically, the quantity of water absorbed is measured by optical microscopy of the thickness of the water-enriched surface layer (hydration rim). Age is computed by an age equation relating the measured hydration rim to an age with controls for temperature history and structural water content of the specimen's geochemical source. We investigate whether archaeological data sets (obsidian-radiocarbon pairings) are accurate enough to determine the mathematical form of the age model. The analysis is based on a Monte Carlo simulation of the site formation and analysis processes and includes all known sources of experimental error. Time association error is quantified, as is the hydration rim uncertainty caused by structural water variations and temperature history. We conclude that archaeological data are not accurate enough to determine the age model. Although it is possible to create an ad hoc best fit equation from archaeological data for a specific analysis, there is no assurance that it will be valid beyond the data set on which it is based, and the procedure is not recommended.

Introduction

In obsidian hydration dating (OHD) the thickness of the hydration layer is converted into time before present by an age equation, so there are two unknowns: the form of the age equation (square root of time, exponential, linear, or other) and the numerical value of the parameters in the age estimation equation. The question addressed here is: are archaeological data sufficiently accurate to determine the form of the age equation with high confidence and its parameter values.

Archaeological data sets typically comprise obsidian hydration rim measurements and associated ages based on radiocarbon dating. The original paper by Friedman and Smith (1960) proposed a form of the age equation based on the physical chemistry of the hydration process, and then estimated the parameter values from archaeological data. Subsequent

developments (Friedman and Long 1976) extended the parameter determination to laboratory induced hydration. In all cases, however, the form of the equation (depth of penetration is proportional to the square root of time) was retained. They also pointed out the need to control for obsidian source and for temperature history. These methods were subsequently developed and refined by Friedman and colleagues and by others (summarized in Liritzis and Laskaris 2011; Rogers and Stevenson 2020).

Accuracy of the method as applied by many archaeologists was poor, however, primarily because mathematically rigorous methods to control for temperature had not been developed. The mathematics to control for temperature were subsequently developed based on diffusion theory (Rogers 2007). Many archaeologists apparently attributed the poor accuracy to the form of the age equation

of Friedman and Smith, and attempted to improve accuracy by determining the age equation empirically based on archaeological data. This led to suggested equations which were linear (Bettinger 1989), exponential (Basgall 1990), or higher-order (Basgall and Giambastiani 1995; Pearson 1995). In no case was accuracy improved significantly, leading to complete disillusionment by some archaeologists (e.g., Ridings 1996, but see rebuttal in Hull 2001). Further, there are no publications extant indicating any attempt to quantify accuracy until Rogers (2010).

The present study explores the analysis process and demonstrates that archaeological data are not sufficiently accurate to establish the form of the age equation. A Monte Carlo simulation is used here to explore parameter sensitivities, and the ultimate results are checked against a previously-published archaeological data set. The accuracy analysis updates the prior work of Rogers (2010), which explored OHD accuracy analytically. In all cases optical microscopy is assumed as the method for measuring the width of the hydration layer.

After a brief overview of obsidian mineralogy, the sources of experimental error in the obsidian-radiocarbon association process are described (note that in the discussion hereafter, the term “error” is used in the sense of “experimental error,” i.e., uncertainty in the data, and does not imply a mistake). The error sources are identified and quantified and typical analytical methods are described with mathematical details. After that, the Monte Carlo simulation model is described and the simulation results presented. Finally, the results are discussed and placed in the larger context of archaeological dating.

Obsidian Properties

Obsidian is an aluminosilicate glass, formed by rapid cooling of rhyolitic magma where the silica content is between 68-72%. Like any other glass, obsidian is not a crystal,

and lacks the lattice structure typical of crystals at the atomic level, but does possess a matrix-like structure exhibiting some degree of short-range spatial order in the molecular structure (Doremus 1994:27, Fig. 2; 2002:59-73; Shelby 2005). The anhydrous composition (chemical composition independent of water) of obsidians from a wide variety of sources has been shown to be remarkably consistent, within a few tenths of a weight percent (Zhang 1997), and has very little effect on hydration rate (Behrens and Nowak 2000; Stevenson et al. 1998, 2000; Zhang and Behrens 2000). All obsidians also contain small amounts of natural water resulting from the incomplete degassing of the rhyolitic melt during its ascent from the magma chamber. The water is present in two species, hydroxyl (OH) and molecular water (H_2O_m). This water is known as structural (or intrinsic) water, to distinguish it from water gained by hydration. The amount is generally < 2.5 wt.% in natural obsidians, although cases of somewhat higher concentration are occasionally encountered (Newman et al. 1986; Stevenson et al. 2019). The structural water content is the primary compositional determinant of hydration rate, and its effects are modeled in this simulation.

Obsidian hydration is a process by which water is absorbed by obsidian by diffusion, and involves both physical and chemical changes in the glass (Anovitz et al. 2008; Doremus 2002; Kuroda et al. 2018, 2019; Kuroda and Tachibana 2019). When a fresh surface of obsidian is exposed to air, water molecules adsorb on the surface (for a detailed description of the process, see Kuroda et al. 2018, 2019; Kuroda and Tachibana 2019). Some of the adsorbed water molecules are absorbed into the glass and diffuse into the interstices in the glass matrix. Water penetration occurs when a water molecule has sufficient energy to stretch the glass matrix and enter one of the interstices; since energy is proportional to temperature, the hydration process is inherently temperature-sensitive.

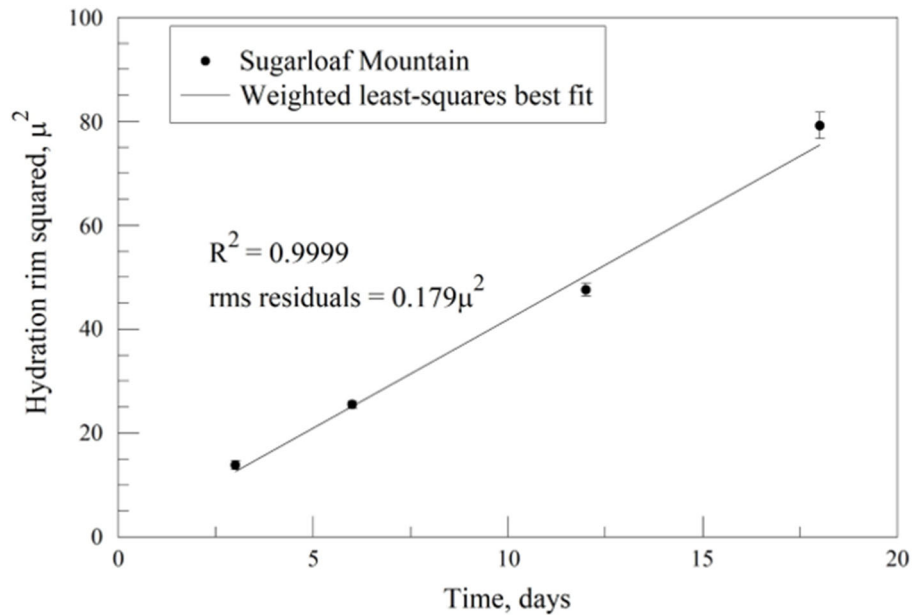


Figure 1. Linear growth of the square of the hydration rim with time, supporting equation (1). Temperature 160°C.

The hydrated region expands due to water penetration while the non-hydrated region is not, so a stress zone is created between the two, which is visible under a polarizing microscope and by the phenomenon of stress birefringence. As time passes, the region of increased water concentration grows thicker, its rate of progress being a function of the initial openness of the glass, temperature, and the dynamics of the process itself. When the hydrated layer becomes thick enough, typically greater than $\sim 20\mu$, the accumulated stresses may cause the layer to spall off as perlite (Friedman et al. 1966). Temperature effects are also modeled in this simulation.

Hydration Growth Model

A simulation of the process of hydration rate computation from the obsidian-radiocarbon association process requires, first, constructing a “ground truth” model of the growth of the hydration rim with time. This growth model is described by the age equation, whose initial form was proposed by Friedman and Smith (1960), derived from the

physics and chemistry of hydration. The hydration of obsidian is a diffusion process (Doremus 2000, 2002), in which mass is transported due to a concentration gradient (Crank 1975). In a diffusion process the depth of penetration is proportional to the square root of time (Crank 1975), which results in an age equation of the form

$$t = r^2/k \quad (1)$$

where: t is age, r is rim thickness in microns, and k is the hydration rate in $\mu^2/\text{unit time}$ (Friedman and Smith 1960; Friedman and Long 1976; Rogers 2007, 2012). This model is supported by laboratory data (e.g., Friedman and Long 1976; Rogers and Duke 2011; Stevenson and Scheetz 1989; Stevenson et al. 1998; Stevenson et al. 2019), diffusion theory (Crank 1975), and glass science (Doremus 2002; Zhang et al. 1991). As confirmation of equation (1), Figure 1 shows growth of the rim vs. time for Coso Sugarloaf Mountain obsidian at a temperature of 160°C (433.15K) (Stevenson and Scheetz 1989:25, Table 1); the

graph shows the linear nature of the relationship between time and the square of the hydration rim, as in equation (1). The least-squares best fit has a rate value of $4.191 \pm 0.118 \mu^2/\text{day}$; rms residuals are $0.179 \mu^2$, and $R^2 = 0.9999$, so the fit is excellent.

These data are for a temperature well above the typical archaeological temperatures range (around 5°C to 25°C , or 278.15K to 298.15K), so the hydration at archaeological temperatures will proceed more slowly than in Figure 1. However, the diffusion process is unchanged over all temperatures below the glass transition temperature ($500 - 700\text{K}$, per Ochs and Lange 1999:1316, Table 2), so equation (1) is expected to be valid for archaeological temperatures as well. The value of k in equation (1) can be determined by a number of methods, described in Rogers and Stevenson (2020 and references therein) and including obsidian-radiocarbon date association.

Error Sources in Archaeological Data Sets

Characterization of the error sources is essential to development of a valid simulation. An archaeological data set typically consists of pairs of radiocarbon-based ages with the obsidian hydration rims from the same archaeological context, both of which are subject to experimental errors. There are four sources of uncertainty (or experimental error) involved in the process, two minor ones which are technical, and two major ones which are related to archaeological site formation processes. The minor ones are the accuracy of the age measurement by radiocarbon, and the accuracy of the hydration rim measured by microscopy. The major ones are the validity of the association and the confidence with which a hydration rim can be projected based on its age. The minor error sources can be quantified easily, as accuracy of the age measurement by radiocarbon is typically $\sim 50 - 150$ years, and the accuracy of hydration rim measurement is typically $\sim 0.08 - 0.1 \mu$.

Time Association Error

The time association error is defined as the difference between a radiocarbon-based measurement and actual age of an obsidian specimen with which it is assumed to be contemporary. This is distinct from the “old wood problem” of radiocarbon (Schiffer 1986). Here as an example, data from the Rose Spring site (CA-INY-372) are used to provide quantitative estimates (Yohe 1992, 1998).

The Rose Spring site in eastern California (CA-INY-372) provides data on the possible magnitude of the error (Yohe 1992, 1998). Locus 1 at Rose Spring exhibited good stratigraphic integrity, and a series of radiocarbon ages to a depth of three meters was obtained (Rogers and Yohe 2014; Yohe 1992, 1998), ten of which were from hearths. Radiocarbon from hearths is typically stationary, although bulk soil radiocarbon is not, so use of hearth dates is the prudent strategy in making obsidian associations. A linear best fit of calibrated age with depth yielded $R^2 = 0.9490$ and rms residuals of 546 years; the good fit shows the stratigraphy is reasonably intact. Obsidian hydration data were obtained on 28 debitage samples, ranging in depth from 5 to 255 cm depth, and ages were computed (Rogers and Yohe 2014). However, the ages exhibited considerable scatter and the fit of age vs. depth was very poor ($R^2 = 0.2748$), showing the stratigraphy was not intact for the obsidian. The rms difference in age between obsidian and radiocarbon at any stratigraphic level was 1189 years, so if radiocarbon ages at the site had been “associated” with the debitage based purely on stratigraphy, an error of approximately 1200 years would likely have resulted. This large uncertainty occurs because obsidian tends to be scavenged for re-use, which causes extreme mixing. Thus, associations based on stratigraphy alone can be seriously in error.

Source	Rate, $\mu^2/1000$ yrs. at 20°C	CV_{rate}	References
Bodie Hills	10.38	0.053	Stevenson et al. 2021
Casa Diablo	13.60	0.067	Haverstock et al. 2023
Coso West Sugarloaf	18.14	0.190	Rogers and Yohe 2013; Rogers 2022
Coso Sugarloaf Mountain	29.87	0.216	Rogers and Yohe 2013; Rogers 2022

Table 1. Hydration rate data for the simulated cases.

At the other extreme would be an obsidian projectile point recovered with organic hafting material adhering to it. In this highly unusual case, the time association error could be less than a human life-time (≈ 50 years), assuming the point type agrees with the OHD age. If the point type does not agree with the OHD age, the point was probably curated and the time association error could be much larger. For example, a Silver Lake point with an OHD age of less than a thousand years would indicate curation and rework and it would be prudent to reject the association.

More typical would be obsidian artifacts recovered from dateable floor features, such as floors with hearths. Here the obsidian could come into proximity with the floor by any number of depositional processes: it could have been left by the person who made the last fire (best case); the floor could have been abandoned for years and the obsidian dropped by a human at a later time; or it could have been washed in by erosion a century or more later. The time association error could be on the order of a few years to a few hundred years, so 100 and 300 years are used here for analysis. These estimates (50, 100, 300 years) probably bracket the association uncertainty in archaeological data sets and are used in the simulation.

Rim Expectation Error

It is well known that two pieces of obsidian from the same geochemical source may hydrate at different rates, due to intra-source variations in structural water content and differing temperature and humidity history (Rogers 2010; Rogers and Stevenson

2022; Stevenson et al. 1993), and would thus exhibit different hydration rims after the same time. Thus, even if the age of a specimen is known, there is uncertainty in what the resulting hydration rim value should be, and this uncertainty must be incorporated in any simulation of the process.

The standard deviation of the expected hydration rim due to intra-source water variations, σ_{rim} , varies by obsidian source and is equal to $r \cdot CV_{rate} / 2$ (Rogers 2010), with the appropriate value of CV_{rate} for the geochemical source (Table 1).

To this standard deviation must be added the uncertainty due to temperature history (effective hydration temperature, EHT). The CV of uncertainty due to EHT has been shown to be (Rogers 2010) $CV_{EHT} \approx 0.11 \cdot \sigma_{EHT}$, and $\sigma_{EHT} \approx 1^\circ\text{C}$. Further, by propagation of error theory (Taylor 1982), the CV of r is one half the CV of the rate, so the CV of the expected hydration rim error is:

$$CV_{rim} = \sqrt{[(CV_{rate}/2)^2 + (0.11 \cdot \sigma_{EHT})^2]} / 2 \quad (2)$$

Numerically, CV_{rim} varies between approximately 0.06 for a slow obsidian such as Bodie Hills and 0.12 for a fast obsidian such as Coso Sugarloaf Mountain, so it is a major source of uncertainty. Equation (2) is incorporated in the simulation model to generate the rim expectation error. The uncertainty is simulated by the product of $r \cdot CV_{rim}$ and a Gaussian random number.

Analytical Methods Simulated

The question here is whether the form of equation (1), or some other form, can be

determined directly from archaeological data. A very powerful, general method to compute an age equation from archaeological data, employed by Basgall (1990), is to assume a general form of

$$t = A * r^S \quad (3)$$

In the analysis below, the constant A is referred to as the age coefficient and S is referred to as the exponent. By taking the natural logarithm of both sides, equation (3) becomes

$$\ln(t) = \ln(A) + S * \ln(r) \quad (4)$$

This is a linear equation of the form

$$y = I + S * x \quad (5)$$

where $y = \ln(t)$ and $x = \ln(r)$; given a set of data points $\{r_i, t_i\}$, linear least-squares methods then yield values for S and $\ln(A) = I$. In principle this method should yield an estimate of the growth equation of the hydration rim, depending upon the accuracy of the basic data.

A linear least-squares solution for I and S is (Cvetanovic et al. 1979)

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

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

where:

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

The w_i factors represent statistical weights. Most archaeologists are expected to solve for I and S by the SLOPE, INTERCEPT, or LINEST functions in MS Excel, which automatically sets the w_i parameters equal to one, i.e., uniform weighting, so this is the scenario simulated. The purpose of non-uniform weighting is briefly discussed below.

Monte Carlo Simulation Structure

A Monte Carlo simulation was developed in MatLab to replicate the obsidian-radiocarbon association process and the computation of the best-fit equation, including the error sources discussed above (computer

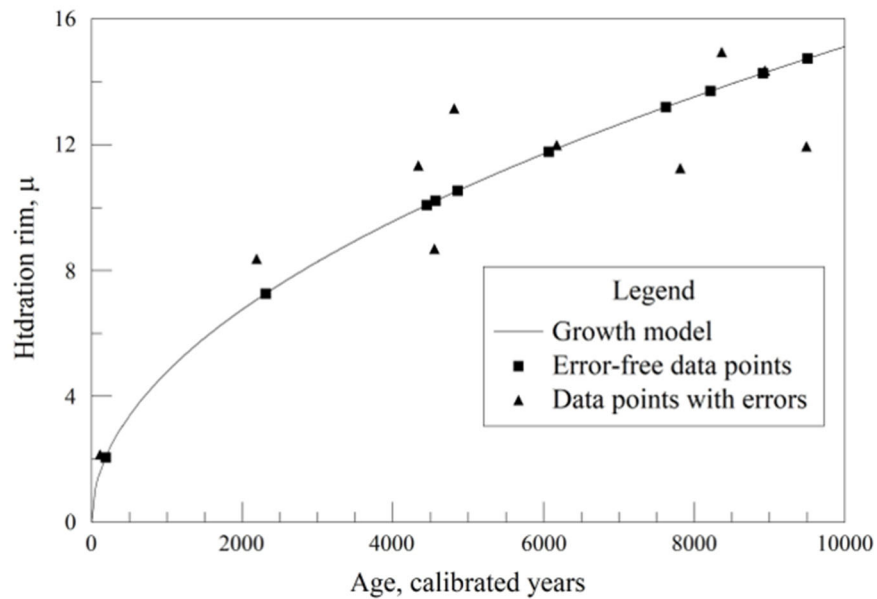


Figure 2. Typical data set generated by the simulation. The hydration rate is typical of the Coso volcanic field, California. The best fit is created using the data points with errors.

code is uploaded to the website of the International Association for Obsidian Studies). The simulation assumes the specimens are from the same geochemical source, although intra-source variations in structural water (and thus hydration rate) are present and are modeled. The simulation creates 10 data points; ages are selected by a uniformly-distributed random number generator between 50 and 10,000 years. Hydration rims are computed with a square-root-of-time growth equation for four obsidian sources, spanning the range from slow to fast: Bodie Hills, Casa Diablo, Coso West Sugarloaf, Coso Sugarloaf Mountain (Table 1). Rim expectation error is added by equation (2) and a Gaussian random number. Figure 2 shows a typical data set generated by the simulation, showing the growth model curve, the error-free data points selected, and the resulting data points with errors in time association and rim expectation.

Once the data set is created, the measurement process is simulated by introducing the two measurement error sources, the radiocarbon age uncertainty (a

nominal value of 100 years) and the measurement accuracy of the hydration rim (assumed to be 0.1μ); again normally-distributed random numbers are used. The least-squares linear best fit is computed for each iteration, using uniform weighting. The age coefficient and exponent derived from the simulated data set are computed on each iteration, and are then used to compute a set of ages which are compared with the data set. The simulation was run for 20,000 replications, at the end of which the statistics of S and I were computed, as well as the age coefficient (A in equation (3)). The rms residual error is also computed as a measure of the accuracy with which an equation derived from empirical data can predict ages; the better the fit, the smaller the rms residuals.

Evaluation is based on two measures: the value of the root-mean-square (rms) residual error between the equation and the data set, which defines the accuracy of the fit, and the probability of success, the probability that the computed values of both the exponential and (simultaneously) the computed age coefficient are within 5% of their growth model values.

Source	T	Model A value	Sim A mean	Sim A std. dev.	CV _A	Bias in A
BH	50	96.34	118.17	67.53	57.1%	22.7%
BH	100	96.34	118.45	67.57	57.0%	23.0%
BH	300	96.34	131.17	111.79	85.2%	36.2%
CD	50	73.53	92.56	57.21	61.8%	25.9%
CD	100	73.53	94.15	60.94	64.7%	28.0%
CD	300	73.53	104.80	95.40	91.0%	42.5%
WSL	50	55.13	92.53	77.28	83.5%	67.9%
WSL	100	55.13	96.30	103.29	107.3%	74.7%
WSL	300	55.13	105.36	130.72	124.1%	91.1%
SLM	50	33.48	69.89	105.96	151.6%	108.8%
SLM	100	33.48	69.35	91.57	132.0%	107.1%
SLM	300	33.48	78.66	127.17	161.7%	135.0%

Table 2. Monte Carlo Simulation Results, Age Coefficient. Rim measurement error = 0.1μ , age measurement error = 100 yrs., T = time association error, yrs. A = Age coefficients in $\text{yrs.}/\mu^2$. 20,000 replications. BH = Bodie Hills; CD = Casa Diablo; WSL = Coso West Sugarloaf; SLM = Coso Sugarloaf Mountain.

Source	T	<u>Model</u> <u>S value</u>	Sim S mean	Sim S std. dev.	CV _s	Bias in S
BH	50	2	1.95	0.25	12.6%	-2.4%
BH	100	2	1.96	0.27	13.7%	-2.0%
BH	300	2	1.98	0.42	21.0%	-0.8%
CD	50	2	1.95	0.24	12.5%	-2.5%
CD	100	2	1.95	0.27	13.7%	-2.4%
CD	300	2	1.98	0.41	20.8%	-1.1%
WSL	50	2	1.86	0.28	15.1%	-7.0%
WSL	100	2	1.86	0.31	16.8%	-6.9%
WSL	300	2	1.89	0.44	23.1%	-5.5%
SLM	50	2	1.83	0.30	16.5%	-8.5%
SLM	100	2	1.84	0.33	17.8%	-8.0%
SLM	300	2	1.86	0.44	23.8%	-6.9%

Table 3. Monte Carlo Simulation Results, Exponent. Rim measurement error = 0.1μ , age measurement error = 100 yrs., T = time association error, yrs. S = exponent in equation (3). 20,000 replications. BH = Bodie Hills; CD = Casa Diablo; WSL = Coso West Sugarloaf; SLM = Coso Sugarloaf Mountain.

Simulation Results

Data from the simulation runs are summarized in Tables 2 and 3. Table 4 presents the rms residuals for these cases.

The probability of success is defined here as the probability of achieving a value of the age coefficient and the exponent which are both acceptably close to the growth model value. In this case “acceptably close” was taken to be within 5% of the growth model values for both age coefficient and exponent simultaneously. Table 5 presents the results.

Discussion

Examination of Table 1 shows that the CV of the simulated age coefficient (A) and exponent are relatively large, and further that the age coefficient is significantly more sensitive to experimental errors than is the exponent (S). The large values of CV_A arise because A is determined from the equation $A = \exp(I)$, where I is the y-intercept of the least squares best fit. The exponentiation process amplifies the uncertainty, because the standard deviations are related by $\sigma_A = A \cdot \sigma_I$. The values of CV_A vary between 162% and 57%, with a mean of 98%. Similarly, the CV

of the slope varies between 24% and 13%, with a mean of 17%.

There is also significant bias in the mean values relative to the growth model. For the age coefficient, bias ranges between 135% and 23%, with a mean of 64%, and for the slope the bias ranges between -0.5% and -8%, with a mean of -4%. The fact that the bias is generally positive for the age coefficient indicates the logarithmic analysis is tending to compute values that are too high, while the reverse is true for the slope.

The bias arises because the least-squares best fit process has a built-in assumption that the independent variable ($\ln(r)$) is error-free, while in this case it is definitely not. The rim expectation error of equation (2) adds directly to the independent variable error, which adds bias to the best fit solution. Mathematical methods exist to handle such a case (e.g., Oliviera and Aguilar 2013; Tellinghuisen 2020; Van Huffel and Vandewalle 1991), but they are not built in to MS Excel nor MatLab and are very complex to program. Thus, the presence of the rim expectation error severely affects the performance of the logarithmic analysis method.

Source	Time assoc. error, yrs.	Uniform weighting, yrs.
BH	50	752
BH	100	773
BH	300	936
CD	50	775
CD	100	792
CD	300	955
WSL	50	1177
WSL	100	1198
WSL	300	1339
SLM	50	1275
SLM	100	1296
SLM	300	1423

Table 4. RMS Residuals. BH = Bodie Hills; CD = Casa Diablo; WSL = Coso West Sugarloaf; SLM = Coso Sugarloaf Mountain.

Examination of the rms residual errors (Table 4) shows that, for the logarithmic fit with uniform weighting, the rms residuals range from 1423 – 752 years, with a mean of 1058 years. Both bias and CV become worse (larger) for faster-hydrating obsidians and for larger time association errors.

The data in Table 5 show that the probability of getting the correct age equation is surprisingly low, between approximately

10% and 3%, with a mean of 6%. Thus, the logarithmic best fit method does a poor job of extracting the correct age equation from the data set.

For comparison, Table 6 presents the hydration rate accuracy obtained when the form of the age equation (equation (1)) is assumed to be known based on physics and the least squares process is employed to determine the hydration rate.

Source	Time assoc. error, yrs.	Probability of Success
BH	50	10.38%
BH	100	9.69%
BH	300	5.94%
CD	50	9.59%
CD	100	8.74%
CD	300	5.57%
WSL	50	6.27%
WSL	100	5.42%
WSL	300	3.80%
SLM	50	4.75%
SLM	100	4.40%
SLM	300	3.25%

Table 5. Probability of Success. BH = Bodie Hills; CD = Casa Diablo; WSL = Coso West Sugarloaf; SLM = Coso Sugarloaf Mountain.

Source	T	A Model	Sim. A, mean	Sim A, std. dev	CV _A	Bias	RMS residuals	Probability Success
BH	50	96.34	97.41	4.37	4.48%	1.11%	740	73.34%
BH	100	96.34	97.26	4.32	4.44%	0.96%	739	73.49%
BH	300	96.34	96.90	4.80	4.96%	0.59%	777	68.87%
CD	50	73.53	74.41	3.46	4.65%	1.20%	776	70.94%
CD	100	73.53	74.35	3.43	4.61%	1.12%	775	71.57%
CD	300	73.53	74.07	3.79	5.11%	0.74%	811	67.48%
WSL	50	55.13	57.25	4.48	7.82%	3.85%	1376	45.91%
WSL	100	55.13	57.04	4.47	7.83%	3.47%	1359	45.19%
WSL	300	55.13	56.68	4.63	8.17%	2.81%	1357	45.43%
SLM	50	33.48	35.02	3.04	8.67%	4.61%	1531	41.68%
SLM	100	33.48	34.94	3.01	8.60%	4.36%	1519	41.56%
SLM	300	33.48	34.66	3.09	8.92%	3.52%	1508	41.73%

Table 6. Simulation Results for Square-Root-of-Time Model. Rim measurement error = 0.1μ , age measurement error = 100 yrs., T = time association error, yrs. A = Age coefficients in yrs./ μ^2 , rms residuals in yrs. 20,000 replications.

This analysis again suffers from the problem of significant errors in both variables, but here the exponent is known and only the age coefficient is in question. Further, there is no exponentiation involved, which avoids error magnification. The data in Table 6 show that the bias in the mean values of the age coefficient relative to the model is always less than the standard deviation of the simulated value, so the accuracy of the age coefficient can be characterized by its CV alone. The CV varies from around 4% for slow obsidians to 9% for fast ones, with a nominal value somewhere around 6 – 7 %. This accuracy is comparable to the accuracies obtained by laboratory induced hydration (Rogers and Stevenson 2017).

Archaeological Data

The data discussed thus far are based on simulations, and the question always arises of whether they are representative of the real

world. A previously published archaeological data set (Rogers 2009) from the high desert of eastern California was used for comparison. The obsidian specimens had been sourced to the Coso volcanic field but not to subsources therein. The obsidian data were corrected for effective hydration temperature by the method of Rogers (2007) and the radiocarbon ages were calibrated by Calib06 (the latest at the time) and adjusted to the year 2000. A square-root-of-time analysis based on the Total Least Squares method (Rogers 2009; Van Huffel and Vandewalle 1991) yielded an age coefficient of 43.72 ± 1.74 yrs./ μ^2 ; when the data are plotted as years vs. rim squared, the $R^2 = 0.9136$, with the rms residuals of 1.79μ in the rim dimension and 1079 yrs. in the age dimension (N = 26).

For comparison, data sets were simulated using the same age coefficient, $CV_{rim} = 0.12$, and time association errors from 50 – 300

T*, yrs.	Maximum, μ	Minimum, μ	Archaeological, μ
50	2.12	0.47	1.79
100	2.13	0.51	1.79
300	2.18	0.54	1.79

Table 7. RMS Residuals in Hydration Rim. Simulated data represents 10,000 replications.

* T = time association error

T*, yrs.	Maximum, yrs.	Minimum, yrs.	Archaeological, yrs.
50	2235	362	1079
100	2257	374	1079
300	2354	0.54	1079

Table 8. RMS Residuals in Age. Simulated data represents 10,000 replications.

* T = time association error

years. The rms residuals are shown in Table 7 (for rim value) and Table 8 (for age).

The simulated data sets represent 10,000 replications, while the archaeological data set is a single entity, so a direct comparison is not possible; instead, the archaeological residuals can be compared with the maximum and minimum values from the simulation. The archaeological residuals fall in the middle of the range for the simulation, and so the simulation can be accepted as a reasonable representation of reality.

Conclusions

The question which prompted this investigation was whether archaeological data are sufficiently accurate to determine the form of the OHD age equation with high confidence. The simulation shows that the answer is negative – it is not possible to determine the form of the OHD age equation from archaeological data with any degree of certainty. The logarithmic best fit described is the most sophisticated method for such an analysis, but its results are shown to do a poor job of recovering the actual growth equation parameters, yielding large uncertainties in both the age coefficient and exponent. The poor performance is due to the presence of significant experimental errors in both the variables of hydration rim and age, which invalidates a key condition in the mathematics of the standard best fit methods. Any other mathematical form for the best fit, such as linear or polynomial, suffers from the same drawback, which can be avoided only by much more complex methods as summarized by Tellinghuisen (2020). Furthermore, computing the age coefficient in the

logarithmic method requires taking the exponential of the y-intercept, which greatly magnifies experimental error. On the other hand, the hydration rate accuracy obtained when the form of the age equation is accepted based on physics (equation (1)) and the least squares process is employed to determine the hydration rate yields hydration rate accuracies in 6 – 7% range.

It is possible to use archaeological data to create an ad hoc best fit equation, which can be used for a specific analysis, but there is no assurance that it will be valid beyond the actual data set on which it is based. Developing an age equation of more general validity requires starting from the known form, equation (1), which is based on physical chemistry, geochemistry, and glass science.

In light of the above analysis, we find that obsidian-radiocarbon association can be used, with appropriate accuracy checks, to estimate the hydration rate for the square-root-of-time age equation. However, it is not a good idea to attempt to determine an age equation by empirical best-fit to archaeological data, and earlier studies conducted under this research design should be treated with caution.

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A HYDRATION RATE FOR PINE GROVE HILLS OBSIDIAN, WESTERN NEVADA, BASED ON SPECTROSCOPY

Alexander K. Rogers^a and Christopher M. Stevenson^b

^a Maturango Museum, Ridgecrest, California, USA

^b Virginia Commonwealth University, Richmond, Virginia, USA

Abstract

This paper reports a hydration rate for Pine Grove Hills obsidian from western Nevada, computed from the structural water content of the glass as determined by infrared spectroscopy. The structural total water content is found to be 0.1363 ± 0.065 wt.% ($N = 8$); total water equals molecular water plus hydroxyl. The hydration rate at 20°C is $10.25 \pm 0.71 \mu^2/1000$ years. Both the water content and the rate are comparable to those for the near-by Truman-Queen obsidian source.

Introduction

This paper presents a hydration rate for Pine Grove Hills obsidian from western Nevada, computed from the structural water content of the glass. Water content is determined by infrared (IR) spectroscopy and the Beer-Lambert law, and the rate is computed for an effective hydration temperature (EHT) of 20°C by the equation in Rogers and Stevenson (2022a).

The specimens ($N = 8$) were kindly provided by Mr. John Dougherty, of PAR Environmental. He stated that the specimens, which were non-cultural, were collected from near Dead Ox Springs, Lyon County, Nevada, in a canyon bottom. The geographic coordinates in decimal degrees are N 38.9836711/W 119.134832; UTM coordinates are 314091mE/ 4274369mN/ Zone 11S (NAD83 datum). The local geology is a sequence of volcanic mudflows with welded (non-glassy) tephra and basalt or dacite flows. The obsidian, in nodule form, is apparently weathering from the tephra beds.

Method

Hydration rate of obsidian is determined by two parameters, the structural water content and the EHT. Structural water in glass

occurs as two species, hydroxyl (OH) and molecular water (H_2O_m); the sum of the two is total water (H_2O_t), which is required for the hydration rate computation. Both OH and H_2O_m absorb infrared radiation, the amount absorbed being given by the Beer-Lambert law:

$$W = A/(d \cdot t \cdot \epsilon) \quad (1)$$

where W is species concentration in mole fraction, A is absorbance, d is density, t is thickness, and ϵ is the molar absorption coefficient for that species. This equation can be rearranged in terms of weight percent as

$$w = 100 \cdot 18.02 \cdot A/(d \cdot t \cdot \epsilon) \quad (2)$$

The factor of 18.02 is the effective molecular weight of molecular water and hydroxyl in the typical ratios found in obsidian (Newman et al. 1986); other units are: A in absorbance units, d in gm/L, t in cm, and ϵ in L/(mol*cm).

For each specimen a parallel slab was cut on a circular trim saw and ground on a lapidary wheel with aluminum oxide grit. The specimen was then polished to a sheen with abrasive papers and cleaned with ethanol. Specimen density was determined by

Specimen No.	Mass in Air (gm)	Mass in Liquid (gm)	Temp (°C)	Density Liquid (g/cm ³)	Specimen Density (g/cm ³)
PGH 1	3.5367	1.1703	20.9	1.5949	2.3837
PGH 2	6.5200	2.1608	20.9	1.5949	2.3855
PGH 3	11.1700	3.7054	20.9	1.5949	2.3866
PGH 3A*	9.5096	3.1369	20.9	1.5949	2.3800
PGH 4	7.1317	2.3598	20.9	1.5949	2.3836
PGH 5	14.8974	4.9468	21.0	1.5947	2.3875
PGH 6	19.3741	6.4192	21.0	1.5947	2.3849
PGH 7	22.4038	7.4930	21.0	1.5947	2.3961
PGH 8	3.5367	1.1703	20.9	1.5949	2.3837

Table 1. Pine Grove Hills obsidian density.

* Note: Specimen PGH 3A is a repeat of Specimen PGH 3.

gravimetry using the methods described in Stevenson et al. (2019). Table 1 presents the density data.

Absorbance measurements were made at the peak of the 3570 cm⁻¹ band (wavelength 2.8 μ) with a Perkin-Elmer FTIR spectrometer using 32 scans at 16 resolution, and a 1 mm aperture to the specimen. Specimen thickness was measured with Mitutoyo IP65 pointed micrometer ± 0.001mm precision, and the resulting absorbance and thickness measurements and density are in Table 2.

Analysis

Infrared absorption at the 3570 cm⁻¹ band is due to stretching of the O – H chemical bond. This bond occurs in both the OH and

H₂O_m species, and the molar absorption coefficients are significantly different: ε = 100 ± 2 L/(mol*cm) for OH and 56 ± 4 L/(mol*cm) for H₂O_m (Newman et al. 1984; 1537, Table 7). Since both species contribute to the absorbance, the molar absorption coefficient ε in equation (2) is a weighted average of the coefficients for the two species, given by

$$\epsilon_{\text{eff}} = (\epsilon_{\text{OH}} * \text{OH} + \epsilon_{\text{H}_2\text{O}_m} * \text{H}_2\text{O}_m) / (\text{H}_2\text{O}_m + \text{OH}) \quad (3)$$

where OH and H₂O_m refer to concentrations in weight percent.

However, since the relative abundances are not known *a priori*, an iterative computation procedure is required. The

Specimen No.	Peak absorbance at 3570 cm ⁻¹	Thickness, cm	Density, gm/L
PGH 1	0.4680	0.0354	2383
PGH 2	0.5234	0.0442	2385
PGH 3	0.7706	0.0285	2386
PGH 3A	0.6861	0.0260	2386
PGH 4	0.5394	0.0456	2380
PGH 5	0.6264	0.0492	2384
PGH 6	0.6879	0.0404	2388
PGH 7	0.9338	0.0342	2385
PGH 8	0.5746	0.0494	2396

Table 2. Pine Grove Hills specimen data.

* Note: Specimen PGH 3A is a repeat of Specimen PGH 3.

Specimen No.	H ₂ O _t , wt. %	Hydration rate, $\mu^2/1000$ yrs. at 20°C	Activation energy, Kelvins
PGH 1	0.1010	9.80	9969
PGH 2	0.0902	9.68	9973
PGH 3	0.2106	11.19	9930
PGH 3A	0.2054	11.12	9932
PGH 4	0.0903	9.68	9973
PGH 5	0.0972	9.76	9971
PGH 6	0.1306	10.16	9959
PGH 7	0.2129	11.22	9930
PGH 8	0.0882	9.65	9974

Table 3. Pine Grove Hills obsidian hydration parameters by specimen.

* Note: Specimen PGH 3A is a repeat of Specimen PGH 3.

procedure is to assume the water content is composed of one species only, compute the value of w in equation (2) using that species' value of ϵ , compute the relative abundances of OH and H₂O_m by a speciation model, compute ϵ_{eff} by equation (3), and then use ϵ_{eff} in equation (2) to recompute w . Once the change in w between iterations is lower than the resolution limit of the instruments (≈ 0.005 wt.%) the iteration can be terminated.

At the low values of H₂O_t, typical of natural obsidians, OH $\gg$ H₂O_m, so the ϵ for OH was chosen for the initial computation of w , which is an approximation to H₂O_t. Next the relative values of OH and H₂O_m were computed from a Langmuir speciation model (Rogers and Stevenson 2022b):

$$\text{OH} = 2.093 * Y / (1 + Y) \quad (4a)$$

where

$$Y = 0.489 * \text{H}_2\text{O}_t \quad (4b)$$

and

$$\text{H}_2\text{O}_m = \text{H}_2\text{O}_t - \text{OH} \quad (4c)$$

Now ϵ_{eff} can be computed and substituted into equation (2) to compute a new value of H₂O_t. This process can be repeated until the change in H₂O_t becomes negligible. In the present

case the change in H₂O_t from the first to the second step was significant, but subsequent steps yielded changes three orders of magnitude smaller than the instrument limits, so the data resulting from the second step are regarded as valid.

Once H₂O_t is known, the hydration rate for a temperature T can be computed from the equation

$$k = \exp[36.29 - (10005 - 354 * \text{H}_2\text{O}_t) / (T + 273.15)] \quad (5)$$

(Rogers and Stevenson 2022a). Here k is hydration rate in $\mu^2/1000$ years and T is temperature in °C. Finally, the activation energy for the hydration process in Kelvins is

$$Q = 10005 - 354 * \text{H}_2\text{O}_t \quad (6)$$

which is independent of temperature.

Note that this rate only applies at the value of T used for the computation, and, to be used in archaeological analysis, the rate must be adjusted to conditions at the archaeological site. The computations reported below were made for a temperature of 20°C (293.15 K), which is a typical EHT for the high desert of California. If the rate is being applied to a site with different EHT (say, EHT_s, in °C), the rate must be adjusted by the equation

$$k_s = k_{20} * \exp\{Q * [1/293.15 - 1/(EHT_s + 273.15)]\} \quad (7)$$

Parameter	Mean	Std. dev.	CV
H ₂ O _t , wt. %	0.1363	0.056	0.414
Rate, $\mu^2/1000$ yrs. at 20°C	10.25	0.71	0.069
Activation energy, Kelvins	9957	20	0.002

Table 4. Pine Grove Hills obsidian parameter statistics.

where k_s is the hydration rate for the site at EHT_s, k_{20} is the rate computed from equation (5) for 20°C, and Q is the activation energy computed from equation (6).

For Pine Grove Hills, Table 3 presents the H₂O_t, hydration rate, and activation energy. Table 4 gives a statistical summary for this specimen set.

Conclusion

This analysis finds that Pine Grove Hills obsidian is a relatively slow-hydrating glass, comparable to the near-by sources at Truman-Queen and Bodie Hills.

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Department of Anthropology and Geography
Coastal Carolina University
P.O. Box 261954
Conway, SC 29528
U.S.A.
IAOS.Editor@gmail.com

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Lucas Martindale Johnson

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ABOUT THE IAOS

The International Association for Obsidian Studies (IAOS) was formed in 1989 to provide a forum for obsidian researchers throughout the world. Major interest areas include: obsidian hydration dating, obsidian and materials characterization (“sourcing”), geoarchaeological obsidian studies, obsidian and lithic technology, and the prehistoric procurement and utilization of obsidian. In addition to disseminating information about advances in obsidian research to archaeologists and other interested parties, the IAOS was also established to:

1. Develop standards for analytic procedures and ensure inter-laboratory comparability.
2. Develop standards for recording and reporting obsidian hydration and characterization results
3. Provide technical support in the form of training and workshops for those wanting to develop their expertise in the field.
4. Provide a central source of information regarding the advances in obsidian studies and the analytic capabilities of various laboratories and institutions