

# UC Berkeley

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# IAOS

International Association for Obsidian Studies

## Bulletin

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### *International Association for Obsidian Studies*

|                        |                   |
|------------------------|-------------------|
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### NEWS AND INFORMATION

#### **Award Nominations**

Have you seen a student presentation recently that merits recognition? Consider nominating it for an IAOS student paper award. Contact Ana Steffen for more information at [asteffen@vallescaldera.gov](mailto:asteffen@vallescaldera.gov)

#### **Michael D. Glascock Wins SAA Fryxell Award**

Congratulations to Dr. Michael D. Glascock, director of the Archaeometry Lab at the Research Reactor Center, University of Missouri (MURR). The Fryxell Award recognizes a scientist who contributes to interdisciplinary research in archaeology. The award was presented at the 2009 annual meeting of the Society for American Archaeology in Atlanta, Georgia.

#### **38<sup>th</sup> International Symposium on Archaeometry**

The 38th International Symposium on Archaeometry will be held at the University of South Florida, Tampa, May 10-14, 2010. The aim of ISA is to promote the integration of scientific techniques with archaeology and cultural heritage, with participants coming from a variety of backgrounds and subdisciplines. The website (<http://isa2010.cas.usf.edu/>) includes preliminary information, including title/abstract submission and registration deadlines. Additional information on accommodations, payment methods, social activities, publication, sponsors, etc. will be added in the near future.

**Deadline for submission of abstracts:** December 1, 2009

Contact: Robert H. Tykot, Chairman of the Local Organizing Committee, [rtykot@cas.usf.edu](mailto:rtykot@cas.usf.edu)

## NOTES FROM THE PRESIDENT

Greetings! At this year's IAOS Annual Meeting in Atlanta we were able to wrap-up two important pieces of business. The first was to announce the results of our recent election: congratulations and welcome to our new President-Elect, Tristan Carter. Tristan will take over the lead of IAOS next spring at our Annual Meeting in St. Louis. Now also provides an opportunity to thank out-going Past-President, Phil LeTourneau, for his hard work and good cheer.

The second piece of business was the vote and unanimous acceptance of the revised IAOS by-laws. The full text of the by-laws will be available for review on the IAOS website.

We are also pleased to announce two student awards for excellent research presentations at the SAA Meetings:

1. Guadalupe "Pete" Cadena, Department of Anthropology, University of Texas at San Antonio for his poster entitled "Obsidian Tools and Mobility Patterns in a Region between the Great Basin and Columbia Plateau."

2. Adam Joseph Nazaroff, Department of Anthropology, Stanford University for his paper entitled "Examining the Validity of PXRf for Obsidian Sourcing in the Maya Lowlands" (with Lee Drake).

Congratulations to Pete Cadena and Adam Nazaroff. If you are aware of other high-quality student research presentations worthy of recognition by the IAOS, please let me know. Awardees receive a free membership to the society and a letter of recognition from the IAOS President.

Finally, keep an eye on the IAOS website for new postings. Craig Skinner, our webmaster, is pursuing several enhancements to the site and his associated Northwest Research Obsidian Studies Laboratory website (where you can find new maps of state-wide obsidian sources).

Best wishes for the summer season!

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### Laboratory of Archaeometry, University of the Aegean, Places SIMS-SS Tools Online

SIMS-SS (Secondary Ion Mass Spectrometry - Saturation Surface) is a *pioneering dating method* for ancient obsidian artifacts based on the modeling of the water diffusion profile, using the *Saturation Surface Approach*.

The method makes use of the *SIMS* analytical technique to measure the profile of water concentration, which has been defused perpendicular to the surface, versus depth. The profile is properly elaborated for the deduction of the age.

This analytical presentation of the method, an on-line tool for age calculation, and a program download is available: [www.rhodes.aegean.gr/tms/sims-ss](http://www.rhodes.aegean.gr/tms/sims-ss)

Contributed by Ioannis Liritzis, Professor of Archaeometry, University of the Aegean

## NEWS AND NOTES

### University of Washington Acquires Portable XRF Units for Student Research

Contributed by Colby Phillips

The University of Washington's Department of Anthropology has recently acquired two Bruker Tracer III-V portable XRF instruments for undergraduate and graduate student research. The instruments were acquired with a grant obtained through the University of Washington's Student Technology Fee program which was established to supplement the availability of technology to students and provide opportunities for innovative projects that require capital investment. Each year a student-run committee solicits a wide spectrum of student technology proposals, and last year the committee allocated approximately four million dollars to proposals aimed at improving access to technology to further student education and research goals. Graduate students in the Department of Anthropology wrote a grant to acquire two of the Bruker units with the intention that one unit would be made available for students to check out and take into the field or to museum collections, while the second unit would remain on campus for local use.

The two instruments were calibrated this spring for obsidian sourcing using a suite of obsidian reference samples generously loaned by Dr. Michael Glascock at the University of Missouri Research Reactor. Several graduate students in the University of Washington's Department of Anthropology are already using the XRF units for their PhD. research. Colby Phillips is analyzing obsidian debitage excavated from archaeological sites in the Kuril Islands of the Russian Far East for part of his project on using obsidian source provenance data to reconstruct migration and social network patterns in the islands over the last 2,500 years. Amanda Taylor is conducting source provenance analysis of fine-grained volcanic toolstone used by prehistoric people in the San Juan Islands in Washington State. Jack Johnson is measuring potassium and thorium concentrations in sediment samples from Peru that will be used for luminescence dating.

The precision, accuracy, and flexibility of current portable XRF technology provides an array

of options for University of Washington students interested in using XRF analysis for their research, and it is expected that these units will be utilized by students from a variety of departments on campus.

### Northwest Research Obsidian Studies Hydration Lab Reopened April 1, 2009

Contributed by Craig Skinner

Not quite a year after we closed the obsidian hydration laboratory in 2008, we decided to reopen it again and have begun accepting new obsidian hydration analysis projects. Please note that we've begun making the necessary modifications at the lab website (new sample submission and price sheets) but it'll take us just a little while to finish all the changes.

Why the change of heart? Two major reasons:

1. The obsidian analysis services that we provide (XRF and OH analysis) work very well **together** and that it was simply awkward and time-consuming to have to forward obsidian samples after XRF analysis to another laboratory for hydration analysis. To our knowledge, we're the only commercial lab on the planet that can provide both services in one location and it made a lot of sense to once again reunite them here in Corvallis.
2. We arrived at the decision in 2008 to close the hydration lab so that we could devote more time to provide online support for our provenance-related obsidian and fine-grained volcanic (FGV) materials research. For years, we have been planning to produce a variety of maps and documents related to this research and were simply unable to find the time. Since 2008, we've been able to make considerably more headway than anticipated and it was clear that we would soon be in a position to either expand to some new services or to continue with a previous one. We've kept the hydration laboratory busy with various lab research projects and the decision to open it for commercial projects again was an easy one.

Thanks for your patience and your encouragement over the last year for us to restart the hydration lab. We look forward to providing you once again with high-quality and timely information for your archaeological projects.

## OBSIDIAN ARTIFACTS IN LA PAMPA, ARGENTINA, FROM SOURCES IN SOUTHWEST NEUQUÉN

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### Introduction

In a paper recently published in the IOAS Bulletin, Giesso et al., (2008) presented chemical analysis of 16 samples of obsidian from two archaeological sites, Tapera Moreira and El Chenque I, located in the Lihue Calel Provincial Park, province of La Pampa, central Argentina (Fig. 1). These sites were occupied by terrestrial hunter-gatherers during the Late Holocene, between 3,000 and 500 years BP.

The results of their analyses indicate seven chemically distinct types of obsidian. Three types come from known sources, which include 1) Laguna del Maule-Paso Pehuenche in the High Andes along the frontier between Chile and Argentina at latitude 36°S (Fig. 1; Durán et al., 2004); 2) Cerro Huenul along the Colorado river in northern Neuquén province (Durán et al., 2004); and 3) La Bandera, described as being located in central Neuquén, 100 km south of Cerro Huenul. They also identified four other obsidian types from unknown sources they called Unknowns 1 through 4.

Other studies of obsidian sources in central and southern Neuquén have identified two regionally important sources, one at Portada

Covunco area (Fig. 1; Bellelli et al., 2006), and the other in the area of Lolog lake, both at Cerro de las Planicies and along the northern coast of the lake (Pérez and López, 2004; López et al., 2009). These have been the sources of two types of obsidians found in widely distributed archaeological sites, both far to the south in Cholila, Chubut province (Bellelli et al., 2006), and far to the east along the Atlantic coast in Río Negro province (Favier Dubois et al., 2009).

Here we present bulk sample ICP-MS analyses of the most important obsidian types from these two sources, PC1 and CP/LL1, respectively (Table 1 and Fig. 2; López et al., 2009). These data suggest that the obsidian type Unknown 2 found by Giesso et al., (2008) in the Tapera Moreira site located in La Pampa is derived from the Lolog lake source area well to the southwest in Neuquén. The data also suggest that Portada Covunco and La Bandera may be secondary sources of the same obsidian, or alternatively that in this region of central Neuquén there are various sources that have obsidian of very similar chemistry.

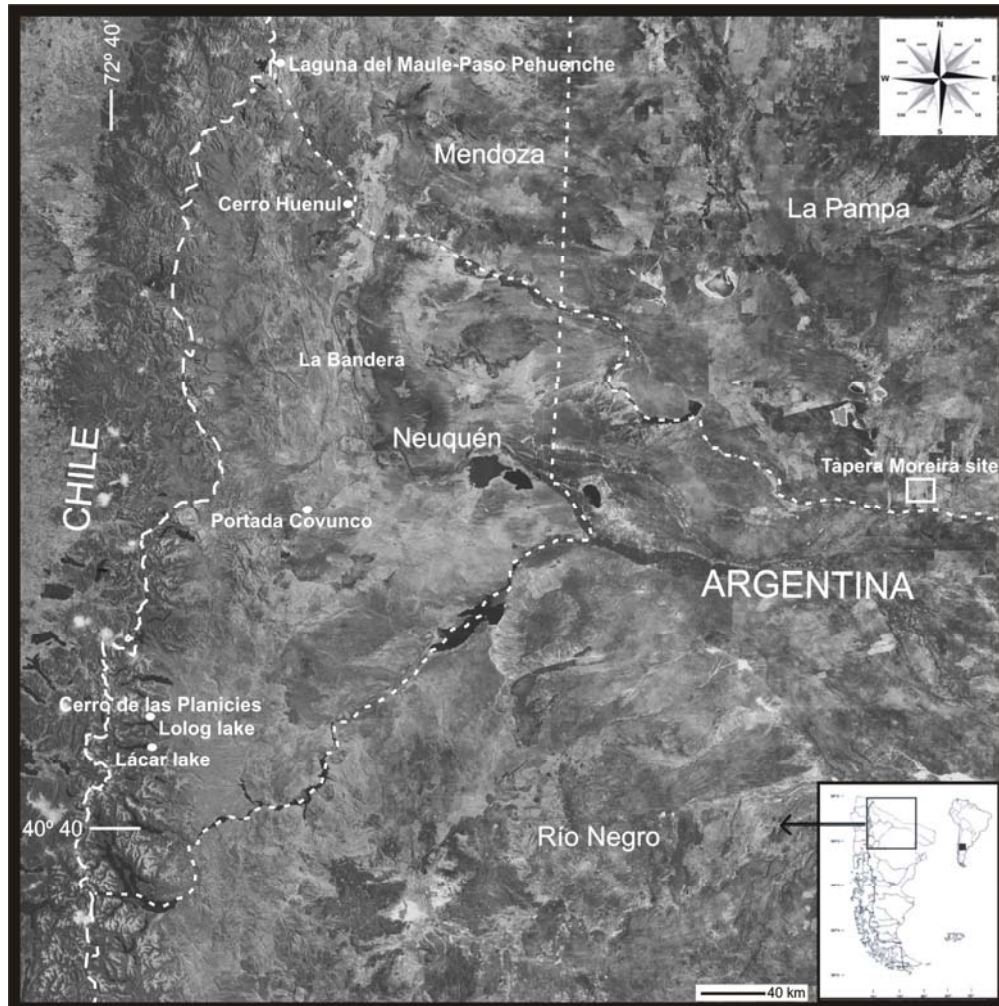


Figure 1. Location map of some of the more regionally important obsidian sources in the provinces of Neuquén and Mendoza, and archaeological site Tapera Moreira, in central Argentina. Dashed lines mark the borders of the provinces, and the frontier between Chile and Argentina.

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sources that have obsidian of very similar chemistry.

### **The Cerro de las Planicies and Lolog lake sources**

Obsidian type Unknown 2 from the Tapera Moreira site in La Pampa is chemically similar to obsidian CP/LL1 from the Cerro de las Planicies and Lolog lake sources located 520 km to the southwest in southern Neuquén province (Fig. 1), with 16 of the 17 elements determined by INAA (Giesso et al., 2008) and

ICP-MS (López et al., 2009), respectively, being within analytical uncertainty (Table 1). For these two data sets, only Zr differs by more than analytical uncertainty. We therefore suggest that Unknown 2 obsidian is derived from the Cerro de las Planicies and Lolog lake sources.

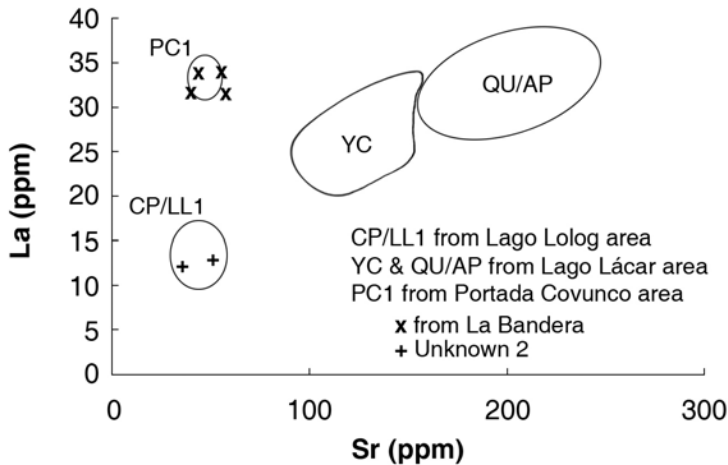


Figure 2. Contents in parts-per-million (ppm) of obsidian from different sources in central and southern Neuquén province (López et al., 2009), compared to values for obsidian from the La Bandera source and obsidian type Unknown 2 found in the Tapera Moreira archaeological site in La Pampa province (Fig. 1).

These sources includes a primary source of large obsidian fragments among the volcanic rocks of Cerro de las Planicies, north of Lolog lake, and secondary sources of small rounded cobbles, typically <5 cm in diameter, along the northern coast of Lolog lake (Fig. 1), principally at Puerto Arturo (López et al., 2009). Of a total of 32 samples analyzed from this source, 30 correspond to the type of obsidian we have called CP/LL1, and 2 correspond to CP/LL2, which has significantly lower concentrations of Sr, Ba and REE.

Previous studies have determined that artifacts fashioned from CP/LL1 obsidian derived from these sources are found in archaeological sites between 20 to 40 km to the south around Lácar and Meliquina lakes,

and that this obsidian has also been transported by terrestrial hunter-gatherers over 560 km to the east, where it is found in sites along the Atlantic coast of Río Negro province (Favier Dubois et al., 2008). The presence of this type of obsidian in Tapera Moreira, located in the region of the southern Dry Pampa, significantly amplifies the spatial distribution for this type of obsidian, and demonstrated the possibility of networks of obsidian interchange between the prehistoric inhabitants of La Pampa and northwest Patagonia.

### The Portada Covunco source

Obsidian derived from the La Bandera source are chemically closely similar to obsidian called PC1 by López et al., (2009), or “Grupo B” by Bellelli et al. (2006) derived from the Portada Covunco source in central Neuquén (Fig. 1; Table 1). Only Mn, Rb and Zr differ by more than analytical uncertainty.

The Portada Covunco source consists of secondary deposits of rounded cobbles of obsidian found in the Covunco arroyo. Obsidian PC1 from the Portada Covunco source area is found locally in the archaeological sites Cuchillo Cura (López et al., 2009) and Alero Tromen IV, and has been transported by hunter-gatherers as far as 430 km to the south where it is found near Cholila, Chubut province (Bellelli et al., 2006). La Bandera source is only poorly located based on the description of Giesso et al., (2008), but if it is actually only 100 km south of Cerro Huenul, it most likely occurs north of Portada Covunco (Fig. 1). Therefore it is unlikely to contain the same obsidian cobbles. Until the location of the La Bandera source is better determined, we suggest that the similarity of the obsidian from the La Bandera source and Portado Covunco may simple reflect the chemical similarity of some of the different obsidian sources in the central Neuquén region.

**Table 1. Composition in parts-per-million of different obsidian types from central Argentina.**

| Obsidian type<br>#No of samples | PC1  |         | LB   |         | CP/LL1 |         | Unknown 2 |         |
|---------------------------------|------|---------|------|---------|--------|---------|-----------|---------|
|                                 | N°=6 | 2 sigma | N°=5 | 2 sigma | N°=19  | 2 sigma | N°=2      | 2 sigma |
| Ti                              | 880  | 58      | -    | -       | 790    | 90      | -         | -       |
| Mn                              | 498  | 18      | 424  | 9       | 971    | 70      | 924       | 7.1     |
| Cs                              | 8.4  | 0.4     | 7.6  | 0.2     | 5.2    | 0.4     | 5.0       | 0.02    |
| Rb                              | 177  | 9.8     | 158  | 3.2     | 145    | 9.8     | 131       | 0       |
| Sr                              | 46   | 2.7     | 49   | 11.1    | 44     | 5.3     | 35        | 8.35    |
| Ba                              | 278  | 16      | 278  | 13.4    | 765    | 72      | 708       | 2.8     |
| Y                               | 18   | 0.5     | -    | -       | 22     | 1.9     | -         | -       |
| Zr                              | 157  | 8.8     | 194  | 9.3     | 96     | 8.3     | 118       | 4.9     |
| Nb                              | 29   | 3.3     | -    | -       | 17     | 1.7     | -         | -       |
| Hf                              | 4.8  | 0.3     | 5.2  | 0.2     | 3.7    | 1.2     | 3.5       | 0.02    |
| Pb                              | 22.4 | 0.9     | -    | -       | 20.3   | 2.2     | -         | -       |
| Th                              | 26.8 | 1.1     | 25.1 | 0.8     | 11.6   | 1.7     | 10.7      | 0.07    |
| U                               | 7.9  | 0.4     | 7.6  | 0.3     | 3.6    | 0.4     | 3.6       | 0.03    |
| La                              | 33.4 | 1.00    | 32.3 | 0.4     | 13.3   | 1.4     | 13        | 0.07    |
| Ce                              | 63.7 | 5.80    | 57.6 | 1.9     | 29.9   | 4.3     | 28.4      | 0.7     |
| Pr                              | 5.85 | 0.43    | -    | -       | 3.27   | 0.21    | -         | -       |
| Nd                              | 18.7 | 0.40    | 19.4 | 0.9     | 11.99  | 1.06    | 11.8      | 0.042   |
| Sm                              | 2.79 | 0.35    | 3.78 | 0.07    | 2.95   | 0.37    | 3.32      | 0.04    |
| Eu                              | 0.46 | 0.04    | 0.37 | 0.01    | 0.53   | 0.11    | 0.48      | 0.03    |
| Gd                              | 3.08 | 0.29    | -    | -       | 3.16   | 0.45    | -         | -       |
| Tb                              | 0.55 | 0.09    | 0.43 | 0.02    | 0.59   | 0.08    | 0.52      | 0.02    |
| Dy                              | 2.95 | 0.12    | -    | -       | 3.3    | 0.42    | -         | -       |
| Ho                              | 0.60 | 0.05    | -    | -       | 0.73   | 0.11    | -         | -       |
| Er                              | 1.78 | 0.08    | -    | -       | 1.93   | 0.25    | -         | -       |
| Tm                              | 0.32 | 0.03    | -    | -       | 0.34   | 0.06    | -         | -       |
| Yb                              | 2.19 | 0.18    | 2.35 | 0.06    | 2.14   | 0.37    | 2.33      | 0.06    |
| Lu                              | 0.36 | 0.06    | 0.4  | 0.04    | 0.35   | 0.04    | 0.39      | 0.02    |



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# AN ESTIMATE OF COSO OBSIDIAN HYDRATION RATE, BASED ON OBSIDIAN-RADIOCARBON PAIRINGS AND THE “WEIGHTED TOTAL LEAST SQUARES” METHOD

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

## Abstract

Many hydration rates have been published for Coso obsidian over the years, most of which, although adequate at the time they were proposed, now suffer from conceptual or analytical shortcomings. This paper reports a hydration rate for the Coso Volcanic Field as a whole based on the physics of obsidian hydration, effective hydration temperature (EHT) correction by time-dependent diffusion theory, regional temperature scaling, and a detailed consideration of the mathematical techniques used to estimate hydration rates from obsidian-radiocarbon pairing data. The resulting form is quadratic,  $t = mr^2$ , where  $m$  equals 43.72 cal years before 2000 (cyb2k)/ $\mu^2$ , or 38.87 radiocarbon years before 1950 (rcybp)/ $\mu^2$ . These equations provide an accuracy of approximately  $\pm 20\%$  of age, 1-sigma, for EHT-corrected rims  $0 < r < 16\mu$ . Accuracies are limited by errors introduced by obsidian-radiocarbon association and rate variations caused by intra-source chemical variability.

## Introduction

Previous estimates of Coso hydration rate (e.g. Basgall 1990, Pearson 1995, Basgall and Hall 2000) represented the state of the art at the time, but the researchers did not have access to newer theoretical developments or numerical techniques. This paper re-examines the problem of developing a hydration rate from obsidian-radiocarbon association data, and differs from previous treatments in four respects. First, it explicitly uses the physics of the hydration process to provide the framework for the analysis, based on the diffusion-reaction hydration model of Doremus (1994, 2000, 2002). Second, it uses a newly-published and more accurate method for correcting for effective hydration temperature (EHT), which includes a correction for burial depth (Rogers 2007a). Third, it determines temperature at sites by means of regional temperature scaling (Rogers 2007b). Finally, it employs a weighted two-variable least squares technique (“total least squares”, per Van Huffel and Vandewalle

1991) which explicitly includes weighting for change of variable (Cvetanovic et al. 1979) and accounts for the effects of measurement uncertainties in both rim thickness and time. Hydration equations are developed relating EHT-corrected rim thickness to radiocarbon age (radiocarbon years before 1950) and physical age (calendar years before 2000). Estimation accuracy is quantified, error sources discussed and limits of validity defined. The resulting rates are based on current conditions, so any adjustments for paleotemperature changes must be taken into account when age computations are made (Rogers 2007c).

## Hydration Theory

Hydration of obsidian has both a physical and a chemical aspect, and is known as a diffusion-reaction process (Doremus 1994, 2000, 2002). All that is known of the physics and chemistry of the process suggests the

relationship between age and rim thickness should be quadratic, i.e. of the form

$$r^2 = mt \quad (1)$$

where  $t$  is age in calendar years,  $r$  is rim thickness in microns, and  $m$  is the hydration rate (e.g. Ebert et al. 1991; Zhang et al. 1991; Doremus 2000, 2002; Stevenson et al. 1989, 1998, 2004). Doremus demonstrated the quadratic form experimentally (Doremus 1994), as did Stevenson et al. (1998, 2000). Furthermore, no other form of functional dependence is currently suggested by theory; Haller argued, based on the physical chemistry of diffusion, that if any dependence other than quadratic is found, "it is more likely the fault of the experiment rather than any inherent feature of the diffusion process" (Haller 1963:217). When obsidian data are expressed in radiocarbon years before the present (rcybp, by convention referenced to 1950), the quadratic form is still the best fit, giving the smallest overall error in age estimation, but with a different rate constant (Rogers 2006a).

The hydration coefficient varies with EHT (see e.g. Hull 2001; Onken 2006; Ridings 1996; Rogers 2007a; Stevenson et al. 1989, 1998, 2004), with relative humidity (Friedman et al. 1994; Mazer et al. 1991; Onken 2006), and with structural water concentration in the obsidian (Ambrose and Stevenson 2004; Friedman et al. 1966; Rogers 2008c; Stevenson et al. 1998, 2000).

The analysis reported here controls for EHT by the time-dependent diffusion technique (Rogers 2007a), which specifically accounts for average annual temperature, annual variation, diurnal variation, and burial depth. The equation for EHT is

$$\text{EHT} = T_a \times (1 - Y \times 3.8 \times 10^{-5}) + 0.0096 \times Y^{0.95} \quad (2)$$

where  $T_a$  is annual average temperature, and the variation factor  $Y$  is defined by

$$Y = V_a^2 + V_d^2 \quad (3a)$$

in which  $V_a$  is annual temperature variation (July mean minus January mean) and  $V_d$  is mean diurnal temperature variation (Rogers 2007a). All temperatures are in degrees C.

The variation parameters  $V_a$  and  $V_d$  represent the temperature variations at the artifact burial depth; if the artifacts were buried, variations at the artifact depth are related to surface conditions by

$$V_a = V_{a0} \exp(-0.44z) \quad (3b)$$

and

$$V_d = V_{d0} \exp(-8.5z) \quad (3c)$$

where  $V_{a0}$  and  $V_{d0}$  represent nominal surface conditions and  $z$  is burial depth in meters (Carslaw and Jaeger 1959:81). This dependence of temperature variation on depth is well attested in physics, geology, and soil science. The numerical parameters determining attenuation with depth were experimentally determined by the author in desert conditions, and the resulting thermal diffusivities agree well with the published values for sand (Carslaw and Jaeger 1959; App. 4).

Once EHT has been computed, the measured rim thickness is multiplied by a rim correction factor (RCF) to adjust the rims to be comparable to conditions at a reference site:

$$\text{RCF} = \exp[-0.06(\text{EHT} - \text{EHT}_r)] \quad (4)$$

where  $\text{EHT}_r$  is effective hydration temperature at the reference site. The EHT-corrected rim value  $r_c$  is then

$$r_c = \text{RCF} \times r \quad (5)$$

The value of  $\text{EHT}_r$  for Coso obsidian is conventionally taken to be that of Lubkin

Creek, or CA-INY-30 (20.4°C, per Rogers 2007a). Since most Coso work uses CA-INY-30 as a reference, correcting the rim to these conditions allows direct comparison of EHT-corrected rim data with other published data.

It has been shown that depth correction for EHT is desirable, even in the presence of site turbation (Rogers 2007d), because the depth correction, on the average, gives a better age estimate.

Since climate has not been stable over the periods of archaeological interest, the effects of resulting temperature changes must be included. West et al (2007) presented a graph of mean temperature fluctuations over the past 18,000 years. Data from this graph are used to model the effects of climate change on obsidian hydration (Rogers 2007c), computed as a weighted average of effective diffusion rates over time (Rogers 2007c).

## Analysis

### *Archaeological and Temperature Data*

The archaeological data set employed consists of 26 pairs of rim readings and associated radiocarbon data from 10 desert sites; all are on Coso obsidian with known excavation depths and corresponding radiocarbon dates. Subsource within Coso is not known, so the values refer to the volcanic field as a whole. Table 1 summarizes the site data and sources.

Temperature parameters were estimated from data for 13 sites in the southwestern Great Basin and northern Mojave Desert, reported by the Western Regional Climate Center, corrected for altitude. All represent 30 years of meteorological data, which is the standard length of time for establishing seasonal norms (Cole 1970). It has been shown that that the annual average temperature in this region decreases by 1.8°C/1000 ft altitude increase, and to be predicted by the equation

$$T_a = 22.25 - 1.8h, \quad 0.94 \leq h \leq 11.8 \quad (6)$$

where  $h$  is altitude in thousands of feet (Rogers 2007b). The accuracy of this model is 0.98°C, 1-sigma.

The annual temperature variation was found to decrease by 1.7°C/1000 ft. altitude increase, and to be predicted by

$$V_a = 1.65 + 0.94T_a \quad (7)$$

with  $T_a$  defined as above. The accuracy of the prediction is 0.27°C, 1-sigma.

The best fit between  $V_d$  and altitude is relatively poor, and, in the absence of other data about a site, the best estimate is 15.8°C for locations in the western Great Basin and deserts. The accuracy of this estimate is 1.67°C, 1-sigma.

These equations are for air temperatures. Obsidian on the surface is exposed to surface temperatures, which can be significantly higher than air temperatures in areas devoid of vegetation (Johnson et al. 2002; Rogers 2007d). However, for surfaces which have intermittent foliage coverage, the air temperatures are, on average, a good approximation to surface temperatures (Rogers 2008c)

### *Linear Best Fit Theory*

For most practical applications, hydration rates are determined by correlation of obsidian hydration rims with radiocarbon data. Since equation 1 is quadratic, the usual process is to compute a linear least-squares best fit between  $x^2$  and  $t$ , with the resulting slope being the rate:

$$t = kr_c^2 \quad (8)$$

where  $k$  is the slope of the line,  $t$  is age, and  $r_c$  is the EHT-corrected hydration rim. Obviously  $k = 1/m$  from equation 1.

Table 1. Radiocarbon-obsidian data base and sources.

| Site       | Sample ID | RC Age | Rim mean in u, uncorrected | Depth, m. | References  |
|------------|-----------|--------|----------------------------|-----------|---|
| INY-30     | 30.1      | 760    | 4.10                       | 0.85      | Basgall and McGuire 1988:116, Table 12; Basgall and McGuire 1988, App. B. |
| INY-30     | 30.2      | 960    | 4.73                       | 0.65      | Basgall and McGuire 1988:116, Table 12; Basgall and McGuire 1988, App. B. |
| INY-30     | 30.3      | 1220   | 4.43                       | 0.55      | Basgall and McGuire 1988:116, Table 12; Basgall and McGuire 1988, App. B. |
| INY-30     | 30.4      | 1600   | 4.43                       | 0.55      | Basgall and McGuire 1988:116, Table 12; Basgall and McGuire 1988, App. B. |
| INY-30     | 30.5      | 1860   | 5.31                       | 0.70      | Basgall and McGuire 1988:116, Table 12; Basgall and McGuire 1988, App. B. |
| INY-30     | 30.6      | 1530   | 5.31                       | 0.70      | Basgall and McGuire 1988:116, Table 12; Basgall and McGuire 1988, App. B. |
| INY-30     | 30.7      | 1840   | 4.50                       | 0.60      | Basgall and McGuire 1988:116, Table 12; Basgall and McGuire 1988, App. B. |
| INY-30     | 30.8      | 1650   | 4.50                       | 0.60      | Basgall and McGuire 1988:116, Table 12; Basgall and McGuire 1988, App. B. |
| INY-372    | 372.1     | 2900   | 8.04                       | 2.55      | Lanning 1963; Jenkins and Warren 1984:57.                                 |
| INY-372    | 372.2     | 3520   | 8.20                       | 2.89      | Lanning 1963; Jenkins and Warren 1984:57.                                 |
| INY-372    | 372.3     | 3580   | 8.16                       | 3.21      | Lanning 1963; Jenkins and Warren 1984:57.                                 |
| INY-372    | 372.4     | 3900   | 8.16                       | 3.74      | Lanning 1963; Jenkins and Warren 1984:57.                                 |
| INY-372    | 372.5     | 3240   | 7.32                       | 2.30      | Yohe 1992:140, Table 5; Yohe 1992 App.                                    |
| INY-372    | 372.6     | 4460   | 8.05                       | 2.65      | Yohe 1992:140, Table 5; Yohe 1992 App.                                    |
| SBR-5250   | 5250.1    | 8410   | 15.19                      | 0.60      | Jenkins 1985, App. D; Haynes 2001:121, Table 1; Jenkins 1987.             |
| SBR-5250   | 5250.1    | 8420   | 18.27                      | 0.25      | Jenkins 1985, App. D; Haynes 2001:121, Table 1; Jenkins 1987.             |
| SBR-4562   | 4562.1    | 9470   | 13.50                      | 0.85      | Jenkins and Warren 1986, App. D, p. 8, Table 3; Haynes 2001:121, Table 1. |
| SBR-4562   | 4562.2    | 9410   | 11.58                      | 0.95      | Jenkins and Warren 1986, App. D, p. 8, Table 3; Haynes 2001:121, Table 1. |
| INY-3806/H | 3806.1    | 1600   | 3.64                       | 0.85      | Delacorte and McGuire 1993:67ff, App. T                                   |
| INY-3806/H | 3806.2    | 1160   | 3.64                       | 0.85      | Delacorte and McGuire 1993:67ff, App. T                                   |
| INY-3812   | 3812.1    | 1600   | 4.71                       | 0.95      | Delacorte and McGuire 1993:67ff, App. T                                   |
| INY-3812   | 3812.2    | 1340   | 5.60                       | 1.15      | Delacorte and McGuire 1993:67ff, App. T                                   |
| INY-4554   | 4554      | 6740   | 10.30                      | 0.90      | FWARG 1994:A17, 233.  |
| INY-1428   | 1428      | 990    | 4.30                       | 0.35      | Gilreath 1995, App. A   |
| INY-328/H  | 328       | 9440   | 11.07                      | 0.66      | Delacorte 1999:39-40,48.  |
| INY-2750   | 2750      | 1330   | 4.03                       | 0.50      | Delacorte 1999:41.  |

Table 2. Analysis data, arranged in order of increasing age.

| Site   | Site Alt, kft amsl | RC Age, RCYB1950 | RC Age SD | Cal Age, Yrs B1950 | Phys Age Yrs B2000 | Depth, m. | N  | Rim mean in u, uncorrected | Rim sd in u, uncorrected | Rim mean in u, EHT corrected | Rim sd in u, EHT corrected |
|--------|--------------------|------------------|-----------|--------------------|--------------------|-----------|----|----------------------------|--------------------------|------------------------------|----------------------------|
| 30.1   | 3.28               | 760              | 100       | 710                | 760                | 0.85      | 5  | 4.10                       | 1.47                     | 4.98                         | 1.78                       |
| 30.2   | 3.28               | 960              | 100       | 867                | 917                | 0.65      | 6  | 4.73                       | 1.17                     | 5.67                         | 1.40                       |
| 1428   | 3.71               | 990              | 80        | 893                | 943                | 0.35      | 6  | 4.30                       | 0.25                     | 5.33                         | 0.31                       |
| 3806.2 | 3.6                | 1160             | 90        | 1088               | 1138               | 0.85      | 5  | 3.64                       | 0.97                     | 4.61                         | 1.23                       |
| 30.3   | 3.28               | 1220             | 70        | 1146               | 1196               | 0.55      | 3  | 4.43                       | 0.45                     | 5.28                         | 0.54                       |
| 2750   | 3.66               | 1330             | 70        | 1247               | 1297               | 0.50      | 5  | 4.03                       | 0.23                     | 5.02                         | 0.29                       |
| 3812.2 | 4.21               | 1340             | 50        | 1268               | 1318               | 1.15      | 5  | 5.60                       | 0.80                     | 7.67                         | 1.10                       |
| 30.6   | 3.28               | 1530             | 70        | 1428               | 1478               | 0.70      | 11 | 5.31                       | 0.50                     | 6.39                         | 0.60                       |
| 3812.1 | 4.21               | 1600             | 60        | 1485               | 1535               | 0.95      | 5  | 4.71                       | 0.44                     | 6.39                         | 0.60                       |
| 30.4   | 3.28               | 1600             | 70        | 1488               | 1538               | 0.55      | 3  | 4.43                       | 0.45                     | 5.28                         | 0.54                       |
| 3806.1 | 3.6                | 1600             | 100       | 1497               | 1547               | 0.85      | 5  | 3.64                       | 0.97                     | 4.61                         | 1.23                       |
| 30.8   | 3.28               | 1650             | 100       | 1554               | 1604               | 0.60      | 7  | 4.50                       | 1.08                     | 5.38                         | 1.29                       |
| 30.7   | 3.28               | 1840             | 80        | 1771               | 1821               | 0.60      | 7  | 4.50                       | 1.08                     | 5.38                         | 1.29                       |
| 30.5   | 3.28               | 1860             | 70        | 1793               | 1843               | 0.70      | 11 | 5.31                       | 0.50                     | 6.39                         | 0.60                       |
| 372.1  | 3.58               | 2900             | 80        | 3051               | 3101               | 2.55      | 7  | 8.04                       | 1.09                     | 10.55                        | 1.43                       |
| 372.5  | 3.58               | 3240             | 60        | 3466               | 3516               | 2.30      | 6  | 7.32                       | 1.40                     | 9.63                         | 1.84                       |
| 372.2  | 3.58               | 3520             | 80        | 3798               | 3848               | 2.89      | 4  | 8.20                       | 0.20                     | 10.76                        | 0.26                       |
| 372.3  | 3.58               | 3580             | 80        | 3883               | 3933               | 3.21      | 9  | 8.16                       | 0.22                     | 10.73                        | 0.29                       |
| 372.4  | 3.58               | 3900             | 80        | 4324               | 4374               | 3.74      | 5  | 8.16                       | 0.42                     | 10.76                        | 0.55                       |
| 372.6  | 3.58               | 4460             | 110       | 5106               | 5156               | 2.65      | 2  | 8.05                       | 0.35                     | 10.57                        | 0.46                       |
| 4554   | 3.68               | 6740             | 90        | 7602               | 7652               | 0.90      | 14 | 10.30                      | 1.34                     | 12.78                        | 1.66                       |
| 5250.1 | 1.44               | 8410             | 140       | 9379               | 9429               | 0.60      | 9  | 15.19                      | 1.00                     | 14.17                        | 0.93                       |
| 5250.1 | 1.44               | 8420             | 140       | 9391               | 9441               | 0.25      | 10 | 18.27                      | 4.03                     | 16.79                        | 3.70                       |
| 4562.2 | 3.28               | 9410             | 115       | 10662              | 10712              | 0.95      | 4  | 11.58                      | 3.09                     | 13.71                        | 3.66                       |
| 328    | 3.73               | 9440             | 150       | 10722              | 10752              | 0.66      | 5  | 11.07                      | 0.65                     | 13.64                        | 0.80                       |
| 4562.1 | 3.28               | 9470             | 115       | 10767              | 10817              | 0.85      | 5  | 13.50                      | 1.46                     | 16.06                        | 1.74                       |

The simple linear best fit is well known mathematically and can be found in many text books (e.g. Meyer 1975). It is also built into Microsoft Excel. Equation 9 shows the best-fit slope, under the constraint that the line must pass through the origin (which is required by the physics of hydration):

$$k = [\sum(x_i y_i)] / [\sum(x_i)^2] \quad (9)$$

where  $m$  is the best-fit slope and the sum is taken over all  $N$  data points. However, the assumption is implicit in equation 9 (and in Excel) that the  $x$ -coordinate of each data point is error-free, and all experimental uncertainties are in the  $y$ -coordinate. There are many classes of problems for which this is, indeed, a reasonable assumption, but not for obsidian, since significant experimental error exists in both coordinates from at least five error sources, and the error variance can change point by point. First, radiocarbon dates have statistical uncertainties associated with them, as does the calibration curve. Second, obsidian rim thicknesses have their own measurement errors. Third, EHT correction is probably no better than 1°C, even with modern techniques (Rogers 2007a). Fourth, there is the well-known range of rim thicknesses which results even after EHT correction, possibly due to uncorrected chemical composition variables such as intrinsic water concentration (Ambrose and Stevenson 2004; Rogers 2008a; Stevenson et al. 1998). Finally, and probably most significant, an association uncertainty exists between radiocarbon and obsidian, arising from site formation processes (Schiffer 1987). Thus, each obsidian-radiocarbon data point contains significant experimental uncertainties (of the order of >10%) in both dimensions. Because these errors affect both dimensions, use of equation 9 is inappropriate.

The “total least squares” (TLS) algorithm is specifically designed for the case where both variables contain uncertainties. The

algorithm minimizes sum-square error in the  $y$  dimension between the data points and best-fit line, weighted by the error variance *measured perpendicular to the best-fit line* (Meyer 1975; Van Huffel and Vandewalle 1991). The form applied here was derived by the present author from the starting point of Meyer (1975:75, last two equations).

The TLS equation for  $k$  (see equation 8) is

$$k = [-B + \sqrt{B^2 + 4AC}] / 2A \quad (10a)$$

where

$$A = \sum x_i y_i (\Delta x_i)^2 / \sigma_i^4 \quad (10b)$$

$$B = \sum [x_i^2 (\Delta y_i)^2 - y_i^2 (\Delta x_i)^2] / \sigma_i^4 \quad (10c)$$

$$C = \sum x_i y_i (\Delta y_i)^2 / \sigma_i^4 \quad (10d)$$

$$\sigma_i^2 = (\sigma_y)^2 + k^2 (\sigma_x)^2 \quad (10e)$$

For this analysis, age  $t$  is chosen as the dependent variable and the square of the rim as the independent variable, because the resulting slope will be used to compute age based on rim measurements. The analysis must include change of variable weighting, in accordance with the theory of propagation of errors (Cvetanovic et al. 1979; Taylor 1982:153ff.). Change of variable weighting is required whenever the analysis is based on composite variables; this is the case here, because the fit is between  $x = r^2$  and  $y = t$ , so  $x$  is a composite variable. It can be shown that, for this case,

$$\sigma_x^2 = 4r^2 \sigma_r^2$$

and

$$\sigma_y^2 = \sigma_t^2 .$$

With  $\sigma_x^2$  and  $\sigma_y^2$  defined as above, and  $x = r^2$  and  $y = t$ , equations 10b – e become

$$A = \sum t_i r_i^2 (\sigma_{t_i})^2 / \sigma_{k_i}^4 \quad (11a)$$

$$B = \sum [r_i^4(\sigma_{ti})^2 - t_i^2(\sigma_{ri})^2] / \sigma_{ki}^4 \quad (11b)$$

$$C = \sum 4t_i r_i^4 (\sigma_{ri})^2 / \sigma_{ki}^4 \quad (11c)$$

$$\sigma_{mi}^2 = (\sigma_{ti})^2 + k^2 4r_i^2 (\sigma_{ri})^2 \quad (11d)$$

This is the algorithm implemented here; its output  $k$ , in years/ $\mu^2$ , is the reciprocal of the hydration rate. Its implementation is iterative, because the unknown ( $k$ ) occurs on both sides of equation 10a.

### Linear Best Fit Process and Results

Effective hydration temperature was computed for each specimen based on equations 2 and 3 above. Following this, the rim thickness for each sample was corrected for EHT by equation 4 and 5 above, which forms the basis for the obsidian-radiocarbon best fit. Also, radiocarbon ages were converted to physical age (calendar years referenced to 2000) using Calib 501; no correction was made for  $\delta^{13}C$ , since the data were not available. Table 2 presents the data set used in the analysis.

An approximate best fit slope  $k_0$  was computed from the data of Table 2 by equation 9 to give a starting estimate. Next an error analysis was performed using the value of  $k_0$  to estimate the error variances, or residual errors, in both dimensions. Since variances were not reported in the original source data (Table 1), *a posteriori* variances were computed based on the data and the initial linear best fit. The data were found to fall naturally into three age-rim groupings, as shown in Figure 1 for the fit to radiocarbon age, and a variance in both age and rim thickness was computed for each grouping. The total least squares method of equation 10, allowing for errors in both variables, was then applied to the data set and variances, using  $k_0$  as the starting value for the slope. This resulted in a new (and different) value of slope,  $k_1$ ;  $k_1$  was then input to equation 10 and

to the error computations for  $r$  and  $t$ , and a new value  $k_2$  obtained. The process was repeated, and on the fourth iteration the difference between successive values of  $k_n$  was found to be confined to the third decimal place, so the process was stopped.

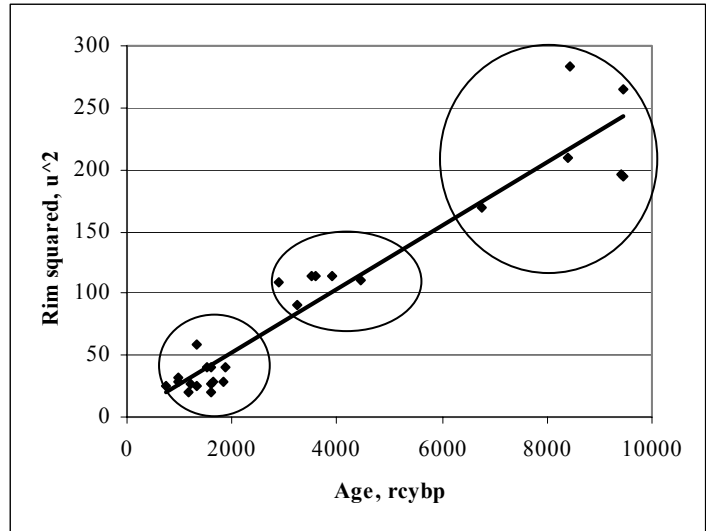


Figure 1. Initial linear fit to physical age data, showing grouping of data. Curve for radiocarbon age similar. Note that the slope is the hydration rate.

The resulting best-fit models for this data set are

$$t_{\text{cal yrs before 2000}} = 43.72r^2 \quad 0 \leq r \leq 16 \quad (12)$$

and

$$t_{\text{RCYB1950}} = 38.87r^2 \quad 0 \leq r \leq 16 \quad (13)$$

with  $r$  being the EHT-corrected rim thickness in microns, referenced to an EHT of 20.4°C (i.e. conditions at Lubkin Creek, CA-INY-30).

Accuracy of the best-fit models was estimated by comparing ages computed from equations 12 and 13 with the data set. The standard deviation of the age estimates is presented in Table 3, and shows 1-sigma errors ranging from 454 years to 1931 years (for purposes of error assessment, radiocarbon years and calibrated years may be treated as

equivalent). The errors become larger with increasing age, and are roughly 20% of age.

Table 3. Error standard deviation from TLS best fit

| EHT-corrected rim, $\mu$ | Fit to Physical Age         | Fit to Radiocarbon Age      |
|--------------------------|-----------------------------|-----------------------------|
|                          | Standard Deviation<br>cyb2k | Standard Deviation<br>rcybp |
| $0 < r < 6$              | 486                         | 454                         |
| $9 < r < 11$             | 701                         | 542                         |
| $13 < r < 16$            | 1931                        | 1677                        |

The fit in equations 12 and 13 is quadratic (i.e. of the form of equation 1), based on the physics of obsidian hydration; as pointed out earlier, no other functional form is suggested by theory. Inclusion of higher-order terms was explicitly avoided, since the apparent accuracy thus achieved is spurious: adding higher order terms to the equation increases the apparent goodness of fit, as measured by residuals, but since each data point is a combination of valid data and experimental error, the higher degree polynomial is simply a better fit to the experimental error. Indeed, it can be shown (Hanning 1973; Matthews 1992) that the lower the order of the fit, the better the fit suppresses experimental error. Generally the appropriate order of the equation should be suggested by the nature of the problem, i.e. the physical or chemical model; in the case of obsidian, physics suggests that a quadratic relationship such as equation 1 is appropriate, so no higher order terms were included.

In using the rates in equations 12 and 13, best results are obtained by including a correction for paleoclimatic temperature change (Rogers 2007c). Figure 2 shows the fit between radiocarbon age data and best fit visually, with and without the paleoclimatic correction.

## Conclusions

The analysis has led to two new equations for Coso obsidian, equations 12 and 13. Equation 12 is a best-fit for calendar years before 2000, and equation 13 gives RCYBP prior to 1950. Both are based on 26 data points (plus the origin, zero rim at zero time), with the rim values corrected for EHT including effects of burial depth. The EHT was computed for INY-30 conditions at the ground surface, or 20.4°C.

It is clear that significant residual error remains. This error probably arises from two sources, the first being variations in obsidian chemistry. Obsidian chemistry enters the picture because the specimens may not be from the same obsidian flow at Coso, and hence may exhibit different rates due to chemistry (Stevenson and Scheetz 1989; Stevenson et al. 1993). Alternatively, they may be from the same flow and the variability may be due to intra-flow variations in chemistry and rate (Stevenson et al. 1993). The idea that rate is a function of chemical composition has

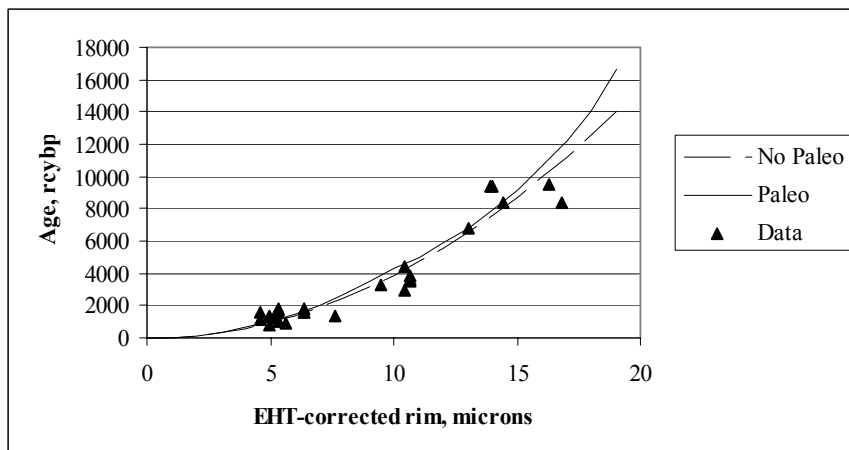


Figure 2. Fit of radiocarbon age data to total least squares best fit. Ages computed with and without paleotemperature correction. “No Paleo” case represents equation 13; “Paleo” case computed by method of Rogers 2007c.



been accepted since Friedman and Long 1976; currently researchers in glass science generally attribute the majority of the variability to water content (molecular and hydroxyl), with anhydrous composition playing a minor role (Ambrose and Stevenson 2004; Doremus 1994, 2002; Behrens and Nowak 1997; Steffen 2005). Furthermore, Stevenson et al. (1993) have shown that Coso obsidian exhibits significant variability in water content. The effects of water variability in Coso obsidian imply a similar variability in hydration rate and hence in hydration rim thickness for a given age and temperature history (Rogers 2008a; Stevenson et al. 1998, 2000); indeed, the variability in hydration rim thickness due to variations in intrinsic water content for the Coso volcanic field as a whole has a CV = 0.21 (Rogers 2008a).

The second major limitation is site formation processes, which also place a limit on accuracy, because the analysis is based on the assumption that the obsidian and radiocarbon values are associated, with some degree of experimental error. A recent analysis of the data set from Rose Spring (CA-INY-372) showed that an upward vertical shift of between 50 and 100 cm had occurred in obsidian relative to radiocarbon, due probably to artifact reuse and to site aggradation (Rogers 2008c). It is likely that these two factors place a limit on further refinement of hydration rate based on this data set.

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## ABOUT OUR WEB SITE

The IAOS maintains a website at <http://www.peak.org/obsidian/>  
The site has some great resources available to the public, and our webmaster, Craig Skinner, continues to update the list of publications and must-have volumes.

You can now become a member online or renew your current IAOS membership using PayPal. Please take advantage of this opportunity to continue your support of the IAOS.

Other items on our website include:

- World obsidian source catalog
- Back issues of the *Bulletin*.
- An obsidian bibliography
- An obsidian laboratory directory
- Photos and maps of some source locations
- Links

Thanks to Craig Skinner for maintaining the website. Please check it out!

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Submissions of articles, short reports, abstracts, or announcements for inclusion in the *Bulletin* are always welcome. We accept electronic media on CD in MS Word. Tables should be submitted as Excel files and images as .jpg files. Please use the *American Antiquity* style guide (available at [www.saa.org/publications/StyleGuide/styFrame.html](http://www.saa.org/publications/StyleGuide/styFrame.html)) for formatting references and bibliographies.

Submissions can also be emailed to the *Bulletin* at [cdillian@princeton.edu](mailto:cdillian@princeton.edu) Please include the phrase "IAOS Bulletin" in the subject line. An acknowledgement email will be sent in reply, so if you do not hear from us, please email again and inquire.

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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.

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