Redefining the Working Assumptions of Obsidian Hydration Dating

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Recent experimental work has shown that the rate of hydration is significantly influenced by the amount of intrinsic water (OH-) contained within the unweathered obsidian. A value for the intrinsic water concentration may be obtained through a nondestructive measurement of glass density, thereby permitting obsidian hydration rates to be determined for individual artifacts. As a result of these discoveries, many of the assumptions used in the normal application of obsidian hydration dating are now in need of revision. This article presents a revised set of working assumptions and procedures for implementation of the obsidian dating method and evaluates the ability of calibrations to produce chronometric dates that correspond with radiocarbon assays.

Since the initial publication of the paper on the obsidian hydration dating (OHD) technique by Friedman and Smith (1960), the field of glass science has seen a wide variety of developments that have increased our understanding of the hydration process. These studies have been largely laboratory-based studies that have addressed the problem of hydration rate compositional dependence (Friedman and Long 1976; Stevenson et al. 1998; Anovitz et al. 1999) and the environmental factors that influence the hydration process (Mazer et al. 1991; Friedman et al. 1994, 1997; Jones et al. 1997). However, field applications of the dating method have generally not incorporated the new advances. Instead, archaeologists have held to several basic working assumptions that have been viewed as well-grounded and preferable to the results of complex experimental procedures.

This article reviews four fundamental assumptions of OHD that have been in use since the development of the method. It is maintained herein that each of these assumptions is now unsuitable in light of new theoretical advances in the dating method. We propose alternate, easy to use strategies for the application of OHD that rely upon experimental results observed under controlled conditions. These new methods are then applied to a case example, showing that reliable age estimates can be obtained for archaeological contexts.

WORKING ASSUMPTIONS OF OBSIDIAN HYDRATION DATING

The application of OHD in the western United States (principally California) is viewed as a relative dating method. In the generally accepted procedure, artifacts from site assemblages are first provenienced to geological source by elemental analysis (e.g., X-ray fluorescence analysis, instrumental neutron activation analysis), or by visual categorization based upon color and type of crystal inclusions. The hydration rim thicknesses obtained from artifacts of known geological source are then compared on a within or between site basis. These comparisons are used to develop statements about which contexts are earlier or later. If clusters of rim measurements
are present, generalizations may also be made about the relative length of site occupations or the number of past settlement episodes.

The application of this simple method is based upon four fundamental assumptions about the properties of obsidian. These assumptions are:

**Assumption No. 1:** Artifacts derived from the same geological source will hydrate at the same rate. This assumption likely stems from an early statement by Friedman and Smith (1960: 484) on the influence of chemical composition, where they observed that “[t]he variation within one petrographic province is usually small, but greater variation can be expected from province to province.” This was reinforced in a second publication by Friedman and Long (1976), where they presented data in graphical form that demonstrated the uniformity of hydration rate for a large number of glass fragments described as coming from the same source. In addition, they presented a single set of high temperature hydration rate constants for each source. Since that time, these reporting standards—and all that they imply—have become the convention for most subsequent studies that have been concerned with estimating hydration rates for geological sources (Ericson 1981; Stevenson and Scheetz 1989; Stevenson and McCurry 1990).

**Assumption No. 2:** Trace element uniformity implies obsidian major element and minor element uniformity, those factors thought to have the most influence on hydration rate. This assumption is closely related to Assumption No. 1. It has developed over the years as the ability to characterize samples for trace element concentrations has become a routine procedure. The ability to characterize a source with high precision, and to subdivide that source into unique flows or geological events, raises the question of how many rates are represented in the source material. Is one rate still representative of the entire source, or is a rate needed for each flow? In many cases, the researcher is guided by the trace element chemistry and assumes that flow-specific rates are required (Ericson 1989).

**Assumption No. 3:** Ambient temperature significantly affects the hydration rate, while environmental conditions, such as relative humidity, have little or no influence on the rate of hydration. Early in the development of OHD, it was proposed that atmospheric relative humidity had no effect on the rate of hydration (Friedman and Smith 1960; Friedman and Long 1976). As a result, this variable has not been routinely considered, although the effects on hydration rate have been investigated (Friedman et al. 1994; Mazer et al. 1991). Temperature has always been seen as an influential variable both between regions and to a lesser degree over time. However, users of this method who rely upon externally correlated hydration rates have not been able to account for this variable with any level of precision. Thus, although known to be influential, it is generally ignored (Ericson 1988).

**Assumption No. 4:** Accurate hydration rates may be empirically developed using field data. In their initial paper, Friedman and Long (1960) presented the basic strategy for hydration rate development where hydration rim thicknesses are correlated with dated contexts. In recent applications, it is typical for samples from the same geological source to be located in numerous dated contexts within a larger region. Hydration rates that follow the square root of time or other rate equations are typically proposed (Bettinger 1980, 1989).

**THE HYDRATION PROCESS**

**Scientific Background**

Obsidian hydration dating converts a hydration layer of measured thickness to an absolute date with an established rate for the inward diffusion of molecular water using the equation:

\[
x = kt^{1/2}
\]

where \( x \) is the hydration rim width in microns (\( \mu \)), \( k \) is the hydration rate at a particular temper-
ature/relative humidity, and t is time.

The major tasks in OHD are to determine the thickness of the hydration rim (x) and the value of the hydration rate for specific archaeological site conditions (k). Hydration rims are presently measured by optical microscopy on prepared thin sections. The current approach to rate determination is to develop a rate at high temperature (160° C) and extrapolate to ambient site conditions using the Arrhenius equation (Friedman and Long 1976):

\[ k = A \, (RH) \exp \left( \frac{E}{RT} \right) \]  

where \( k \) is the archaeological hydration rate, \( A \) is the preexponential at 160° C, \( RH \) is relative humidity, \( E \) is activation energy, \( R \) is universal gas constant, and \( T \) is site ambient temperature.

The geochemical approach to hydration rate development offers a precise way to integrate all of the rate-influencing variables into a single equation. However, in order for OHD to provide reliable age estimates, the values of \( A \), \( E \), \( RH \), and \( T \) must be accurately determined.

The Compositional Dependence of Obsidian Hydration

The development of obsidian hydration rates has been a fundamental issue for users of the method. Conventional methods of hydration rate determination for specific obsidian sources have included the correlation of hydration rim widths with associated radiocarbon dates and/or high temperature induced hydration on geological samples. The latter approach has been extensively investigated using a variety of reaction media and temperature settings (Ambrose 1976; Friedman and Long 1976; Ericson 1981; Michels et al. 1983; Stevenson and Scheetz 1989; Stevenson et al. 1989; Stevenson and McCurry 1990; Mazer et al. 1992). In these experimental designs, fresh obsidian surfaces were exposed to either a liquid or vapor atmosphere within an open or sealed reaction vessel maintained at temperatures between 95° C and 250° C. The hydration rims formed at elevated temperatures were measured and used to calculate the hydration rate constants (A, E). In studies conducted by the authors over the last five years, a vapor environment kept at 100% RH has been used as a model of natural conditions.

The dependence of hydration rate on obsidian chemical composition has been addressed through theoretical considerations (Ericson 1981) and by correlation of high temperature hydration rates with glass chemical constituents (Friedman and Long 1976). Recent work by Mazer et al. (1992) and Stevenson et al. (1996, 1998) has shown a strong dependence between the structural water content (OH-) of the glass with the 100% relative humidity hydration rate constants developed at high temperature (Fig. 1). With this calibration established, it was now possible to estimate archaeological hydration rates from the concentration of OH- contained within the glass.

Once the rate controlling parameter had been identified, several quarry locations in the Coso Volcanic Field were examined to look at the potential effect of intrinsic water on the hydration rate (Stevenson et al. 1993). Infrared water analyses indicated that the water content of obsidian samples had a large range within many of the quarry locations, a factor that would result in correspondingly large hydration rate ranges. Additional studies completed since that time (Stevenson et al. 1996) have demonstrated that a range of intrinsic water values (exceeding analytical error) is present in some source locations while others exhibit only limited variation.

In order to develop the hydration rate calibration (Fig. 1), the structural water content was precisely determined on transparent obsidian sections using the infrared spectroscopy protocol of Newman et al. (1986). However, the application of the calibration to archaeological obsidians was significantly hindered by the lack of infrared transparency in many obsidians. A method to avoid this limitation was proposed (Ambrose and Stevenson 1995; Stevenson et al. 1996). Gravi-
Fig. 1. Relationship between OH- concentration and the hydration rate at 160° C (top), and OH- concentration and the activation energy (bottom).
metric analysis of samples with known water contents were used to demonstrate a mathematical relationship between water content and density (Fig. 2). High-density obsidians have low quantities of structural water and hydrate slowly, while low-density glasses have higher water concentrations and faster hydration rates (Stevenson et al. 1998). With this relationship precisely established, water values—and thus hydration rates—for virtually all archaeological obsidians can be nondestructively estimated.

**Effective Hydration Temperature and Relative Humidity**

As noted above in the discussion of method, the rate of hydration is exponentially dependent upon ambient temperature and is thus very sensitive to this variable. However, new experimentation has contradicted earlier statements about the effects of RH and has shown that low humidity levels can significantly slow the hydration rate. Mazer et al. (1991) demonstrated that the rate reduction was most pronounced when the relative humidity was reduced from 100% to 90%. This observation was generally confirmed by Friedman et al. (1994), who found a linear reduction in hydration rate in the 80% to 100% relative humidity range. They also provided a correction equation to adjust the 100% RH hydration rate (Friedman et al. 1994:187). Control over these variables is currently monitored with the use of thermal cells that precisely record ambient conditions over the course of a one-year period (Ambrose 1982, 1984; Leach and Hamel 1984; Trembour et al. 1988).

**REVISED WORKING ASSUMPTIONS FOR OBSIDIAN HYDRATION DATING**

The scientific background presented above has illustrated the complexity of the obsidian hydration process. Yet, experimentation on rhyolitic obsidian and other glass compositions has shown repeatedly that many glasses hydrate at the square root of time and that the hydration rate is influenced by the intrinsic water content and the ambient context within which the artifact has resided. We find these data compelling to the point where the current working assumptions in the application of OHD are in need of revision. We therefore propose the following revised assumptions:

**Assumption No. 1:** Obsidian sources will have a range of hydration rates that is a function of the variation in intrinsic water content. Intrinsic water concentration values for obsidian flows generally fall between 0.08% and 1.3%. Based on only a few studies to date, it appears that the internal variation of water content is greater for sources with an overall higher average water content (0.4% to 01.3%) than those sources that have relatively little water (0.08% to 0.4%). The water concentration range for each geological source should be empirically determined using either infrared or gravimetric methods.

**Assumption No. 2:** There is no observable relationship between trace element concentrations and the uniformity of obsidian intrinsic water content. As with sources containing one flow event, sources with multiple flows may exhibit a range of intrinsic water content values within each flow defined through trace element analysis. The range of hydration rates for each flow needs to be empirically determined.

**Assumption No. 3:** Ambient temperature and relative humidity conditions significantly influence the rate of obsidian hydration. The assumption that aerially extensive regions will be uniform with respect to their ambient conditions is no longer supportable. Temperature and relative humidity are significantly influenced by elevation, slope, and ground cover, all of which affect the long-term averages. It has been shown that microvariation with respect to these variables will form significantly different climatic settings even within small areas (Ridings 1991; Jones et al. 1997).

**Assumption No. 4:** Archaeological field data may not be used to estimate the long-term hydra-
As currently structured, studies that estimate hydration rates from archaeological data do not control for any of the pertinent variables that affect the rate of hydration. The chemical sourcing of samples does not ensure that all of the samples have the same hydration constants. In addition, the use of samples from multiple contexts within a region does not account for variation in ground temperature or relative humidity. This is compounded by the fact that the sample may not be in situ so it may not reflect the dated context (Hall and Jackson 1989). Even if all of the potential errors are minimized at a particular location, such as a stratified cave deposit, the utility of an empirically derived rate is dubious once applied to a different environmental setting. We therefore consider it unadvisable to work with uncontrolled contexts in order to provide a precise estimate for a physical process.

RESEARCH DESIGN CONSIDERATIONS

The discussion presented above has argued that assumptions about the weathering process of obsidian and the variables that affect the rate of hydration be replaced with a new approach, one based on demonstrated processes established through controlled experimentation. Prior laboratory modeling of the hydration process in nature was problematic as hydration parameters were not estimated to reflect actual site conditions. We consider induced hydration within a noncorrosive vapor environment (100% RH) to be representative of many ambient contexts. In addition, this permits the hydration rate for each glass composition to be adjusted in accordance
with the temperature and relative humidity conditions measured at the site.

In light of these developments, it is proposed herein that OHD results may be significantly improved by employing the following simple research design:

1. From noncorrosive contexts (e.g., non-tropical), select flake or tool samples that are free of cortex or internal flaws, such as large perlite inclusions or open cracks. In corrosive contexts, it may be necessary to select samples with visible microfissures that contain protected hydrated surfaces (Ambrose 1994).

2. Determine the water concentration of each sample through a density analysis or by infrared spectroscopy.

3. Estimate or measure the effective hydration temperature (EHT) and RH conditions at the archaeological site.

4. Calculate absolute or relative ages for the samples in question. Samples of different composition are directly comparable at this stage.

It is our opinion that the procedures outlined above will produce superior results in the application of OHD. To help evaluate the procedures and identify potential problem areas, these methods were applied to a prehistoric site (CA-ORA-64) that has been well dated.

APPLICATION OF THE REVISED OHD APPROACH AT CA-ORA-64

In order to provide support for the revised OHD approach delineated above, a case example from California (CA-ORA-64) is presented. In this dating exercise, the research design discussed above is illustrated and evaluated through a comparison with other chronological data.

Located on the east bluffs of Newport Bay in Newport Beach, Orange County, CA-ORA-64 is a prehistoric open-air site. Three previous studies in the 1970s and 1980s (Archaeological Research, Inc. 1977; Drover et al. 1983; LSA 1987) documented the rich variety of cultural materials and established that CA-ORA-64 was one of the earliest sites in southern California, with occupations dated between approximately 7,000 and 2,300 B.C. The most recent research at the site was conducted by Macko (1998), and it is from this work that we have drawn the case example to illustrate the application of our revised OHD approach.

CA-ORA-64 encompasses an area of approximately 79,000 m² (Macko 1998). Controlled surface collection in the 1970s identified two spatially distinct core areas of high artifact density. A pre-mitigation magnetometer survey revealed that the upper surface layers had been heavily disturbed through plow agriculture and rodent burrowing. This was confirmed through excavation, where intact cultural features were not encountered until a depth of approximately 70 cm. below the surface was reached. At this depth and below, several hundred cultural features were identified. Obsidian samples used for an initial age assessment were selected from systematic unit (nonfeature) contexts between 10 and 80 cm. below the surface, from which specimens for accelerator mass spectrometry (AMS) dates were also obtained. These items were submitted to the University of California, Los Angeles, Obsidian Hydration Dating Laboratory or Diffusion Laboratory for analysis. The objective of the dating exercise was to determine if the same dating range and patterns of occupation revealed by the numerous radiocarbon dates could be matched by OHD. In addition, the degree of correspondence was assessed between obsidian dates and AMS radiocarbon dates recovered from the same feature contexts (Macko 1998).

High-precision AMS dating of CA-ORA-64 was conducted by Macko (1998) as part of the site mitigation effort. A total of 42 AMS dates was obtained on shell (n = 41) and bone (n = 1) located within features. The corrected radiocarbon dates revealed an occupational range that spanned the period from approximately 7,000 to 2,300 B.C. Within this age range, the data revealed a nearly continuous occupation from
7,000 to 5,500 B.C., which was followed by a 1,000-year hiatus. At 4,500 B.C., the occupation resumed, although it was broken by shorter periods of nonuse between 4,000 and 3,500 B.C. and between 3,000 and 2,500 B.C. An additional 22 conventional radiocarbon dates on pooled shell samples collected previous to the mitigation fell within the 7,000 to 2,300 B.C. age range, but because of the large standard deviations in the reported ages, periods of site abandonment could not be identified (Macko 1998).

Soil Temperature and Relative Humidity

Monitoring of the soil temperature and relative humidity was conducted within the site boundaries of CA-ORA-64 using the saline based cells developed by Trembour et al. (1988). Two separate columns of cell pairs (one temperature cell/one relative humidity cell) were installed a few meters apart. The cell pairs in each column were buried at depths between 0 and 100 cm. and recovered at the end of one year. The monitoring results in Table 1 revealed that the EHT decreased from the surface to a depth of 100 cm., consistent with the general trends noted by Friedman et al. (1994). The greatest decrease was in the 0 to 10 cm. range in Trench 1, where a difference of 3°C was recorded. Smaller temperature decreases occurred at greater depths. In Trench 1, from a depth of 10 to 100 cm., the temperature decreased by 1.3°C and in Trench 2 the temperature dropped by 0.83°C between 10 and 90 cm.

In contrast to the temperature trend, the percent relative humidity values increased with depth (Friedman et al. 1994; Table 1) and ranged between 96% and 98% at deeper levels and 81% and 82% at 10 cm. below the surface. The surface cell in Trench 1 was nearly desiccated upon retrieval and returned a relative humidity value of 43%. Because of the degraded cell condition, this value most likely does not represent an accurate determination for this context.

Hydration Rate Estimation

Estimations of the hydration rate constants were made from the OH- concentration of the glass as estimated from density values. In applying the Archimedes method, density determinations were made on an analytical balance with a Mettler density kit. A heavy liquid (Unigrav) was used as the immersion media (1.45 to 1.6 g/ml at 15.5°C) and a mercury thermometer was used to measure the temperature of the liquid to ± 0.5°C. The results are presented in Table 2.

Prior to determination of artifact density, it is advised that samples with obvious open cracks or bubbles be removed or an unflawed sample cut from the body of the flake. Although surface cortex does not appear to affect the overall density result (Torrence and Victor 1995), it is suggested that high proportions of cortex on the surface be avoided since air bubbles may become trapped, lowering the density value. Despite these precautions, a portion of the samples in this study produced very low and inaccurate density values. The first two samples (UCLA-19647 and -3853; Table 2) returned OH- values of 1.9% and 2.5% and fall outside the known density range of obsidian. The next four samples (UCLA-22998, -7155, -2099, and -5333) returned high OH- values ranging between 0.48% and 0.90%.

Table 1

<table>
<thead>
<tr>
<th>Cell No.</th>
<th>Trench No.</th>
<th>Depth (cm.)</th>
<th>EHT (°C)</th>
<th>%RH</th>
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<tbody>
<tr>
<td>4/11</td>
<td>1</td>
<td>0</td>
<td>29.55</td>
<td>43</td>
</tr>
<tr>
<td>3/12</td>
<td>1</td>
<td>10</td>
<td>26.68</td>
<td>81</td>
</tr>
<tr>
<td>2/13</td>
<td>1</td>
<td>50</td>
<td>26.08</td>
<td>96</td>
</tr>
<tr>
<td>1/14</td>
<td>1</td>
<td>100</td>
<td>25.38</td>
<td>96</td>
</tr>
<tr>
<td>7/8</td>
<td>2</td>
<td>10</td>
<td>26.03</td>
<td>82</td>
</tr>
<tr>
<td>6/9</td>
<td>2</td>
<td>50</td>
<td>25.48</td>
<td>96</td>
</tr>
<tr>
<td>5/10</td>
<td>2</td>
<td>90</td>
<td>25.20</td>
<td>98</td>
</tr>
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</table>
Table 2

OBSIDIAN HYDRATION DATES FOR NONFEATURE CONTEXTS AT CA-ORA-64

<table>
<thead>
<tr>
<th>UCLA Lab No.</th>
<th>Depth (cm.)</th>
<th>Rim (μ)</th>
<th>Density&lt;sup&gt;a&lt;/sup&gt;</th>
<th>%OH-</th>
<th>Rate&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Age A.D./B.C.</th>
<th>S.D.&lt;sup&gt;c&lt;/sup&gt;</th>
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<td>70</td>
<td>9.8</td>
<td>2.3094</td>
<td>1.90</td>
<td>236.09</td>
<td>A.D. 1543</td>
<td>8.0</td>
</tr>
<tr>
<td>3853</td>
<td>50</td>
<td>12.4</td>
<td>2.2995</td>
<td>2.48</td>
<td>299.14</td>
<td>A.D. 1436</td>
<td>8.0</td>
</tr>
<tr>
<td>22998</td>
<td>40</td>
<td>9.3</td>
<td>2.3286</td>
<td>0.78</td>
<td>101.72</td>
<td>A.D. 1100</td>
<td>18.0</td>
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<td>7155</td>
<td>60</td>
<td>10.5</td>
<td>2.3267</td>
<td>0.90</td>
<td>115.96</td>
<td>A.D. 999</td>
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<td>2099</td>
<td>50</td>
<td>11.9</td>
<td>2.3338</td>
<td>0.48</td>
<td>61.33</td>
<td>359 B.C.</td>
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<td>0.13</td>
<td>11.76</td>
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<td>7,601 B.C.</td>
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<td>0.09</td>
<td>7.00</td>
<td>25,259 B.C.</td>
<td>396.0</td>
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</table>

<sup>a</sup>Density in g/cm.³

<sup>b</sup>Rate in μ²/1,000 years (based on Equation 2).

<sup>c</sup>Standard deviation.

Although significant in comparison to many obsidians, these concentrations are well within the range exhibited for the Coso Volcanic Field (Stevenson et al. 1993). The remainder of the artifacts has a limited density range that falls between 0.09 and 0.13% (Table 2).

After completion of the density analysis, a thin section was prepared for each sample. The hydration rim thickness measurement was made using a Jenaval polarizing microscope with a Leitz filar micrometer at a magnification of 625X. Five independent measurements were taken within the field of view on clear and well-defined hydration and a mean value computed. A measurement error of ±0.2μ is associated with each thickness value. If a second hydration rim was measured and found to be greater or lesser than the first hydration rim by 0.4μ, then a second band measurement was reported. This was observed on four samples (UCLA-1965, -2099, -7154, and -22998). However, the larger rim on each sample was omitted from the data set as it does not reflect the last depositional event. It cannot be assumed that the scavenged artifact originated at CA-ORA-64 since it is also possible that the item may have been imported from an-
other nearby site. At this stage, all of the measured variables (EHT, RH, OH-, hydration rim width) were used to calculate the hydration rate at ambient temperature and an age for each of the samples (Table 2).

Results

Successful obsidian hydration analyses were obtained on 23 samples (Table 2). Only a single sample had no visible hydration on the surface and is not listed. The age range (based on Equations 1 and 2) for the samples extends from 25,259 B.C. to A.D. 1543. This range is significantly greater than the 7,000 to 2,300 B.C. radiocarbon determination for site use. What the data in Table 2 do not reflect are the analytical decisions that were made to account for error and inappropriate context. In this study, all the data were purposefully included in order to illustrate what post-processing considerations may need to be addressed.

An examination of the data in Table 2 reveals several sources of introduced variation. The first source of error is that of faulty analysis. Two of the most recent samples (UCLA-3853 and -19647) have very low densities and thus very high water contents. These water content values are 1.90% and 2.48%, levels that are significantly greater than that reported for water-rich obsidian sources (0.10% to 1.20%), such as the Coso Volcanic Field (Stevenson et al. 1993). Although these individual items have not been assigned to their geological source, five other specimens within the set of dated samples are from West Sugarloaf or West Cactus Peak in the Coso field [Macko 1998]. It is therefore recommended that the samples be eliminated from further consideration.

At the other end of the continuum, there are four dates (11,770, 15,417, 19,329, and 25,259 B.C.) that are very old and much earlier than the generally accepted age for humans in the New World. Although pre-Wisconsin glacial age occupations have been documented in the western hemisphere (Adovasio et al. 1983; Dillehay 1997), there is no additional artifactual or radiocarbon dating evidence to support their occurrence at CA-ORA-64. It is likely that the hydrations observed on these samples are geological surfaces that were included in the sample because they could not be visually identified as such; therefore, the samples were removed from further consideration as the hydration does not reflect the appropriate context.

After the removal of samples that reflected obvious analytical error or a geological origin, an age range of 9,384 B.C. to A.D. 1100 remains. At this point, it is interesting to note that there is a large 1,700-year gap between the youngest cluster of samples (359 B.C. to A.D. 1100) and the older cluster (9,384 to 2,041 B.C.). The three samples in the latest cluster also happen to be more water rich, with concentrations between 0.48% and 0.90%. With one exception, all of the other samples have water concentration values between 0.09% and 0.13%. However, we were reluctant to eliminate this water-rich group of samples, since the reported concentrations fall within the range documented for the Coso Volcanic Field and one of the water-rich samples (UCLA-5333) is within the radiocarbon age range. It is unlikely that these results represent analytical errors. Thus, there appears to have been a single, nearly continuous occupation between 9,384 and 2,041 B.C., as well as a small and younger set of occupations occurring between 359 B.C. and A.D. 1100. The earliest and larger occupation correlates well with the documented radiocarbon age span of 7,000 to 2,300 B.C., although there are several outliers at the early end of the distribution. The smaller and more recent period of site use is not represented in the radiocarbon ages.

At this point, additional obsidian samples were processed from AMS-dated feature contexts to assess the degree of correspondence that might be obtained. Thirteen samples associated with four cultural features (Features 1, 2, 8, and 12)
Table 3
OBSIDIAN HYDRATION DATES FROM FEATURE CONTEXTS AT CA-ORA-64

<table>
<thead>
<tr>
<th>Lab No.</th>
<th>Feature No.</th>
<th>Rim (µ)</th>
<th>%OH-</th>
<th>2-Sigma AMS Date</th>
<th>Hydration Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>DL-99-13*</td>
<td>1</td>
<td>7.7</td>
<td>0.13</td>
<td>6,188-5,956 B.C.</td>
<td>3,213 B.C. ± 135</td>
</tr>
<tr>
<td>DL-99-14</td>
<td>1</td>
<td>9.4</td>
<td>0.13</td>
<td>-</td>
<td>5,660 B.C. ± 162</td>
</tr>
<tr>
<td>DL-99-15</td>
<td>1</td>
<td>10.4</td>
<td>0.13</td>
<td>-</td>
<td>7,179 B.C. ± 176</td>
</tr>
<tr>
<td>DL-99-2</td>
<td>2</td>
<td>8.2</td>
<td>0.13</td>
<td>7,586-7,420 B.C.</td>
<td>3,673 B.C. ± 138</td>
</tr>
<tr>
<td>DL-99-3</td>
<td>2</td>
<td>6.9</td>
<td>0.13</td>
<td>and</td>
<td>2,186 B.C. ± 120</td>
</tr>
<tr>
<td>DL-99-4</td>
<td>2</td>
<td>9.2</td>
<td>0.13</td>
<td>7,073-6,758 B.C.</td>
<td>5,164 B.C. ± 156</td>
</tr>
<tr>
<td>DL-99-5</td>
<td>2</td>
<td>9.2</td>
<td>0.13</td>
<td>-</td>
<td>5,132 B.C. ± 155</td>
</tr>
<tr>
<td>DL-99-6</td>
<td>2</td>
<td>11.0</td>
<td>0.65</td>
<td>-</td>
<td>A.D. 522 ± 26</td>
</tr>
<tr>
<td>DL-99-8</td>
<td>2</td>
<td>9.1</td>
<td>0.13</td>
<td>-</td>
<td>5,146 B.C. ± 156</td>
</tr>
<tr>
<td>DL-99-10</td>
<td>8</td>
<td>11.4</td>
<td>0.13</td>
<td>5,950-5,691 B.C.</td>
<td>8,871 B.C. ± 191</td>
</tr>
<tr>
<td>DL-99-9</td>
<td>12</td>
<td>7.4</td>
<td>0.13</td>
<td>7,147-6,813 B.C.</td>
<td>2,651 B.C. ± 125</td>
</tr>
<tr>
<td>DL-99-11</td>
<td>12</td>
<td>7.9</td>
<td>0.13</td>
<td>-</td>
<td>3,189 B.C. ± 132</td>
</tr>
<tr>
<td>DL-99-17</td>
<td>12</td>
<td>6.7</td>
<td>0.13</td>
<td>-</td>
<td>1,948 B.C. ± 117</td>
</tr>
</tbody>
</table>

* DL = Diffusion Laboratory.

were processed (Table 3). The degree of correspondence between the age determinations of the two methods is very poor and in no instances do the obsidian dates fall within the two-sigma age range of the AMS dates. The obsidian dates show no consistent pattern and are either considerably older or younger than the AMS range. What is encouraging, however, is that the overall obsidian date range for these samples (7,179 to 1,948 B.C.) again correlates very well with the overall AMS date range, with the exception of one outlier at each end (8,871 B.C. and A.D. 522). While the poor matches suggest that the integrity of the specific features may have been compromised, the overall correspondence in range is encouraging. This example also demonstrates the difficulty of empirically developing a hydration rate from archaeological field data.

**DISCUSSION AND CONCLUSION**

The objective of this article is to address the long-term assumptions of obsidian hydration dating in light of the new experimental results that have been published over the last few years. It has been argued that the new water dependence model of glass hydration has a strong foundation in the experimental literature and is the most appropriate approach to the absolute and/or relative dating of glass artifacts. With this empirical foundation, certain long-held assumptions about the behavior of natural glasses in the environment are less secure. We believe that a high potential for intraflow variability in hydration rate exists within volcanic glass sources and flows, and that the degree of water variation should be explored by those wish to apply the method to their region of study. We maintain that the trace element composition and variability within a geological flow is probably unrelated to the quantity of volatile components in the magma and hardened glass. Consequently, major or trace element compositional analysis may not always be the appropriate analytical technique, unless additional research demonstrates that a specific flow is uniform in its water content.

It has further been argued that obsidian hydration is a complex process within its natural context. Soil temperature and relative humidity are two influential factors that require long-term monitoring with sensors to arrive at estimates for
these variables under current ambient conditions. With this as background, we have great difficulty with the tradition of estimating hydration rates using contexts where the critical parameters of glass hydration are poorly controlled. It is our opinion that archaeological contexts and their chronometric dates should be the proving grounds for the modeling processes behind the dating procedures rather than the empirical foundation for hydration rate development. The approach outlined herein starts with an explicit model and extrapolates to the past to arrive at an estimated age for the archaeological context. If the age is inexact in comparison to the radiocarbon age, one must question not only the integrity of the archaeological context but the parameters of the model and the analytical techniques used to develop it. The transformations that create the archaeological context are vague and only partly reconstructable, and as a result, validation comes through repeated application.

In that light, a case study from CA-ORA-64 has been presented. The correspondence between the large suite of high-precision AMS shell dates and the obsidian dates is encouraging. The vast majority of the samples with low intrinsic water values fall within or slightly exceed the radiocarbon age range of 7,000 to 2,300 B.C. This is indeed a positive sign. Less encouraging is the small set of outlier dates for the water-rich glasses (>0.4% OH-), which have returned dates far removed from the last radiocarbon dated event. Is this an undetected set of occupations or the consequence of a faulty estimate of the intrinsic water content? For the present, it is proposed that the late dates are valid, since they are expected outcomes from the hydration model and are equivalent to those dates that fall within the range of expected age determinations. If late dates on water-rich samples become repeated outliers in the evaluation process, then a reconsideration of the water content model would certainly be in order. Until then, we are confident that the new model of glass hydration and the dates it produces, when rigorously applied, will provide accurate chronometric dates for archaeological contexts.

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