



IAOS

International Association for Obsidian Studies

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International Association for Obsidian Studies

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Web Site: <http://www.deschutesmeridian.com/IAOS/>

NEWS AND INFORMATION

Skinner Poster Award Winner

The Craig E. Skinner Best Poster Award for the 2022 SAAs was awarded to Megan Whitehead for the poster *Artifact Density Analysis of Tlajinga: A Neighborhood in Teotihuacan*.

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!

IAOS President Candidate Statement Now Available

Nominations are now in hand for the position of IAOS President. You may find the candidate statement on page 3 of this issue of the *IAOS Bulletin*. The President oversees the annual IAOS business meeting, makes decisions in conjunction with the executive board on IAOS activities, and steers the organization in the fulfillment of its mission. Watch for an email with instructions to vote. The winner will be announced at the 2023 IAOS meeting at the SAAs. The winner will then serve as President-Elect for one year and begin the term of President in 2024.

NOTES FROM THE PRESIDENT

Hello, IAOS members. Several members of the IAOS Board gave presentations at the Society for American Archaeology (SAA) meeting in Chicago, Illinois this past March/April. Lucas Johnson and Kyle Freund were on two papers, Carolyn Dillian presented a paper, and I presented a paper on my research about Pachuca obsidian in the U.S. Southwest. In addition, we had our annual IAOS business meeting in Chicago, and it was our first in-person meeting since the 2019 SAA in Albuquerque. Unfortunately, the meeting was lightly attended, but we still discussed several items like the Treasurer's report, the *IAOS Bulletin* report, new business like the Craig E. Skinner Poster award, future IAOS sponsorships, and upcoming elections for a new IAOS President.

For the Treasurer's Report, Lucas Johnson reported that membership is down compared to 2021, which is likely associated with the lack of a substantial event (e.g., the International Obsidian Conference) to recruit members. During our meeting, we discussed a potential trip to an obsidian source during next year's SAA meeting because it is in Portland, Oregon. A trip may occur to the Glass Buttes obsidian source before the meeting, and I sent out an informal poll in May to see how many IAOS members might be interested in attending this trip. More information to come!

In other news, this was the first SAA meeting we awarded the Craig E. Skinner Best Poster Award. The IAOS Board looked at the posters related to obsidian, and we voted on Megan Whitehead's poster, *Artifact Density Analysis of Tlajinga: A Neighborhood in Teotihuacan*. Congratulations, Megan! We also passed IAOS pamphlets around the meeting to gain new members and increase our visibility.

In November 2021, I sent out an email seeking interest for a new IAOS President since my term is up. However, no one sent in nomination statements, but I've reached out

individually, and one candidate has provided a statement. You can read her statement in this *IAOS Bulletin* issue. I will be sending out another email for everyone to vote.

Finally, if you presented a research poster or talk at the SAA, please consider submitting an article, research update, news, or lab report projects to the *IAOS Bulletin*. You can submit your work to Carolyn Dillian at IAOS.Editor@gmail.com. Also, please take care of your IAOS membership dues if you haven't done so already. Membership dues help the IAOS host conferences like the International Obsidian Conference (IOC). The next IOC will be in Japan in July 2023. Please see the IOC circular for additional information.

Sean Dolan, IAOS President
sgdolan@gmail.com

**INTERNATIONAL ASSOCIATION FOR OBSIDIAN STUDIES
PRESIDENT CANDIDATE STATEMENT**

Dr. Theodora Moutsiou

My interest in obsidian began over twenty years ago when I first realised that there was surprisingly little known about the use of this unique material in the earliest human past. Investigating Palaeolithic obsidian became the focus of my PhD thesis that brought together all the available information on use and movement of obsidian spanning three continents – Africa, Europe, Asia. I have excavated obsidian-bearing sites, analysed material and investigated obsidian sources in east Africa, central and southeastern Europe, and Japan.

I have studied obsidian as a proxy of past human behaviour and cognition and, recently, my research focus has expanded to the application of geochemical characterisation methods for sourcing. I am a Special Scientist at the Archaeological Research Unit, University of Cyprus (<http://www.ucy.ac.cy/dir/en/cb-profile/tmouts01>), researching island colonisation, human adaptation and raw material selectivity mainly through the study of provenance and distribution of Palaeolithic, Epipalaeolithic and early Neolithic obsidian and other rare raw materials in Cyprus and the broader eastern Mediterranean.

As President of the IAOS, I will continue the efforts made by our previous presidents in managing the Association's business activities, including the newsletter, document library and website. I am very interested to see our membership grow and I will utilise social media to expand IAOS online presence. As a European researcher I believe that I am ideally positioned to increase IAOS visibility outside North America (where the bulk of our members are based) and attract new members from regions not traditionally linked to the IAOS. To this effect, I will also work towards increasing IAOS visibility in international conferences/workshops. Moreover, through my involvement in outreach activities, such as the popular annual *Researchers' Nights* events, I will initiate actions to raise public awareness and interest in archaeology and geology through obsidian, a material that has attracted people's imagination for over one million years. Finally, an important issue within the scientific community I wish to address is the continuing lack of a shared global reference library of geochemical data on obsidian sources. It was one of the founding principles of IAOS and I believe it remains an important goal that we should work together towards. I look forward to serving the needs and interests of the IAOS community.



International Obsidian Conference (IOC) Engaru 2023

Engaru Metro Plaza, Engaru Town, Hokkaido, Japan
3–6 July 2023

Website for IOC Engaru 2023: <http://geopark.engaru.jp/ioc2023/> 

First circular

We invite those interested in all aspects of obsidian studies, from natural sciences to archaeology, to IOC Engaru 2023. We hope to maintain a global scope by highlighting obsidian studies throughout Northeast Asia at the conference. In addition, we will focus on geological heritage studies with regard to the development of public education and tourism in rural areas. Finally, we expect the further development of transdisciplinary research regarding obsidian studies and the sustaining of our communities through this conference.

General information

IOC Scientific Committee

Biró, Katalin T. — Hungarian National Museum, Budapest, Hungary

Glascock, Michael — University of Missouri, Columbia, MO, USA

Kuzmin, Yaroslav — Institute of Geology & Mineralogy, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, Russia

Le Bourdonnec, François-Xavier — University Bordeaux Montaigne, Pessac, France

Lexa, Jaroslav — Earth Sciences Institute of the Slovak Academy of Sciences, Bratislava, Slovakia

Markó, András — Hungarian National Museum, Budapest, Hungary

Ono, Akira — Professor Emeritus of Tokyo Metropolitan University, Tokyo, Japan

Torrence, Robin — Australian Museum, Sydney, Australia

Tykot, Robert — University of South Florida, Tampa, FL, USA

Vianello, Andrea — University of South Florida, Tampa, FL, USA

Local Organizing Committee

Ono, Akira (**Chair**) — Professor Emeritus of Tokyo Metropolitan University, Tokyo, Japan
Matsumura, Yoshifumi (**Secretariat**) — Engaru Town Office, Hokkaido, Japan
Hashizume, Jun — Niigata Prefectural Museum of History, Niigata, Japan
Ikeya, Nobuyuki — Meiji University, Tokyo, Japan
Kumagai, Makoto — Geo. Labo Co., Ltd., Engaru, Hokkaido, Japan
Sano, Kyohei — University of Hyogo, Hyogo, Japan
Shimada, Kazutaka — Meiji University, Tokyo, Japan
Suda, Yoshimitsu — Nagasaki University, Nagasaki, Japan
Takase, Katsunori — Hokkaido University, Hokkaido, Japan
Wada, Keiji — Professor Emeritus of Hokkaido University of Education, Hokkaido, Japan
Yamada, Satoru — Kitami City Board of Education, Hokkaido, Japan

Registration

Full registration	15,000 (JPY)
Early-bird full registration (before 15 January 2023)	10,000 (JPY)
Students and accompanying persons	5,000 (JPY)
Early-bird student registration (before 15 January 2023)	4,000 (JPY)
Conference dinner	5,000 (JPY)
Post-conference field trip (optional)	TBC

Online registration will be available **from October 2022** on the website for IOC Engaru 2023.

Deadlines

Registration for presenters:	17:00 JST, 1 March 2023
Registration for attendees not presenting a paper or poster:	17:00 JST, 1 June 2023
Submission of abstracts:	17:00 JST, 1 March 2023

Contact persons

Ono, Akira (ono@tmu.ac.jp ✉)
Suda, Yoshimitsu (geosuda@nagasaki-u.ac.jp ✉)
Matsumura, Yoshifumi (y.matsumura@engaru.jp ✉)

Note: If you require a **visa** to visit Japan, please contact us as soon as possible.

Detailed information

Conference details

Venue: Engaru Metro Plaza, Engaru Town (<https://engaru-metroplaza.jp> ↗)

Duration: 4 days, 3–6 July 2023 (including a one-day field trip)

Post-conference field trip (optional): 2 days, 6–7 July 2023 (details to be announced)

Transportation

Participants can reach Engaru Town by train from New Chitose Airport (CTS). The journey takes about five hours. For more information, see the following websites:

Engaru Town (<https://engaru.jp/information/page.php?id=224> ↗)

New Chitose Airport (<https://www.new-chitose-airport.jp/en/> ↗)

Accommodation

We are considering a hotel booking system for participants because there are few hotels in Engaru Town. Therefore, please wait until we provide further information before attempting to book a hotel.

Conference sessions (to be confirmed)

1. Formation of obsidian from a geological perspective
2. Obsidian sources and their characterization
3. Analytical methods and databases of obsidian data
4. Cultural aspects of obsidian during different archaeological periods
5. Lithic technology and traceological studies
6. Regional development in relation to geological heritage and archaeological obsidian

Conference format

In the second circular (October 2022), we will state **the final conference format** (i.e., onsite, virtual, or hybrid).

Styles of abstract and presentation

Conference participants can submit an abstract for an oral presentation and/or poster. The abstract must not exceed 300 words (including the author affiliation details). Oral presentations are limited to 15 minutes, followed by a 5-minute discussion. Presenters are asked to use a standard presentation format (i.e., PPT or PDF). Details on poster style and the format of the poster session will be announced in the second circular (October 2022). The official language of the conference is English.

Day field trip during the conference

During the conference, attendees will visit the Shirataki obsidian source and Engaru Archaeological Center as a day trip. For information, please see the following websites:

<https://www.google.com/maps/d/edit?mid=1CSJs5dN25IyZQSZcpXsnXcLNRjQvfFOb&ll=43.96735560106864%2C143.307415&z=12> ↗

<https://my.matterport.com/show/?m=UbN2JmumPzw> ↗

Post-conference field trip (optional)

A two-day post-conference field trip is still under consideration, with the intention to visit obsidian sources around Shirataki in Hokkaido. There will be an extra fee for attending the field trip.

Notes for online registration

Online registration will be available **from October 2022** on the website for [IOC Engaru 2023](#) ↗. Registration will require the following information:

- Name (family name, first name)
- Title
- Gender
- Affiliation (institution, department, position)
- Institution or home address (city, country, postal code)
- Telephone number
- Email address
- Presentation style (onsite or virtual; oral and/or poster)
- Student registration (confirmation needed; i.e., student ID card)
- Details of accompanying persons
- Special request(s)

About Engaru Town and Geopark

Shirataki Geopark is a National Geopark that includes the Shirataki obsidian source and Upper Paleolithic sites of geological and archaeological importance, mainly distributed in Engaru Town. For detailed information on the Geopark and Engaru Town, see the following files and website:

<http://geopark.engaru.jp/wp-content/uploads/2021/09/SHIRATAKI-GEOPARK-GUIDEBOOK2009.pdf> ↗

<http://geopark.engaru.jp/wp-content/uploads/2021/09/The-Shirataki-GeoparkProject2009.pdf> ↗

<https://engaru.jp> ↗

The mean daily temperature in Engaru Town during early July is about 20°C, with a possibility of cold nights.

OBSIDIAN HYDRATION DATING WITH OPTICAL MICROSCOPY: IS AGE ACCURACY IMPROVED BY MEASURING STRUCTURAL WATER CONTENT OF A SPECIMEN?

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

^a Maturango Museum, Ridgecrest, California, USA

^b Virginia Commonwealth University, Richmond, Virginia, USA

Abstract

In archaeological obsidian hydration dating (OHD), the age of an obsidian artifact is computed by using optical microscopy to measure depth of penetration of water absorbed since the artifact was created. The primary compositional determinant of the absorption (hydration) rate is intrinsic (or structural) water content, which varies between geochemical sources and also within a source. Currently the geochemical source of each specimen is determined and a hydration rate ascribed to that source. Water content of each specimen is not measured, and intra-source water variation limits the age accuracy achievable. We analyze the benefits of determining the hydration rate for individual specimens by measuring water content with infrared spectroscopy, which we term the calibrated rate method. We conclude that this provides significant improvement in age accuracy, and the improvement increases with obsidian water content. However, to be useful in a practical sense, a method of measuring intrinsic water content must be devised which is inexpensive and is not destructive to the specimen. We further conclude that OHD age accuracies on the order of 5% are feasible in the future with this method, but only with improvements in effective hydration temperature (EHT) accuracy.

Introduction

Obsidian hydration dating (OHD) is based on computing the age of an obsidian artifact by measuring the amount of surface diffused water absorbed since the artifact was created, and converting the gain to an age with the appropriate hydration rate. The method is widely used in the Great Basin and the Inter-Mountain west. Major advances have been made in the past decade in understanding and applying the basic science of OHD (Rogers 2007, 2012; Stevenson et al. 2019, 2021). It is known that the intrinsic (or structural) water content of obsidian is variable (Stevenson et al. 1993) and is the primary compositional determinant of hydration rate (Stevenson et al. 2000, 2021).

The most commonly applied method of OHD involves determining the geochemical source of each artifact to be dated and ascribing a hydration rate to that source, so we

describe it as the ascribed rate method (ARM). In this method, no attempt is made to measure the water content of each specimen. Previous analyses have shown that this method, although widely used, has fundamental limitations to the achievable accuracy (Rogers 2008a, 2010; Rogers and Yohe 2021). In this paper we investigate an alternative method that determines the hydration rate of each individual specimen based on its structural water content, the calibrated rate method (CRM). Using propagation-of-error analysis, we identify the factors contributing to age accuracy and estimate their magnitude. We also identify the parameters that are most likely to yield significant improvements, and suggest a potential best accuracy achievable by OHD.

The analysis is based on measurement of water gain by optical microscopy, and we only address other methods of water measurement

(Secondary Ion Mass Spectrometry – SIMS – or infrared spectrometry) in terms of the accuracy requirements they should meet to be useful. Similarly, we discuss the benefits of possible improvements in measuring effective hydration temperature (EHT), but do not specify how the improvements should be accomplished. Accuracy is discussed in terms of standard deviation or coefficient of variation ($CV = \text{standard deviation}/\text{mean}$). The standard deviation (or CV) of the computed age is due to experimental error in measurements and in approximations in mathematical models, and we refer to it as "error" or "uncertainty" interchangeably.

Obsidian Chemistry

Obsidian is an aluminosilicate, or rhyolitic, glass, formed by rapid cooling of silica-rich 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, but it does possess a matrix-like structure exhibiting some degree of spatial order (Doremus 1994: 27 Fig. 2, 2002: 59-73). Obsidians are typically about 74% SiO_2 and about 14% Al_2O_3 by weight, the remainder being matrix modifiers (mostly alkaline oxides) and trace elements (mostly rare-earth elements) whose concentrations are source-specific (Doremus 2002: 109, Table 8.1; Hughes 1988; Stevenson et al. 1998; Zhang et al. 1997). 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 et al. 1997). The minute interstices within the glass matrix, on the order of 0.1-0.2nm in diameter, are the pathways where water diffusion takes place.

Obsidian anhydrous chemistry has traditionally been regarded as having a major influence on hydration rate and was the basis of hydration rate prediction equations (e.g.

Friedman and Long 1976; Stevenson and Scheetz 1989). 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 in their high temperature diffusion studies, although Karsten et al. (1982) reported that Ca^{2+} concentration may influence hydration rate to a very slight extent. It appears that anhydrous chemistry has a negligible effect on the magnitude of the hydration rate and attempts to predict rates from anhydrous composition are unlikely to succeed.

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 (wt%) in natural obsidians, although cases of somewhat higher concentration are occasionally encountered (e.g. Mono Craters, Newman et al. 1986: 1528, Table 1). The structural water exists as two species: molecular water (H_2O_m) and hydroxyl (OH). The water trapped in the glass as the melt cools is H_2O_m , some of which reacts with oxygen atoms bound to the glass matrix to form SiOH. The molecular water is free to diffuse, while the hydroxyl is chemically bound to the glass matrix (Doremus 1994: 198, 2001: 129). The sum of H_2O_m and OH is total water (H_2O_t), which is the basis of this analysis.

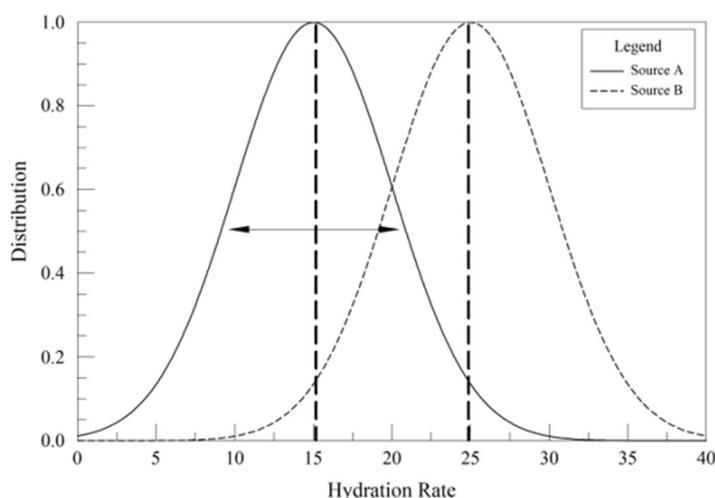
Obsidian forms from a melt which is primarily silica and alumina, and the melt is a liquid, with no internal order at the molecular level. As the temperature decreases, the glass network forms and the degree of order increases. If no modifier ions are present, the network forms with an interatomic spacing characteristic of its composition, about 0.086nm (Doremus 2002: 67) for silica. Modifier ions present in the melt, such as water, cause the glass to form interstices around them (Shelby 2005: 145). A water

molecule has a radius in the range of 0.138-0.233nm (Doremus 2002: 63), so its diameter is roughly 0.3 to 0.5nm. This leads to much larger interstices than for the water-free obsidian, which results in a greater openness leading to a more rapid hydration rate (Garofalini 2020; Kuroda et al 2018, 2019; Kuroda and Tachibana 2019). Thus, intrinsic water has a profound effect on hydration rate, and the effect increases with increasing water content (Behrens and Nowak 1997; Delaney and Karsten 1981; Karsten et al. 1982; Lapham et al. 1984; Rogers 2015; Rogers and Stevenson 2017; Stevenson et al. 1998, 2000, 2019; 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; Stevenson et al. 2019); mass loss when obsidian powder is heated (Newman et al. 1986; Steffen 2005); infrared (IR) transmission spectrometry (Newman et al. 1986); and IR photo-acoustic spectrometry (IR-PAS, Stevenson and Novak 2011). However, micro-densitometry has proven to be unreliable in some cases of archaeological interest (e.g. the Coso volcanic field and the Bodie Hills volcanic field, both in California), and the other three techniques are costly and, as currently practiced, are destructive to the artifact. As a result, intrinsic water measurement is not conducted for most practical archaeological investigations in the United States today, which apply the ARM.

Stevenson et al. (1993) analyzed the intrinsic water content of obsidian from the Coso source in eastern California. Coso was known to have four geochemically distinct subsources (Hughes 1988), and Stevenson demonstrated that the mean intrinsic water content of the subsources varied, and also that there was significant variation within each subsource. The variation in intrinsic water within a geochemical source or subsource leads to variations in hydration rate, which in

turn increase the uncertainty (statistical error) in computed ages. From a practical standpoint, controlling for geochemical source in the ARM functions as a proxy for controlling for intrinsic water (Stevenson et al. 2000), albeit rather poorly (Stevenson et al. 1993; Rogers 2008a). Figure 1 illustrates the process. Sourcing controls for the mean value (central tendency) of intrinsic water in the obsidian from that source. The uncontrolled intra-source variation in water content contributes to uncertainty in the age, and is reflected in the



standard deviation of age in the ARM.

Figure 1. Hydration rate distributions for two hypothetical obsidian sources. The spread in rates is caused by intra-source water variations. Geochemical sourcing controls for central tendency, but cannot control for the spread, which contributes to uncertainty in age (CV_{ke}).

Current OHD Method Overview

In the conventional method of performing an OHD analysis (ARM), the geochemical source of the specimen is determined and a single hydration rate is ascribed to all specimens from that source. A mean rate for a geochemical source may be determined by any of a number of methods which include radiocarbon association, temporally sensitive artifacts, or accelerated hydration in the laboratory (summarized in Rogers and

Stevenson 2020). The intrinsic water content of the individual specimen is not measured in this method.

The sources of error in the age computation by the ARM have been analyzed in detail (Rogers 2008a, 2010; Rogers and Yohe 2021). The contributors to error are measurement uncertainty of the hydration rim (typically $\approx 0.08\mu$ today), uncertainty in effective hydration temperature (EHT), errors in rate ascribed to the geochemical source, and errors due to intra-source water variation. Current practice is to compute EHT based on the temperature parameters determined from meteorological records (Rogers 2007, 2012) or from on-site sensors (Onken 1991; Stevenson et al. 1998). The accuracy of this procedure is approximately 1°C (one- σ) (Rogers 2007, 2008b). Errors due to intra-source variation in intrinsic water, and possible errors due to fluctuations in soil humidity, are included in the age standard deviation.

The analysis of Rogers and Yohe (2021) includes humidity effects, but may be unnecessarily pessimistic. Humidity effects on hydration have been examined in the laboratory by Ebert et al. (1991), Friedman et al. (1994), and Mazer et al. (1991). However, soil interstitial relative humidity is typically over 95%, even in desert conditions, for depths greater than approximately 20cm (Campbell 2021). Most archaeological specimens are recovered from buried contexts, so humidity variation is not expected to have a large effect archaeologically. Humidity effects are not considered here, but can be included by the method of Rogers and Yohe (2021:10, equation 11).

The Calibrated Rate Method (CRM)

An alternative approach, the CRM, would determine the hydration rate individually for each specimen from its structural water content, which resolves the problem of intra-source water variation, but not the

computation of EHT. Conceptually, the method involves the following steps:

1. *Measure the water gained during hydration:* Obsidian hydration is a water (H_2O_m) diffusion process. The amount of water absorbed and retained within the hydration layer increases with the square root of time (Crank 1975; Friedman and Long 1976) although alternate rate exponents have been proposed (Riciputi et al. 2002; Stevenson and Novak 2011). The quantity absorbed can be measured by optical microscopy (thickness), secondary ion mass spectroscopy (SIMS) (thickness), or transmission IR spectroscopy (H_2O_m mass increase). For the purposes of this analysis we examine the conventional method of optical microscopy.

2. *Measure intrinsic (structural) water content of the specimen:* This can be done by IR transmission spectroscopy or by IR photoacoustic spectroscopy (Stevenson et al. 2013) and conversion of the infrared absorbance values to concentration using the Beer-Lambert law (Newman et al. 1986).

3. *Determine the EHT:* Calculate the EHT from meteorological data or sensors. This analysis assumes the current method, which infers EHT of the specimen from the temperature history of the site.

4. *Compute a hydration rate:* Compute a hydration rate for the individual specimen based on the EHT and the structural water content, using a calibration equation. The rate k is a function of absolute temperature (T), by the Arrhenius equation:

$$k = k_0(w) * \exp[-E(w)/(R*T)] \quad (1)$$

where: $k_0(w)$ is the pre-exponential and $E(w)$ is the activation energy, both of which are a function of water content w . Note that k_0 is in the same units as k , and is not a function of

temperature; E is in J/mol, and R is the universal gas constant in J/(mol*K). The activation energy is a function of intrinsic water content, which causes the hydration rate to vary with water content as well. The form of the calibration equation is discussed below.

5. *Compute age*: Use the equation:

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

where t is years before present, r is hydration rim thickness in micrometers (μ), and k is the hydration rate ($\mu^2/1000$ years)

6. *Compute age accuracy*: Each age will have a standard deviation in years (or alternatively a CV) that is computed by the method described below.

Step 4 of the proposed method requires a calibration equation, relating water content and temperature to hydration rate. Zhang (2008: 245) and Zhang and Behrens (1997) published such equations, which also included the effects of pressure. However, the data on which the equations are based were for geological conditions (700-1000K, and pressures up to 0.5gPa), and when the equations are applied to archaeological conditions (290K, 0.1mPa) they yield hydration rates which are over an order of magnitude too small. An equation for archaeological conditions has been published (Rogers 2015; Rogers and Stevenson 2017), but it was based on a small data set with a limited range of temperatures. An alternative equation is proposed below based on a larger archaeological data set with a much larger range of temperatures. The equation has the same form as that of Zhang and yields archaeologically valid hydration rates. This is the equation applied in this analysis (equation 9 below).

Accuracy Analysis for the CRM

The computation of age based on obsidian hydration employs the model of equation (2), so the ultimate accuracy achievable is determined by the uncertainties in r and k. Analysis of uncertainties is based on propagation-of-error theory (Cvetanovic et al. 1979: 51ff., Taylor 1982: 173-175). If a dependent variable y is a function of a number of independent variables x_1, x_2, \dots, x_n , and the errors are independent, the standard deviation of y, σ_y , is given by:

$$\sigma_y^2 = \sum (\partial y / \partial x_i)^2 * \sigma_{x_i}^2 \quad (3)$$

where the sum is taken over all n variables. In this case the dependent variable is t in equation (2), so

$$\sigma_t^2 = (\partial t / \partial r)^2 * \sigma_r^2 + (\partial t / \partial k)^2 * \sigma_k^2 \quad (4)$$

After some algebra this reduces to:

$$CV_t^2 = (2 * CV_r)^2 + CV_k^2 \quad (5)$$

Where CV = coefficient of variation (standard deviation divided by mean value) and the subscripts refer to the specific variable. Thus, CV_t is the coefficient of variation of the computed OHD age.

Determining the uncertainty in hydration rate (CV_k) follows the same logic, but depends on the relationship between rate, temperature, and water content. We developed an equation by a least-squares best fit to an archaeological data set based on published data on two obsidian sources in eastern California: the Coso volcanic field in Inyo County and the Bodie Hills volcanic field in Mono County. The data set is made up of five distinct subsets: laboratory hydration measurements for two Coso obsidian subsources (Stevenson and Scheetz 1989: 25, Table 1); measurements of water content in all four Coso subsources (Stevenson et al. 1993; Rogers 2008); archaeologically-determined hydration rates

for all four Coso subsources (Rogers 2011); laboratory hydration data with aggregated measurements of water content for the two subsources in the Bodie Hills; and laboratory hydration data for two Bodie Hills specimens with specimen-specific water content data (Stevenson et al. 2021; Stevenson et al. n.d.: Tables 5 and 7). The size of the resulting data set is $N = 29$, the range of total water represented is 0.1 wt% to 1.02 wt%, and the temperature range is from 20°C to 170°C.

The data set was used as an input to the curve-fitting routine in PSIPlot (v.9), by PolySoftware International, which computes best-fit parameters for any specified equation and data set, plus goodness-of-fit statistics. The resulting calibration equation is

$$k = \exp[36.29 - (10005 - 354*w)/T] \quad (6)$$

where k is in $\mu^2/1000$ years, w is total water in wt%, and T is in kelvin. The fit between this equation and an archaeological data set ($N = 7$) is $R^2 = 0.9998$, with rms residuals = 0.342 $\mu^2/1000$ yrs. This equation is an improvement over a previous equation in Rogers (2015) and Rogers and Stevenson (2017) in terms of accuracy, size of data set, and range of variation of temperature.

Again, by equation (3) above, the uncertainty in rate is

$$\sigma_k^2 = (\partial k/\partial T)^2 * \sigma_T^2 + (\partial k/\partial w)^2 * \sigma_w^2 \quad (7)$$

The uncertainty in rate due to uncertainty in EHT, expressed as the CV, is the first term of equation (7)

$$CV_{EHT} = [E/(R*T^2)] * \sigma_{EHT} \quad (8)$$

Where σ_{EHT} is the standard deviation of EHT. For typical archaeological conditions, T is approximately 293K, and $[E/(R*T^2)] \approx 0.11$, so:

$$CV_{EHT} \approx 0.11 * \sigma_{EHT} \quad (9)$$

The second term of equation (7) is found by applying equation (3) to equation (6) and is

$$CV_{kw} = (354/T) * \sigma_w \quad (10a)$$

or, if $T = 293K$

$$CV_{kw} \approx 1.2 * \sigma_w \quad (10b)$$

where σ_w is the standard deviation of intrinsic water content in wt%. (The previous equation of Rogers (2015) and Rogers and Stevenson (2017) yields the same value for CV_{kw}). Thus the overall uncertainty in OHD age is

$$CV_t^2 = (2*CV_r)^2 + CV_{kw}^2 + CV_{EHT}^2 \quad (11)$$

Again, the uncertainties are treated as independent, since there is no reason to expect mutual dependence. Note that the accuracy is a function of hydration rim value (r), while the other two terms are constants; it is not a function of water content or EHT.

The numerical value of CV_{kw} is determined by two factors: the accuracy of the IR measurement of water content (w), and by the inherent accuracy of equation (6) itself. Water content is determined by measurements of IR absorbance and the Beer-Lambert law (Levine 2002; Newman et al. 1986; Stevenson and Novak 2011). The accuracy of the water content can be computed from equation (10b), where σ_w is now the inherent uncertainty in measuring intrinsic water by the Beer-Lambert method, or about 0.02 wt% (Newman et al. 1986). The second factor, the accuracy of equation (9) itself, is given by the rms residuals and is $\approx 0.34 \mu^2/1000$ years, resulting in a $CV_{kw} \approx 0.01 - 0.02$. Combining the two by the square root of the sum of the squares gives $CV_{kw} \approx 0.03$. Substituting this value and equation (8) into equation (11), and assuming the accuracy of rim reading setting $\sigma_r = 0.08\mu$, yields the age uncertainty by the CRM to be

$$CV_t^2 = (0.16/r)^2 + (0.11 * \sigma_{EHT})^2 + 0.03^2 \quad (12)$$

Quantification of Uncertainty

We made numerical computations to estimate the effects of the error sources in equation (11). Three typical obsidians were considered. Two are relatively water rich, fast hydrating obsidians (Coso West Sugarloaf, mean water content 0.62 wt%, rate 18.14 $\mu^2/1000$ years at 20°C; Coso Sugarloaf Mountain, mean water content 1.02 wt%, rate 29.87 $\mu^2/1000$ years at 20°C) (Rogers 2008a, 2011; Stevenson et al. 1993). The other is a low water content, slow hydrating obsidian (Bodie Hills Group 2, mean water content 0.11 wt%, rate 10.03 $\mu^2/1000$ years at 20°C) (Stevenson et al. 2021, n.d.). Computations were made for both the ARM and CRM.

The Ascribed Rate Method (ARM)

Error computations were initially made for the ARM as a basis for comparison. As pointed out above, for this case there are four sources contributing to the age error: hydration rim measurement ($CV_r = \sigma_r/r$); error in computing EHT; errors in the rate ascribed to the geochemical source (CV_{ks}); and errors due to intra-source variations in water content (CV_{ke}). The CV of age is computed by the equation:

$$CV_t^2 = (2 * \sigma_r/r)^2 + CV_{ks}^2 + CV_{EHT}^2 + CV_{ke}^2 \quad (13)$$

(Rogers and Yohe 2021: 10, Eq. 12, with CV_{hum} omitted).

Numerical values for the first three terms are: $\sigma_r = 0.8\mu$, $\sigma_{EHT} = 1.0^\circ\text{C}$, and $CV_{ks} = 0.05$. To quantify the fourth term, CV_{ke} , Rogers and Yohe (2021: 10, Table 1) analyzed the variation in structural water content across five geochemical sources with water content varying an order of magnitude (approximately 0.1 to 1.02 wt%). They found that the coefficient of variation of the structural water content consistently lies in the region of 20 – 35%, regardless of the mean value; here we use 30% as a conservative value for analysis, so the value of CV_{ke} is computed by equation

(10b) above, using 0.30 as the nominal value of CV_w . Thus $CV_{ke} = 0.36 * w$ where w is total water in wt%. The age uncertainty for the ARM then becomes

$$CV_t^2 = (0.16/r)^2 + (0.11 * \sigma_{EHT})^2 + 0.05^2 + (0.36 * w)^2 \quad (14)$$

Figure 2 shows a plot of this equation for WSL and BH2 obsidians as a function of hydration rim value (r) at an EHT of 20°C. The results clearly show that the CV of age is a function of rim thickness when rim value is small, because of the r in the denominator of the first term on the right in equation (13); in fact, the $CV_t \rightarrow \infty$ as $r \rightarrow 0$, although this case is not of archaeological interest. Examination of equation (14) shows that the accuracy is a function of both the hydration rim value (r) and the specimen water content (and hence hydration rate) via the CV_{ke} term.

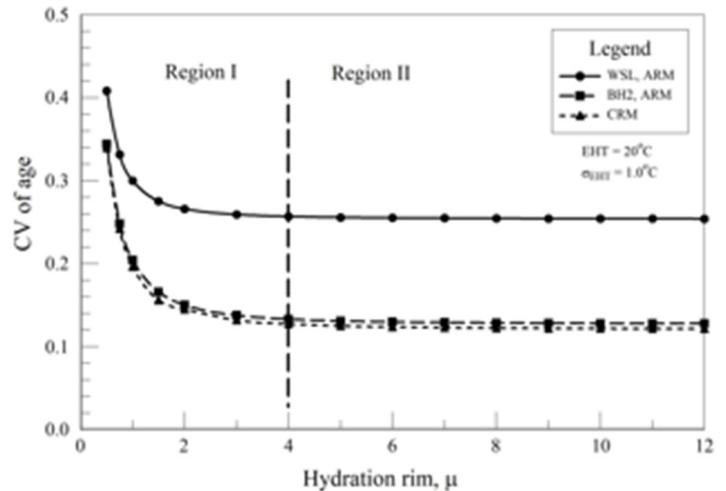


Figure 2. Age coefficient of variation as a function of hydration rim. Three cases are shown: a relatively fast obsidian (Coso West Sugarloaf) and a slow obsidian (Bodie Hills Group 2), computed by the ARM; and age CV computed by CRM. Age accuracy is better in Region II than in Region I because the error contribution due to hydration rim measurement becomes negligible for rims $> 4\mu$.

When the rim values are less than approximately 4μ (Region I) the measurement accuracy strongly affects the age accuracy, while greater than approximately 4μ (Region

II), the CV of age becomes essentially constant. This observation applies regardless of hydration rate or temperature; it is simply a function of σ_r , and better accuracy (a smaller value of σ_r) means a smaller Region I. It is also independent of the method used to measure water gained during hydration, and it applies to the CRM as well. Figure 3 shows the phenomenon graphically.

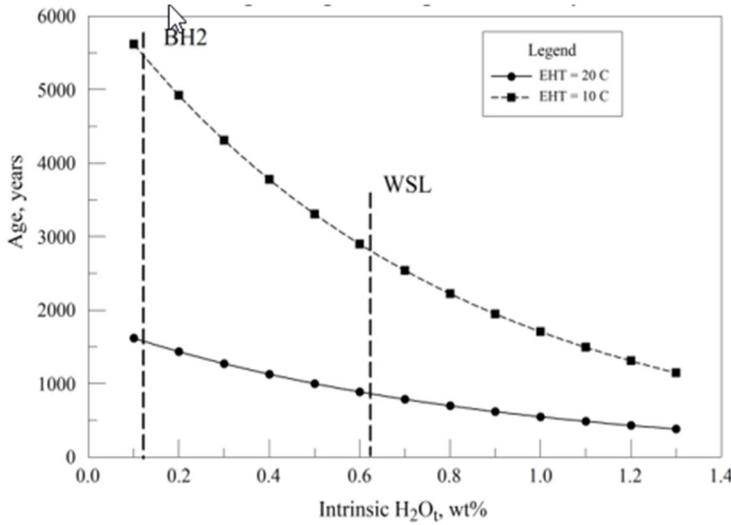


Figure 3. Age of the boundary between Regions I and II as a function of total intrinsic water content, for two values of EHT. Water content for Coso West Sugarloaf (WSL) and Bodie Hills Group 2 (BH2) are shown for comparison. Artifacts at a low temperature site, and made from a slow obsidian ($w \approx 1\%$), will not be in Region II unless the age > 5500 years; more recent specimens will be in Region I, where accuracy is poorer. This dichotomy occurs with either ARM or CRM.

The importance of this phenomenon is that, for Region I, the age accuracy is dominated by the rim measurement and improvements in other parameters are less important. This phenomenon is significant archaeologically, because a slow-hydrating obsidian such as Bodie Hills Group 2, in a low-temperature environment such as mountains, may take 6,000 years to reach 4μ , so most of the archaeological data from such a site will be subject to this degraded accuracy.

Ten cases were analyzed numerically, covering slow and fast obsidians, with variations in σ_{EHT} . Table 1 summarizes the cases and the resulting values of CV_t . Accuracies are shown for two values of the hydration rim, Region I ($r = 1\mu$) and Region II ($r = 7\mu$).

The first point to be observed is that the value of EHT does not affect accuracy. Cases AR1 and AR2 are at different EHT, but the accuracy is the same, so the results are independent of temperature. Next, Figure 4 shows the contributions of each error source for WSL obsidian, a relatively fast-hydrating obsidian, at $EHT = 20^\circ C$. Note that intra-source variations in water content (CV_{ke}) are by far the largest contributor to age uncertainty in Region II, followed by errors in EHT. Note also that the error contribution of the hydration rim measurement is significant in Region I but decreases as mean rim value increases and for rim values above

Case	Source	Total water, wt%	EHT, °C	σ_{EHT} , °C	CV_t , Region I, $r = 1\mu$	CV_t , Region II, $r = 7\mu$
AR1	WSL	0.62	20	1.00	0.30	0.25
AR2	WSL	0.62	12	1.00	0.30	0.25
AR3	BH2	0.11	20	1.00	0.20	0.13
AR4	BH2	0.11	12	1.00	0.20	0.13
AR5	SLM	1.00	20	1.00	0.41	0.38
AR6	SLM	1.00	12	1.00	0.41	0.38
AR7	WSL	0.62	20	0.50	0.28	0.24
AR8	WSL	0.62	20	0.10	0.28	0.23
AR9	BH2	0.11	20	0.50	0.18	0.09
AR10	BH2	0.11	20	0.10	0.17	0.07

* $CV_{ke} = 0.05$, $\sigma_{EHT} = 0.08\mu$, $CV_{ke} = 0.36*w$

Table 1. Current OHD Method (Ascribed Rate Method)*

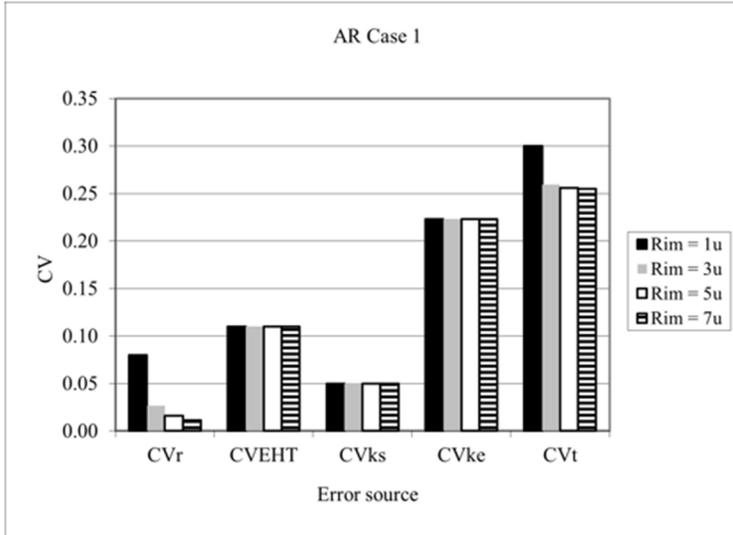


Figure 4. Error term contributions for the ARM for Coso West Sugarloaf (WSL) obsidian at 20°C. Rim values < 4μ fall within Region I. Note the accuracy is worse in Region I due to rim measurement error (CV_r), and improves with increasing rim value; also note the large error contribution from intra-source variations in intrinsic water (CV_{ke}).

approximately 4μ the contribution is negligible. Figure 4 shows the overwhelming importance of controlling for intra-source variations in water content in any effort to improve OHD age accuracy, which is the goal of the Calibrated Rate Method.

The Calibrated Rate Method (CRM)

For the CRM the age uncertainty is computed by equation (12) above. Table 2

Case	Source	Total water, wt%	EHT, °C	σ _{EHT} , °C	CV _r , Region I, r = 1μ	CV _r , Region II, r = 7μ
CR1	WSL	0.62	20	1.00	0.20	0.12
CR2	WSL	0.62	12	1.00	0.20	0.12
CR3	BH2	0.11	20	1.00	0.20	0.12
CR4	BH2	0.11	12	1.00	0.20	0.12
CR5	SLM	1.00	20	1.00	0.20	0.12
CR6	SLM	1.00	12	1.00	0.20	0.12
CR7	WSL	0.62	20	0.50	0.17	0.06
CR8	WSL	0.62	20	0.10	0.16	0.05
CR9	BH2	0.11	20	0.50	0.17	0.07
CR10	BH2	0.11	20	0.10	0.16	0.04

Table 2. Improved Method (Calibrated Rate Method)

summarizes results for the same ten cases, and shows that the accuracy is again independent of EHT, and is now also independent of water content. The calibration process significantly reduces the errors in Region II which were caused in the ARM by unmeasured intrinsic water variation for fast obsidians like WSL; the reduction in uncertainty is from approximately 22% to 12%. There is very little improvement in the BH2 case (13% to 12%), since the intra-source variation is much lower with a dry, slow-hydrating obsidian and EHT uncertainty now becomes the dominant error source for Region II. Rim measurement errors again dominate Region I.

Figure 5 shows the contributions of the error sources for σ_{EHT} = 1.0°C. The results were computed for WSL obsidian, but are independent of EHT and of hydration rate, so they apply equally well to other obsidians and temperatures. Here EHT accuracy is the dominant term in Region II, and roughly co-equal with rim measurement accuracy in Region I.

Figures 6 and 7 summarize the data of Tables 1 and 2 by showing the improvement achieved by the CRM. Three obsidian sources are shown: a dry, slow obsidian, Bodie Hills Group 2; a moderately fast obsidian, Coso West Sugarloaf; and a fast, high-water content obsidian, Coso Sugarloaf Mountain. In all cases the improvement is greater in Region II than in Region I because of the error

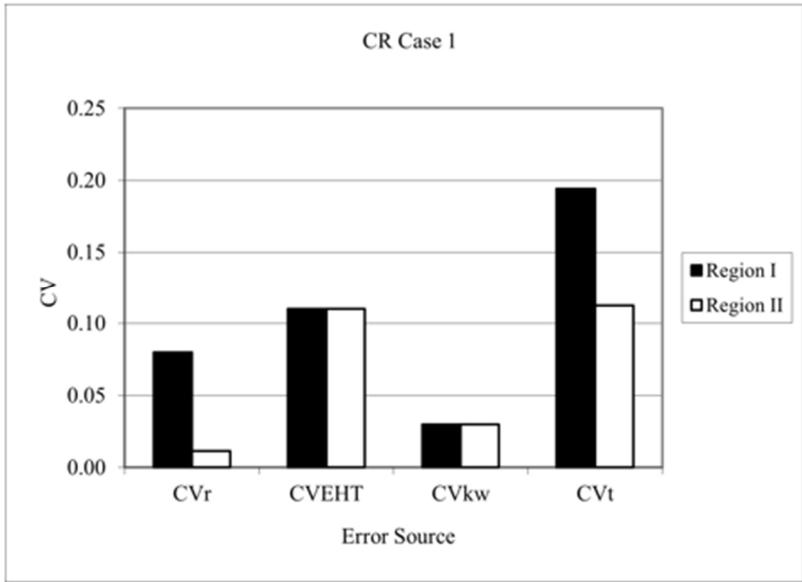


Figure 5. Error term contributions for the CRM for Coso West Sugarloaf (WSL) obsidian at 20°C, showing the improvement due to the method. The current uncertainty in EHT ($\sigma_{EHT} = 1.0^\circ\text{C}$) is assumed. The calibration process has greatly reduced the effects of intra-source water variation; accuracy in Region I is again limited by rim measurement (CV_r), and in Region II by EHT (CV_{EHT}).

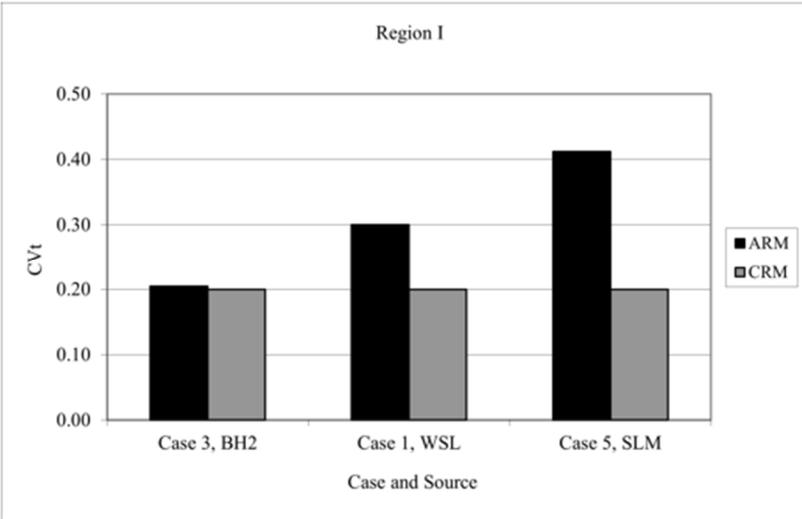


Figure 6. Comparison of age CV for the ARM and CRM in Region I for three typical obsidians, showing the improvement due to the CRM. Bodie Hills Group 2 (BH2) is a dry obsidian which hydrates slowly, Coso West Sugarloaf (WSL) is a moderately wet obsidian, and Coso Sugarloaf Mountain (SLM) is a wet, fast-hydrating obsidian.

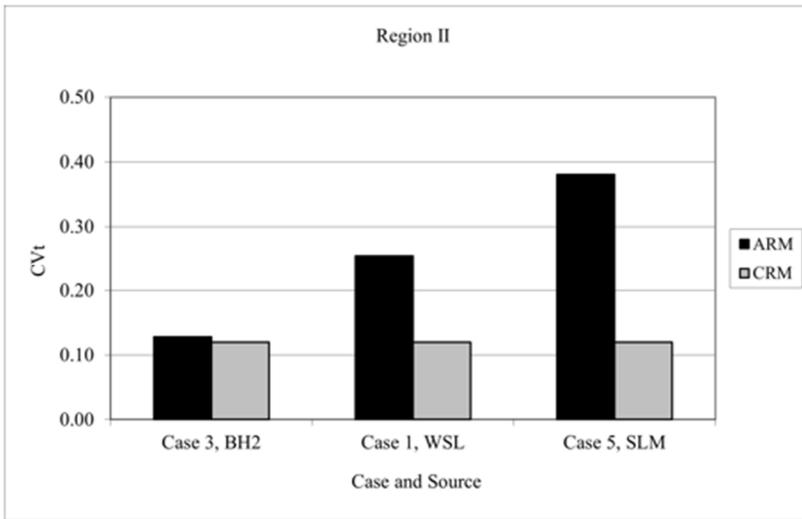


Figure 7. Comparison of age CV for the ARM and CRM in Region II, showing the improvement due to the CRM. Bodie Hills Group 2 (BH2) is a dry obsidian which hydrates slowly, Coso West Sugarloaf (WSL) is a moderately wet obsidian, and Coso Sugarloaf Mountain (SLM) is a wet, fast-hydrating obsidian.

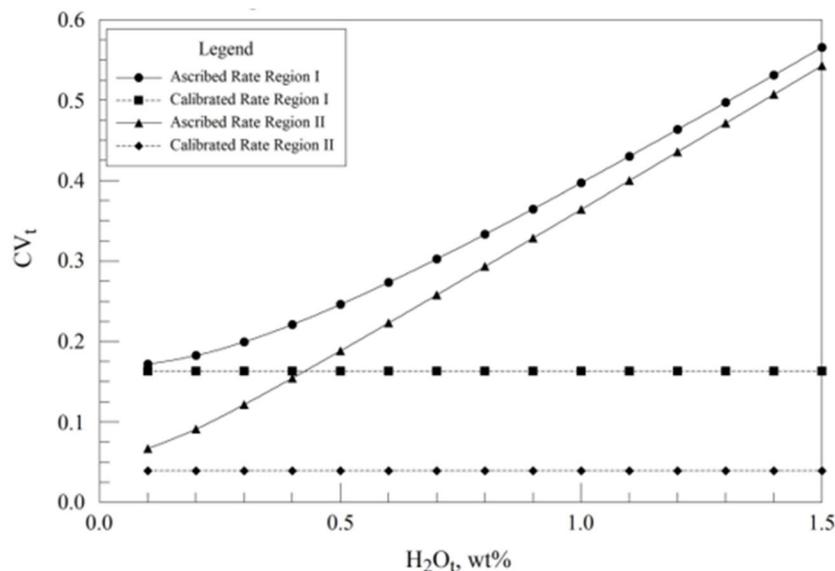


Figure 8. Age CV for ARM and CRM, as a function of total water content. Note that use of the CRM leads to improved accuracy, but the accuracy in Region I is always worse than in Region II.

contribution of hydration rim measurement. There is little improvement for the dry obsidian in either region, because the intra-source variation in water content is small to begin with, but the improvement increases with increasing water content for both regions.

Figure 8 summarizes the variation of age accuracy (CV_t) as a function of total water content for both methods and both regions. It shows graphically that the age accuracy depends on total water content for the ARM in both regions, but not for the CRM, where the Region II accuracy is independent of water content and hence is independent of rate. It also shows that accuracy is worse in Region I than in Region II in both methods.

Alternative Measurement Techniques

The discussion thus far has been based on measurement of water penetration depth by optical microscopy and EHT computed from meteorological data or on-site sensors. We now address possible alternatives.

The quantity of water absorbed can be measured by either of two fundamental methods: depth of penetration by the water, or measurement of water mass gained. Penetration depth can be measured by optical microscopy (the standard in American archaeology today) or by SIMS; water mass gained can be measured by IR spectroscopy or

by mass loss on heating. In either case, the hydration process is one of diffusion, so equation (2) holds. Equation (11) holds as well, so the critical parameter in determining the extent of Region I is $CV_x = \sigma_x/x$, where x is either water mass or penetration depth. For optical microscopy, with current laboratory accuracy, $\sigma_r \approx 0.08\mu$ and the point where $r = 4\mu$ corresponds to $CV_r = 0.02$. Thus, for any alternative technique to be competitive, its CV_x should be less than 0.02 as well, for the same archaeological cases. Ideally Region I should be made as small as possible, because within that region improvements in EHT or calibration uncertainty tend to be dominated by the measurement error.

As pointed out above, current practice in computing EHT based on meteorological records or on-site sensors yields an accuracy of approximately 1°C (one- σ) (Rogers 2007, 2008b), and it is unlikely that significant improvements are possible with this method. For fast obsidians analyzed by the ARM, EHT has much smaller effects than intra-source water variations, so improving σ_{EHT} will yield little improvement; however, reducing σ_{EHT} will pay off for slow obsidians analyzed by the ARM. It would also improve accuracy in the CRM, especially in Region II. Figure 9 shows the error terms which result if σ_{EHT} could be

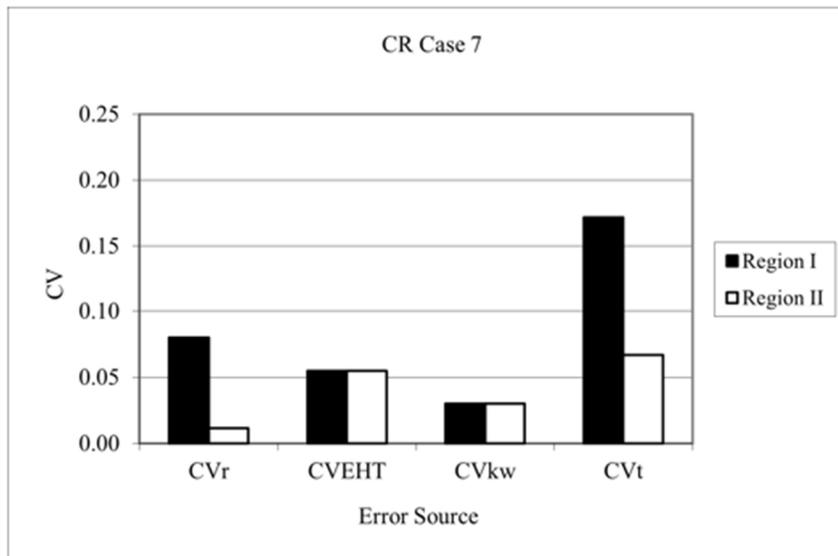


Figure 9. Error term contributions for the CRM for both Coso West Sugarloaf (WSL) and Bodie Hills Group 2 (BH2) obsidian at 20°C, with the uncertainty in EHT reduced to $\sigma_{\text{EHT}} = 0.5^\circ\text{C}$. In Region II the error sources are well balanced, with a total $\text{CV}_t \approx 7\%$. In Region I the accuracy is limited by rim measurement (CV_r).

reduced to 0.5°C . Here the overall error is reduced to approximately 6 – 7% for Region II. Reducing σ_{EHT} to less than 0.5° does not lead to further improvement because of the calibration uncertainty of $\text{CV}_{\text{kw}} = 0.03$.

The ideal solution to the EHT problem would be the identification of some physical or chemical property of the obsidian specimen whose measurement would give the effects of temperature history alone, in other words, an intrinsic method for determining EHT. Stevenson et al. (2020) have proposed that areal density (profile area/thickness) of the SIMS hydrogen profile may reflect “molecular packing” within the hydration layer and thus the thermal history of an artifact. Water speciation in glass is also a possible method, since it is temperature sensitive, and, once it reaches equilibrium, is not time-sensitive (Ihinger et al. 1991; Zhang 2008). This would necessitate measuring speciation of the water in the hydrated layer of a specimen separately from the intrinsic water. However, the feasibility and accuracy achievable have not been analyzed. Figure 9 suggests that any such a method would need to yield an EHT uncertainty on the order of $< 0.5^\circ\text{C}$ to be useful.

Discussion and Conclusions

Improving the accuracy of OHD is a balancing act. For current methods the major limit to accuracy in Region I is measurement uncertainty, and in Region II it is EHT uncertainty and intra-source water variation. Further, the uncertainty introduced by the latter varies with the water concentration itself, so that a high-water content (fast) obsidian such as Coso is more severely affected than a low-water content (slow) obsidian such as Bodie Hills. The slower obsidian will always yield a more accurate age with the ARM, other parameters being equal. The CRM gives greatly improved accuracy in Region II for fast obsidians, but for slow obsidians the improvement is less significant. In Region I the improvement is also less significant because accuracy is dominated by rim measurement accuracy. Overall, the major limit to accuracy in Region I is measurement uncertainty, and in Region II it is EHT uncertainty.

An archaeologist analyzing obsidian data will always prefer to be working in Region II, due to its greater accuracy than Region I. This implies that the hydration rate, controlled by EHT and water content, must be such that the archaeological specimens have hydration rims $> 4\mu$ in thickness, i.e. $\text{CV}_r < 0.02$. Replacing optical microscopy with another measurement

technique such as FTIR or SIMS does not avoid the Region I/Region II dichotomy, and to be useful, the technique should again give an accuracy $CV_x < 0.02$ for the same archaeological cases.

Measurement of age by OHD causes damage to the specimen, and hence is regarded as “consumptive” testing by the museums and land-management agencies with cognizance over the specimens. In the case of optical microscopy the damage is in cutting a notch in the margin or removing a pressure flake for reading. If SIMS is employed the damage is a micron-size pit in the surface, but in either case, it is regarded as undesirable. Measuring water content by transmission IR spectroscopy currently requires preparation of a transparent billet from the specimen, which typically destroys the specimen. For the CRM to be useful in a practical sense, a method of measuring intrinsic water content must be devised which is inexpensive and is not destructive to the specimen.

We conclude that the CRM provides significant improvement in accuracy over the ARM, and the improvement increases with obsidian water content. We further conclude, based on the data in Figure 9, that OHD age accuracies on the order of 5% are feasible in the future with the CRM, but only if improvements in EHT accuracy are achieved.

References Cited

Ambrose, W.R., and C.M. Stevenson (2004) Obsidian Density, Connate Water, and Hydration Dating. *Mediterranean Archaeology and Archaeometry* 4(2): 5-16.

Behrens, H., and M. Nowak (1997) The Mechanisms of Water Diffusion in Polymerized Silica Melts, *Contributions to Mineralogy and Petrology* 126: 377-385.

Campbell, G. (2021) Estimating Relative Humidity in Soil – How to Stop Doing it

Wrong. Environmental Biophysics Corp. www.environmentalbiophysics.org, accessed December 3, 2021.

Crank, J. (1975) *The Mathematics of Diffusion*. Oxford University Press, Oxford.

Cvetanovic, R.J., D.L. Singleton, and G. Paraskevopoulos (1979) Evaluations of the Mean Values and Standard Errors of Rate Constants and their Temperature Coefficients. *Journal of Physical Chemistry* 83(1): 50-60.

Delaney, J.R., and J.L. Karsten (1981) Ion Microprobe Studies of Water in Silicate Melts: Concentration-Dependent Water Diffusion in Silicon. *Earth and Planetary Science Letters* 52: 191-202.

Doremus, R.H. (1994) *Glass Science*, 2nd ed. Wiley Interscience, New York.

Doremus, R.H. (2002) *Diffusion of Reactive Molecules in Solids and Melts*. Wiley Interscience, New York.

Ebert, W.L., R.F. Hoburg, and J.K. Bates (1991) The Sorption of Water on Obsidian and a Nuclear Waste Glass. *Physics and Chemistry of Glasses* 34(4): 133-137.

Friedman, I., and W. Long (1976) Hydration Rate of Obsidian. *Science* 191(1):347-352.

Friedman, I., F.W. Trembour, F.I. Smith, and G.I. Smith (1994) Is Obsidian Hydration Dating Affected by Relative Humidity? *Quaternary Research* 41(2): 185-190.

Garofalini, S.H., J. Lenz, and M. Homann (2020) Molecular Mechanism of Silica Glass upon Exposure to Moisture. *Journal of the American Ceramic Society* 103: 2421-2431.

- Hughes, R.E. (1988) The Coso Volcanic Field Reexamined: Implications for Obsidian Sourcing and Dating Research. *Geoarchaeology* 3: 253-265.
- Ihinger, P.D., Y. Zhang, and E.M. Stolper (1999) The Speciation of Dissolved Water in Rhyolitic Melt, *Geochimica et Cosmochimica Acta* 63(21): 3567-3578.
- Karsten, J.R., and J.L. Delaney (1981) Ion Microprobe Studies of Water in Silicate Melts: Concentration-Dependent Water Diffusion in Obsidian. *Earth and Planetary Science Letters* 52: 191-202.
- Karsten, J.L., J.R. Holloway, and J.L. Delaney (1982) Ion Microprobe Studies of Water in Silicate Melts: Temperature-Dependent Water Diffusion in Obsidian. *Earth and Planetary Science Letters* 59: 420-428.
- Kuroda, M., S. Tachibana, N. Sakamoto, S. Okumura, M. Nakamura, and N. Yuimoto (2018) Water Diffusion in Silica Glass through Pathways formed by Hydroxyls. *American Mineralogist* 103: 412-417.
- Kuroda, M., S. Tachibana, N. Sakamoto, and H. Yuimoto (2019) Fast Diffusion Path for Water in Silica Glass. *American Mineralogist* 104: 385-390.
- Kuroda, M., and S. Tachibana (2019) Effect of Dynamical Property of Melt on Water Diffusion in Rhyolite Melt. *ACS Earth and Space Chemistry* 3: 2058-2062.
- Lapham, K.E., J.R. Holloway, and J.R. Delaney (1984) Diffusion of H₂O and D₂O in Obsidian at Elevated Temperatures and Pressures. *Journal of Non-Crystalline Solids* 67: 179-191.
- Levine, I.N. (2002) *Physical Chemistry*, 5th ed. McGraw-Hill, New York
- Mazer, J.J., C.M. Stevenson, W.L. Ebert, and J.K. Bates (1991) The Experimental Hydration of Obsidian as a Function of Relative Humidity and Temperature. *American Antiquity* 56(3): 504-513.
- Newman, S., Stolper, E.M., Epstein, S. (1986) Measurement of Water in Rhyolitic Glasses: Calibration of an Infrared Spectroscopic Technique. *American Mineralogist* 71: 1527-1541.
- Onken, J. (1991) *The Effect of Microenvironmental Temperature Variation on the Hydration of Late Holocene Mono Craters Volcanic Ashes from East-Central California*. Unpublished MS Thesis, University of Arizona.
- Riciputi, L.R., J.M. Elam, L.M. Anovitz, and D.R. Cole (2002) Obsidian Diffusion Dating by Secondary Ion Mass Spectrometry: A Test Using Results from Mound 65, Chalco, Mexico. *Journal of Archaeological Science* 29: 1055-1075.
- Rogers, A.K. (2007) Effective Hydration Temperature of Obsidian: A Diffusion-Theory Analysis of Time-Dependent Hydration Rates. *Journal of Archaeological Science* 34: 656-665.
- Rogers, A.K. (2008a) Obsidian Hydration Dating: Accuracy and Resolution Limitations Imposed by Intrinsic Water Variability. *Journal of Archaeological Science* 35: 2009-2016.
- Rogers, A.K. (2008b) Field Data Validation of an Algorithm for Computing Effective Hydration Temperature of Obsidian.

- Journal of Archaeological Science* 35: 441-447.
- Rogers, A.K. (2010) Accuracy of Obsidian Hydration Dating Based on Radiocarbon Association and Optical Microscopy. *Journal of Archaeological Science* 37: 3239-3246.
- Rogers, A.K. (2011) Do Flow-Specific Hydration Rates Improve Chronological Analyses? A Case Study for Coso Obsidian. *International Association for Obsidian Studies Bulletin* 45: 14-25.
- Rogers, A.K. (2012) Temperature Correction for Obsidian Hydration Dating, In *Obsidian and Ancient Manufactured Glasses*, edited by I. Liritzis and C.M. Stevenson, pp. 46-55. University of New Mexico Press, Albuquerque.
- Rogers, A.K. (2015) An Equation for Estimating Hydration Rate of Obsidian from Intrinsic Water Concentration. *International Association for Obsidian Studies Bulletin* 53: 5-13.
- Rogers, A.K., and C.M. Stevenson (2017) A New and Simple Laboratory Method for Estimating Hydration Rate of Obsidian. *Proceedings of the Society for California Archaeology* 31: 165-171.
- Rogers, A.K., and C.M. Stevenson (2020) Archaeological Age Computation Based on Obsidian Hydration: A Summary of the Current State of the Art. *International Association for Obsidian Studies Bulletin* 63: 2-44.
- Rogers, A.K. and R.M. Yohe II (2021) An Equation to Compute Accuracy of Obsidian Hydration Dating Ages. *International Association for Obsidian Studies Bulletin* 67: 5-14.
- Shelby, J.E. (2005) *Introduction to Glass Science and Technology*, 2nd ed. Royal Society of Chemistry, Cambridge.
- Steffen, A. (2005) The Dome Fire Obsidian Study: Investigating the Interaction of Heat, Hydration, and Glass Geochemistry. Unpublished PhD dissertation, University of New Mexico.
- Stevenson, C.M., and B.E. Scheetz (1989) Induced Hydration Rate Development of Obsidians from the Coso Volcanic Field: A Comparison of Experimental Procedures. In *Current Directions in California Obsidian Studies*, edited by R.E. Hughes, pp. 23-30. Contributions of the University of California Archaeological Research Facility No. 48., Berkeley.
- Stevenson, C.M., E. Knauss, J.J. Mazer, J.K. Bates (1993) The Homogeneity of Water Content in Obsidian from the Coso Volcanic Field: Implications for Obsidian Hydration Dating. *Geoarchaeology* 8(5): 371-384.
- Stevenson, C.M., J.J. Mazer, and B.E. Scheetz (1998) Laboratory Obsidian Hydration Rates: Theory, Method, and Application. In *Archaeological Obsidian Studies: Method and Theory. Advances in Archaeological and Museum Science*, Vol. 3, edited by M.S. Shackley, pp.181-204. Plenum Press. New York.
- Stevenson, C.M., M. Gottesman, and M. Macko (2000) Redefining the Working Assumptions for Obsidian Hydration Dating. *Journal of California and Great Basin Anthropology* 22(2): 223-236.
- Stevenson, C.M., and S.W. Novak (2011) Obsidian Hydration Dating by Infrared Spectroscopy: Method and Calibration. *Journal of Archaeological Science* 38: 1716-1726.

- Stevenson, C.M., A.K. Rogers, and M.D. Glascock (2019) Variability in Structural Water Content and its Importance in the Hydration Dating of Cultural Artifacts. *Journal of Archaeological Science: Reports* 23: 231-242.
- Stevenson, C.M., A.K. Rogers, S.W. Novak, W. Ambrose, and T.N. Ladefoged (2021) A Molecular Model for Obsidian Hydration Dating. *Journal of Archaeological Science: Reports* 36: 102824.
- Stevenson, C.M., A.K. Rogers, and G. Haverstock (n.d.) Hydration Rates for the Bodie Hills Obsidian Regional Source, Eastern California, Based on Infrared Spectroscopy and Optical Measurement. Part II. In *Sourcing Obsidian*, edited by F.-X. LeBourdonnec, M. S. Shackley & M. Orange. Forthcoming.
- Stevenson, C.M., A.K. Rogers, and G. Haverstock (2021) A Brief Note on Hydration Rates for the Bodie Hills Obsidian Regional Source, Eastern California, Based on Infrared Spectroscopy and Optical Measurement. *International Association for Obsidian Studies Bulletin* 67: 30-35.
- Taylor, J.R. (1982) *An Introduction to Error Analysis*. University Science Books, Mill Valley, California.
- Zhang, Y. (2008) *Geochemical Kinetics*. Princeton University Press, Princeton, New Jersey.
- Zhang, Y., E.M. Stolper, and G.J. Wasserburg (1991) Diffusion of Water in Rhyolitic Glasses. *Geochimica et Cosmochimica Acta* 55: 441-456.
- Zhang, Y., R. Belcher, L. Wang, and S. Newman (1997) New Calibration of Infrared Measurement of Dissolved Water in Rhyolitic Glasses. *Geochimica et Cosmochimica Acta* 62: 3089-3100.
- Zhang, Y, and H. Behrens (2000) H₂O Diffusion in Rhyolitic Melts and Glasses. *Chemical Geology* 169: 243-262.

WHAT ARE WE MEASURING WITH OBSIDIAN HYDRATION DATING?

Alexander K. Rogers^a and Robert M. Yohe II^b

^a Maturango Museum, Ridgecrest, California, USA

^b California State University, Bakersfield, California, USA

Obsidian hydration dating (OHD) is widely used in Great Basin archaeology, since sites there often provide multiple obsidian samples and few other chronometric clues. But from a “meta” perspective, what we are measuring with OHD and how do we interpret it? We compute an OHD age on a specimen, and now what?

We all know that other chronometric methods have problems of interpretation, starting with the well-known issue with old wood in radiocarbon dating. Dendrochronological ages have their problems too – they can be precise but are notoriously difficult to interpret culturally, since large wooden beams were often cut and then stored for later use (Keet Seel is the classic example), or were recycled when structures were dismantled (often seen in the Mimbres area).

But with obsidian, are we dating what we think we are? When we say we are dating an artifact, what we are actually dating is a *worked surface on the artifact*, which may or may not reflect its use date. Further, OHD dates can be measured on any piece of obsidian, but unless the date is on a culturally modified surface, it may be meaningless. Anyone who has done OHD analysis has seen cases where the age from the dorsal surface of a flake is significantly older than the age from the ventral surface of the same flake, or has found different ages on a margin of an artifact and on a break. The cleanest ages, in terms of interpretation, are probably those on working margins of tools – projectile points, flake tools, core tools (aka “scrapers”), or burins. In these cases, the age probably represents manufacture or rework of the tool.

Bifaces, on the other hand, are not as clean. Large nodules of obsidian were not easy to transport and tended to be wasteful, so obsidian for trade or exchange was usually fashioned into bifaces. These were a convenient and efficient form for transporting obsidian. Since bifaces were often curated for future use, the age of the biface reflects the age of manufacture but does not necessarily indicate the age of use.

Debitage is a separate issue and a big one. We find lots of it, and land managers generally don’t care if it gets cut, so we have lots of ages ondebitage. But what do they represent? The first thing to remember is thatdebitage samples are biased toward specimens which are physically large, simply because it is very difficult to make OH readings on small flakes. It is also difficult to do geochemical sourcing on small flakes. This creates an unrecognized problem: since big pieces ofdebitage were often curated or scavenged for reuse by subsequent occupants of a site, the OH reading may reflect the time thedebitage was created, but not when it was subsequently used. The tiny flakes, on the other hand, reflect the latest human actions but are nearly impossible to read (I say “nearly” because even pressure flakes can sometimes be read, but we don’t often do it.) Thus, inferring ages of site use based ondebitage ages may be inadvertently biased toward older ages. However, a bias in the other direction is also possible if thedebitage is the result of subsequent stone transport and tool rework.

Two thought experiments can illustrate the problem. First, Rose Spring (CA-INY-372) is a major site in eastern California. It is the type site for the Rose Spring projectile

point, and provides clearly-defined ages for the transition from atlatl and dart to archery in the western Great Basin (Yohe 1992, 1998). A subsequent OHD analysis computed OHD ages of projectile points and major debitage (Rogers and Yohe 2014). The OHD age of the Rose Spring projectile points (N = 36) was 1276 ± 570 cyb2k, or Haiwee Period, as they should be; however, the age of the debitage (N = 28) was 3216 ± 1306 cyb2k, or Newberry period. The difference was statistically significant at the 95% confidence level, which suggests the obsidian was being scavenged on-site and re-used. Thus, if pot-hunters had stolen all the Rose Spring points before the excavation (as they did other artifacts), the debitage data would have misclassified the age of the site.

Second, in the late 1970s the late Emma Lou Davis conducted a major excavation on the northwest margin of the playa of Pleistocene Lake China, about 40 miles south of Rose Spring (Davis 1978). Although the Early Man claims have been discredited, both artifacts and faunal remains clearly show the site was Paleoindian in age. A re-examination of the site by Mark Basgall around 2004-2005, resulted in collection of obsidian debitage from well-surveyed surface contexts (Basgall 2006). An analysis of the OHD ages of the debitage (Rogers 2018) showed the peak use in terms of dates/period was Early Archaic (Pinto period), not Paleoindian; further, peak use in terms of intensity (dates/millennium) was late Prehistoric (Marana period). So, in this case, surface obsidian debitage ages reflect subsequent use of the site, including transport and rework of new obsidian. The earlier use of the site, which had been revealed by Davis's excavation, was not indicated.

So, our conclusion is that we need to be careful about how we interpret OHD ages, and what we infer from them. If considered carefully, they shed light on interesting cultural questions. For example, at Rose Spring the ages show definitely that the

inhabitants of the site were recycling obsidian, probably to avoid a long trek to the quarry. But if not so considered, they can be seriously misleading, as in the case of the Emma Lou Davis site.

All chronometric measurements must be considered in context. For radiocarbon, this means accounting for such issues as old wood, inorganic carbon, and marine reservoir; for dendrochronology it means cutting vs. non-cutting dates and storage and reuse of timbers; for dating by projectile point typology it means classification dilemmas and the longevity of each type in a particular area; for OHD the critical context is the manufacturing cycle and use life of the artifacts themselves. No chronometric measurement can be treated as a black box.

References Cited

- Basgall, M.E. (2006) *Prehistoric People in an Evolving Landscape: A Sample Survey of the China Lake Basin and its Implications for Paleoindian Land-Use*. Archaeological Research Center, Sacramento State University Technical Report 06-116.
- Davis, E.L. (1978) *The Ancient Californians: Rancholabrean Hunters of the Mojave Lakes Country*. Natural History Museum of Los Angeles, California.
- Rogers, A.K. (2018) *Obsidian Hydration Dating Analysis for Nineteen Sites on the North-West Margin of the China Lake Playa, NAWA China Lake North Range Complex (Emma Lou Davis Sites)*. Maturango Museum MS218. On file, Maturango Museum.

Rogers, A.K., and R.M. Yohe, II (2014) Obsidian Re-use at the Rose Spring Site (CA-INY-372), Eastern California: Evidence from Obsidian Hydration Studies. *Journal of California and Great Basin Anthropology* 34(2): 273-286.

Yohe, R.M., II (1992) *A Reevaluation of Western Great Basin Cultural Chronology and Evidence for the Timing of the Introduction of the Bow and Arrow to Eastern California based on new Excavations at the Rose Spring Site (CA-INY-372)*. Unpublished PhD Dissertation, Department of Anthropology, University of California, Riverside.

Yohe, R.M., II (1998) The Introduction of the Bow and Arrow and Lithic Resource Use at Rose Spring (CA-INY-372). *Journal of California and Great Basin Anthropology* 20(1): 26-52.

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