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THE EXPERIMENTAL HYDRATION OF OBSIDIAN AS A FUNCTION OF RELATIVE HUMIDITY AND TEMPERATURE

J. J. Mazer, C. M. Stevenson, W. L. Ebert, and J. K. Bates

The experimental hydration of obsidian for up to 30 days is described at relative humidities (RH) of 60, 90, 95, and 100 percent and at temperatures of 150, 160, and 175°C. Under isothermal conditions, the rate of hydration increased by as much as 25 percent between 60 and 100 percent RH. The RH dependence is nonlinear, with the majority of the rate increase occurring between 90 and 100 percent RH. The effect of RH can be related to the driving force for molecular water diffusion in obsidians as described by the chemical potential difference between water sorbed onto the obsidian surface and intrinsic water in the obsidian. The differences in hydration rates caused by RH differences in experiments approximate the error commonly described for obsidian-hydration dating. These results suggest that obsidian-hydration dating requires a knowledge of the site temperature and relative humidity in order to accurately generate age estimates.

Se describe la hidratación experimental de obsidiana por hasta 30 días, a humedades relativas (HR) de 60, 90, 95, y 100 por ciento y a temperaturas de 150, 160 y 175°C. En condiciones isotérmicas, el grado de hidratación aumentó hasta un 25 por ciento entre 60 y 100 por ciento de HR. El efecto de la HR puede estar relacionado con la fuerza que impulsa la difusión molecular del agua en obsidianas, descrita por la diferencia en el potencial químico entre el agua absorbida en la superficie y el agua intrínseca en la obsidiana. La diferencia en los grados de hidratación causada por diferencias en HR durante los experimentos se aproxima al error comunmente descrito para la datación por hidratación de obsidiana. Estos resultados sugieren que la datación por hidratación de obsidiana requiere el conocimiento de la temperatura y humedad relativa del sitio a fin de generar estimaciones de antigüedad exactas.

When the obsidian-hydration dating (OHD) method originally was described by Friedman and Smith (1960) there were hopes that this technique would be an easily implemented absolute-dating technique used by scientists in a variety of disciplines. The basis of OHD uses measurements of the thickness of the birefringent hydration layer formed on an obsidian surface in conjunction with estimates of the ambient temperature to estimate the period of time since the glass surface was exposed to water. The rate of the layer formation was described by Friedman and Smith (1960) as

$$l = k \cdot t^{1/2} \quad (1)$$

where l is the layer thickness, t is time, and the proportionality constant, k , describes the temperature dependence of the process. The dependence of the rate of layer formation with the square root of time is characteristic of a diffusion-controlled process, and subsequent studies have confirmed that the rate-determining step for obsidian hydration is the inward diffusion of molecular water (Bates et al. 1988; Doremus 1964; Lee et al. 1974).

The OHD technique was expanded subsequently in Friedman and Long (1976), where experimental methods were described for inducing hydration at elevated temperatures in water-vapor atmospheres. Later researchers have chosen to perform induced-hydration experiments in hydrothermal apparatuses (e.g., Michels et al. 1983). Differences observed in the compositions and thicknesses of experimentally hydrated obsidians have demonstrated that different reactions can occur in these two systems (Bates et al. 1988). Hydrothermal experiments result in significant amounts of etching of obsidian surfaces and the resultant hydration-layer thickness may not be representative of ambient conditions. In order to avoid these complexities, we have chosen to perform experiments in steam atmospheres.

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Table 1. Obsidians Used in Hydration Experiments.

Element	Coso 4-1	Mule Creek	Orito Quarry
SiO ₂	74.94	73.6	72.11
Al ₂ O ₃	14.20	14.34	14.16
Na ₂ O	4.67	4.62	5.47
K ₂ O	4.59	4.45	4.33
CaO	.53	.65	.69
MgO	.02	.06	.03
MnO	.03	.05	.06
Fe ₂ O ₃	.96	.97	3.17
TiO ₂	.04	.06	.19
Cu	153	—	—
Zn	47	—	222
Rb	198	—	60
Sr	17	—	19
Y	9	—	36
Nb	23	—	45
Pb	35	—	—
Zr	57	—	458
Ba	—	—	593
H ₂ O	.87	.19	.15

Note: — = not analyzed. Oxides are weight percent values analyzed by XRF. Elemental values are in ppm. H₂O analyzed using the Penfield method (Jeffery and Hutchinson 1981).

Ericson (1988) recently has reviewed the development of OHD and outlined several of the weaknesses/problems of the technique. These include errors in measuring hydration rims, an incomplete understanding of the hydration process and its controlling variables, including the effect of obsidian composition, and the effect of environmental variables including relative humidity (Ericson 1988). Presently, OHD relies on an empirical approach that requires the development of a separate hydration rate for each obsidian source.

A relation between relative humidity and alteration rates has been described for experimental studies of glasses with complex reaction mechanisms (Abrajano et al. 1989; Bartholomew et al. 1980; Tomozawa and Tomozawa 1989; Tomozawa et al. 1984; Yoko et al. 1983). Although obsidian artifacts used in OHD have been exposed to a wide range of relative humidities, it has been assumed that this parameter is unimportant to the relatively simple process of obsidian hydration (Friedman and Smith 1960). In this study we investigated the effects of relative humidity on obsidian hydration at elevated temperatures. We have chosen to perform carefully controlled experiments at 60, 90, 95, and 100 percent RH. These values appear to be the bounding range of archaeologically relevant conditions based on the limited results where RH within soils have been reported (Cleland 1990; Friedman et al. 1990).

EXPERIMENTAL METHODS

Obsidians were collected from three sites: the Coso field, California; Mule Creek, New Mexico; and Orito Quarry, Easter Island. Preliminary experiments indicated that these obsidians hydrated at rates ranging from relatively fast (Coso) to relatively slow (Orito Quarry). All samples were collected from the same flow at each source in order to ensure that identical materials were being used in all experiments. X-ray fluorescence (XRF) analyses have been performed on each obsidian to determine their bulk compositions, and are presented in Table 1.

Glass discs were prepared by initially core drilling pieces of each obsidian. Fresh, unhydrated core sections were selected for use in hydration experiments. Each core was sliced into discs approximately 1 mm thick. Two radially opposed notches were made on each disc to allow each sample to be later suspended by a Teflon® thread within a test vessel. Each face of the disc was

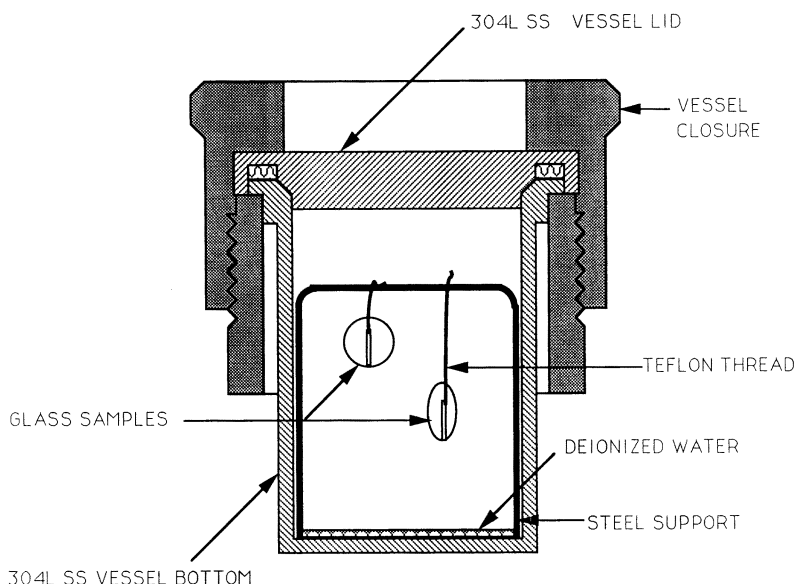


Figure 1. Schematic drawing of a Parr 304L stainless-steel vessel used in 100 percent RH hydration experiments.

polished initially with 600 grit Carborundum paper, using water as a lubricant. Diamond pastes (Buehler) of 6 and 1 μm with oil (Buehler Metadi fluid) as a lubricant were used to achieve the final finish. Between each polishing step, the discs were thoroughly rinsed and ultrasonically cleaned in methanol. Glass preparation was generally performed on the same day that experiments were started to minimize the effects of atmospheric water interaction.

Each polished disc was suspended from a stainless-steel support by a Teflon[®] thread. Samples were arranged so that they contacted neither the vessel walls, the stainless-steel support, nor other samples. Immediately prior to the initiation of each experiment, the suspended samples were thoroughly rinsed in methanol and allowed to air dry.

Experiments were conducted in ovens (Blue-M, model #OV-490A-2) where the temperature was controlled to $\pm 1^\circ\text{C}$. Two experimental setups were used to allow different relative-humidity conditions. Experiments were performed at 100 percent RH using sealed Parr[®] stainless-steel vessels with softened Cu gaskets (Figure 1). The suspended samples were placed in a vessel and preheated to 200°C for approximately two hours. The vessels then were placed in a pan of water and a known volume of distilled water was immediately added to the cooled vessel bottom. The vessel then immediately was sealed and placed in the oven. This step reduced preferential condensation on the glass surface when the experiment was initiated. The experimental method has been described in detail by Ebert and Bates (1990).

Experiments at 95, 90, and 60 percent RH were performed using a dual oven apparatus (Figure 2). This apparatus consisted of two pressure vessels connected by a tube. A supply vessel held the volume of water used to produce vapor at a given pressure within the reaction vessel. Each vessel resided in a separate oven, allowing the temperature and pressure in the reaction vessel to be controlled independently. This technique allowed us to control the relative humidity to ± 2 percent, though in most experiments we maintained an uncertainty of ± 1 percent. The vessels were allowed to heat to the reaction temperature before introducing steam to the reaction vessels.

At the termination of each experiment, each sample was thin-sectioned and the hydration layer measured, using established procedures (Stevenson et al. 1987). An Aus Jena optical microscope with a $40\times$ objective was used to examine $30\text{-}\mu\text{m}$ -thick sections of each sample. The hydration-layer thicknesses reported are the average of seven measurements on each sample with a variation

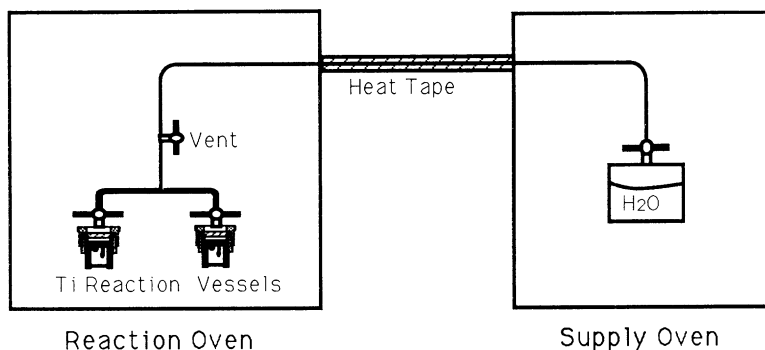


Figure 2. Schematic drawing of the dual oven apparatus used in 90 and 60 percent RH hydration experiments.

of $\pm 2 \mu\text{m}$. All samples were measured by the same operator so that any systematic operator-induced errors would be constant throughout the data set (see Stevenson, Dinsmore, and Scheetz 1989).

RESULTS AND DISCUSSION

To establish whether obsidian hydration in our experiments was similar to that reported by others we considered the nature of the hydration-layer formation with respect to time. Figure 3 shows the relation between the hydration rim and $\text{time}^{1/2}$ for Coso 4-1 obsidian experimentally hydrated at 175°C and 100, 90, or 60 percent RH. At each set of experimental conditions, the rate of growth of the hydration layer is proportional to the square root of time and the trend of the data intercepts at or near the origin. Similar proportionalities between hydration-layer formation and time also were obtained for Mule Creek and Easter Island obsidians. Our results have a time dependence identical to that previously described by Friedman and Long (1976) and are consistent with a diffusional rate-controlling reaction mechanism.

Linear-regression fits to the hydration-rim measurements were used to derive hydration-rate constants, in units of $\mu\text{m}/\text{days}^{1/2}$ (Table 2). The correlation coefficients of each fit were greater than

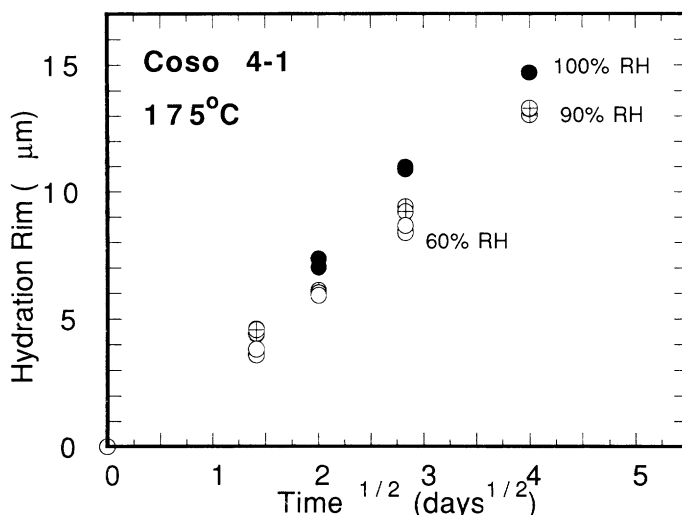


Figure 3. Graph of measured hydration-rim thickness vs. the square root of time for Coso 4-1 obsidian at 175°C and 100 (solid circles), 90 (sectioned circles), and 60 (open circles) percent RH.

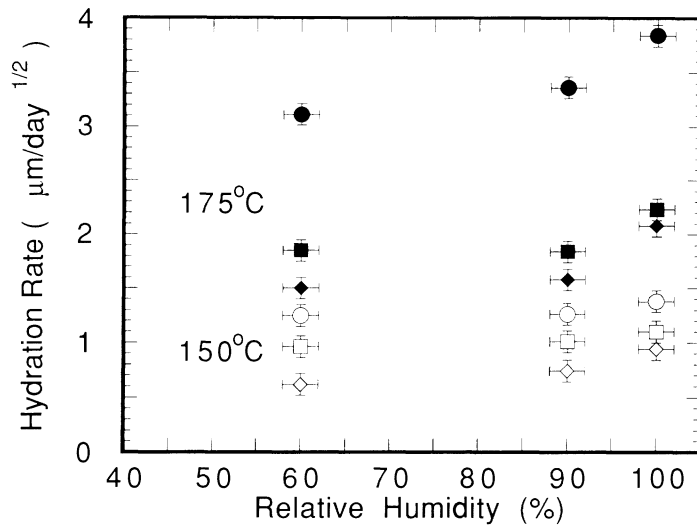


Figure 4. Experimentally determined 150 and 175°C hydration rates as a function of RH. Experiments were performed with obsidian from Coso 4-1 (circles), Mule Creek (squares), and Easter Island (diamonds).

.95 and in most cases were greater than .98. These values have an estimated total error from all sources of no more than $.1 \mu\text{m}/\text{day}^{1/2}$. At 60 and 90 percent RH, at constant temperature, the hydration rates are constant, or nearly so, within experimental error. Between 90 and 100 percent RH, there is a significant difference in the measured hydration rates that range from 10 to 30 percent depending on glass composition. Figure 4 graphically presents the hydration rates given in Table 2 as a function of relative humidity. These results demonstrate that relative humidity significantly affects the experimental hydration rates of obsidian.

It was hypothesized originally that relative-humidity effects could be discounted because an obsidian surface is covered by a monolayer of water at RHs as low as three percent (Friedman and Smith 1960; Friedman et al. 1966). Subsequent additions of water to an obsidian/water system were not believed to affect the reaction. However, our results suggest that the diffusivity of water into obsidian is significantly affected by the vapor pressure in contact with a glass surface. In order to understand how relative humidity affects the hydration of obsidian, we considered water sorption on glass surfaces. The amount of water sorbed onto a crushed sample of Coso 4-1 obsidian was

Table 2. Experimentally Determined Hydration Rates ($\mu\text{m}/\text{days}^{1/2}$).

Temperature (°C)	RH (%)	Coso 4-1	Mule Creek	Easter Island
175	100	3.83	2.23	2.08
175	90	3.36	1.84	1.58
175	60	3.11	1.85	1.50
160	100	2.13	1.35	1.14
160	95	1.92	—	—
160	90	1.78	1.20	.96
160	60	1.79	1.17	.95
150	100	1.38	1.10	1.01
150	90	1.26	1.01	.84
150	60	1.25	.96	.62

Note: — = not determined. These values have an estimated total error from all sources of no more than $.1 \mu\text{m}/\text{day}^{1/2}$.

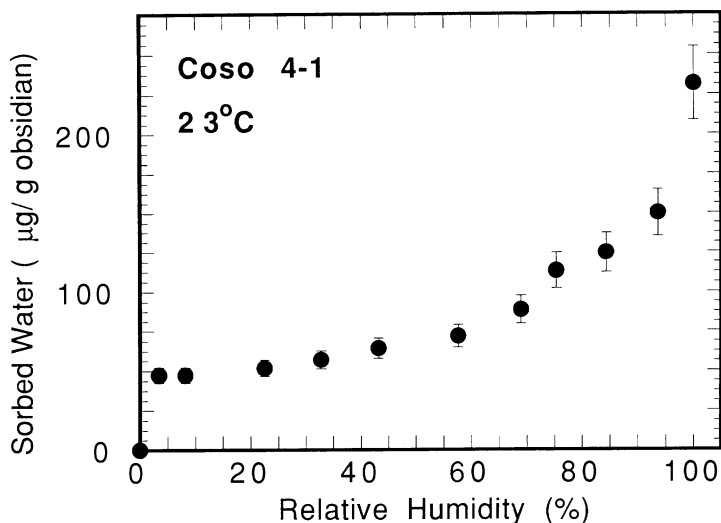


Figure 5. Sorption isotherm collected at room temperature for Coso 4-1 obsidian.

gravimetrically determined as a function of relative humidity at 23°C (Figure 5) (Ebert et al. 1991). Each point represents the mass of water sorbed onto glass at constant relative humidity. Qualitatively, these results show that RH has a similar relation on water sorption as we observe for hydration-rate constants (Figure 4). The sorption data can be fit by the relation

$$\theta = [-b/\ln(\text{RH}/100)]^{1/r} \quad (2)$$

where θ is the number of monolayers of water sorbed onto the glass surface which is proportional to the mass sorbed, b is a constant equal to 1.9 and r is a constant equal to 2.6 that accounts for interactions between the surface and sorbed multilayers (Ebert et al. 1991). Similar isotherms have been measured for water on a large number of simple oxides by Hagymassy et al. (1969), and this shows that the amount of sorbed water increases rapidly above 80 percent RH.

Hagymassy et al. (1969) have described the water that initially sorbs onto a surface at low relative humidities as a statistical monolayer, corresponding to the first 50 µg of sorbed water (Figure 5). After this water initially is sorbed there is little increase in the amount of sorbed water with increasing relative humidity, up to approximately 90 percent RH. Above 90 percent RH the amount of sorbed water rapidly increases with relative humidity, as water saturation of the vapor phase is approached. Near 100 percent RH it is calculated, based on (2), that approximately six statistical monolayers cover the surface.

With respect to glass surfaces, Hagymassy's statistical monolayer describes water molecules hydrogen bonded to surface silanol (SiOH) sites, where sorption is strongest. The weak dependence between RH and additional sorbed water between the sorption of the initial statistical monolayer and approximately 90 percent RH is thought to reflect the accumulation of additional water onto the strongly bound water at surface silanol sites. The rapid increase in sorbed water above 90 percent RH occurs after surface tension causes the coalescence of the sorbed water into a film that covers the entire glass surface (Ebert et al. 1991).

The driving force for a diffusion mechanism can be described thermodynamically by the chemical-potential gradient of the interacting species. In the case of obsidian hydration (molecular water diffusion) this gradient is defined by the difference between the chemical potentials of water sorbed on the glass, $\mu(s)$, and the intrinsic water in the glass, $\mu(gl)$. The force required for a unit of solute to diffuse from the sorbed-water phase into the glass phase over a distance x is then defined by

$$\text{Force} = -(d\mu/dx) = -\left[\frac{\mu_s - \mu_{gl}}{dx}\right] \quad (3)$$

where for a given glass, μ_{gl} is constant. This approach predicts that a change in the chemical potential of the sorbed water will affect the diffusional force, and be reflected in the measured hydration-rate constants. We observe that hydration rates are related to the amount of sorbed water on obsidian surfaces (Figure 5), and therefore, the chemical potential of sorbed water, $\mu(s)$. The chemical potential of water is not readily measured on glass surfaces, but empirical observations can be used to estimate relative-humidity effects on obsidian hydration.

IMPLICATIONS FOR OBSIDIAN-HYDRATION DATING

The results of our experiments suggest that obsidian hydration is a relatively simple process of water diffusion that is controlled by the environmental variables temperature and relative humidity. By carefully controlling these parameters we have demonstrated that reproducible experimental hydration rates can be derived that are consistent with our understanding of the hydration process.

The most important implication for obsidian-hydration dating is that relative humidity is a critical parameter that must be accounted for. Accurate OHD age estimates for obsidian artifacts can be generated using experimental work performed at 100 percent RH only if the artifacts have experienced a similar RH history. Experiments performed at 100 percent RH will tend to underestimate the ages of artifacts exposed predominantly to lower relative humidities, as shown in Figure 6, even though the difference between hydration rates performed at 60 and 90 percent RH is within experimental error. The lines labeled "100 percent RH baseline" on Figure 6 represent the assumption that relative humidity is unimportant to obsidian hydration. The difference between the 100 percent RH baseline and the experimentally determined rate indicate the type of error included in the age estimate when relative humidity is not accounted for.

The application of these findings to field situations will require that site depositional contexts be monitored carefully. Recent studies have demonstrated that both effective hydration temperature (EHT) and relative humidity (RH) may vary appreciably at specific locations. Using various designs of temperature monitoring cells (Ambrose 1976, 1980; Trembour et al. 1988) EHT determinations have been recorded at a variety of locations. Temperatures recorded by Ambrose (1984) for a 1.5-m-deep profile at Lake Mungo, Australia, indicated a 1.2°C difference between 5 and 150 cm for a dry lake floor setting. A similar study by Leach and Hamel (1984) for a coral-sand site in New Guinea documented a 3.2°C difference in EHT between 18 and 90 cm. Within the United States, research at the Coso volcanic field in California has documented a 2°C fluctuation between 5 and 75 cm below the surface (Cleland 1990). As noted in the papers cited above, the variations in ground temperature are due to the combined differences in soil-moisture content, sediment type, aspect and ground cover, and are measurements over relatively short time periods.

Information on annual soil relative humidities has been collected just recently. An ambitious study by Friedman et al. (1990) has recorded soil RH values for a number of "dry" to "very dry" sites in California and Wyoming. In many cases, soil relative humidities are 100 percent at depths of 50 cm below the surface. In the upper regions of the soil horizon RH values of around 80–85 percent were typical for many settings. On subtropical Easter Island, Chile, RH values ranged between 82 and 92 percent for surface contexts at open-air sites but quickly reached 100 percent by a depth of 10 cm (Stevenson and Friedman 1990).

The early investigations into soil EHT and RH suggest that these variables may vary appreciably between and within regions. In subtropical areas the influence of RH may only be significant in near-surface contexts. In more temperate areas, however, the combined effects of RH and EHT may be considerable. For example, Figure 7 graphically depicts the differences in RH and EHT with depth below surface for a 1-m section at the Coso volcanic field (Cleland 1990). In this case, recorded RH values at the site varied between 68 percent (5 cm) and 97 percent (100 cm). The temperature spanned a 1.5°C range (22.0–23.5°C). Based on our experimental results we assumed that the hydration rate for Coso obsidian decreases by approximately 25 percent when RH varies

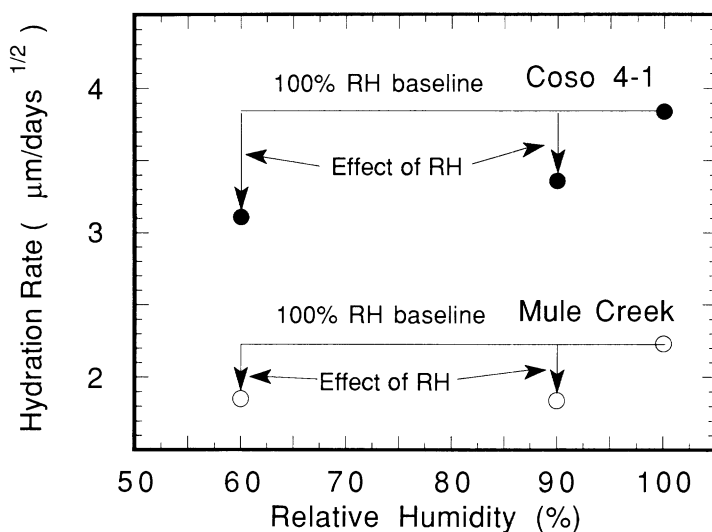


Figure 6. Graph of experimentally determined 175°C hydration rates as a function of RH for Coso 4-1 (filled circles) and Mule Creek (open circles) obsidians. Easter Island obsidian omitted for clarity. The lines labeled “100% RH baseline” represent the assumption that RH is unimportant to obsidian-hydration processes.

from 97 to 68 percent. When the temperature difference also is accounted for in this calculation the result is that the hydration rate varied by nearly an order of magnitude within a 1-m soil profile.

The above case example is probably a “worst-case” scenario, but it has illustrated the importance of recording environmental conditions at prehistoric sites. Accounting for the effects of relative humidity, in addition to temperature, should result in more accurate dating results and provide a basis for more widespread use of obsidian-hydration dating in archaeological and other communities. Recent developments in temperature and relative-humidity monitoring techniques make this more practical. However, they require that the researcher take an active role in the dating process.

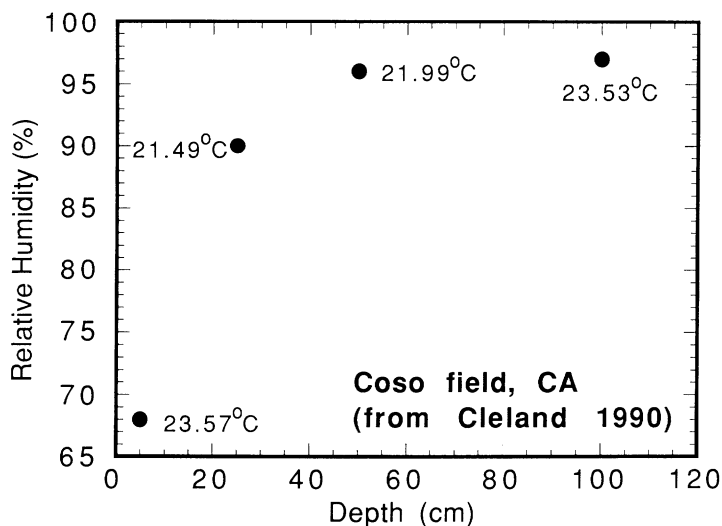


Figure 7. Graph showing the variation of RH and EHT along a 1-m depth profile from Coso volcanic field, California (Cleland 1990).

Nonetheless, these instruments and techniques have the potential to allow OHD to become a simple and routine dating tool including a recognition of the potential error in extrapolating current RH measurements back in time.

CONCLUSIONS

We find a significant effect of relative humidity on the hydration of three obsidians, particularly between 90 and 100 percent RH. This effect can be related qualitatively to the amount of water sorbed onto the glass surface and persists over the entire temperature range examined. This effect is believed to reflect the chemical potential difference of water in the glass and on the glass surface. These results support the assertions of others that careful measurements of temperature and relative humidity at a site are necessary to use obsidian-hydration dating successfully (Stevenson, Carpenter, and Scheetz 1989).

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