

Obsidian Hydration Dating

Ioannis Liritzis*

Laboratory of Archaeometry, Department of Mediterranean Studies, University of the Aegean, Rhodes, Greece

Definition

Obsidian: Obsidian is an aluminosilicate, or rhyolitic, glass, formed by rapid cooling of volcanic magma under the proper geologic conditions. As any other glass, it is not a crystal, and thus it lacks the lattice structure typical of crystals at the atomic level. However, glasses do possess some degree of spatial order. Thus, it is an amorphous natural glass that contains pristine water H₂O and sparse crystals of variable sizes of a few microns. The surface is weathered in the atmosphere and the environmental context. Composition: 70–75 % SiO₂, 10–15 % Al₂O₃, 3–5 % Na₂O, 2–5 % K₂O, 1–5 % FeO₃ + FeO (in contrast to iron-bearing glass and silica-enriched leached rinds on obsidian glass recently discovered on Mars that are representative of global processes of explosive volcanism potentially implying widespread acidic leaching on Mars due to oxidizing and acidic solutions). Obsidian rocks were used by early peoples for the making of their tools and implements.

Obsidian Hydration

In its most basic aspect, hydration simply describes the process by which water is absorbed by obsidian and involves physicochemical changes in the glass (Doremus 2002; Anovitz et al. 2008; Liritzis and Stevenson 2012). The six steps of the process involve:

1. Environmental water molecules adsorb on the surface which exhibits roughness at the nanoscale creating a large surface concentration.
2. Absorption into the glass and diffusion into the interstices in the glass matrix occurs. The diffusion process seems to be driven by two properties of the water molecules: a concentration gradient and osmotic pressure or chemical potential. Although it has been suggested that chemical reactions play a role (Doremus 2002, 108 ff.), it is at present a matter of speculation.
3. A water saturation layer is then formed within a short period of time after the start of the diffusion process. Following this period, the saturated layer increases with depth as time progresses. The saturation conditions on the surface represent the average conditions of the physical surroundings for the diffusion system during the elapsed time in a particular archaeological context. It depends on factors that include the kinetics of the diffusion mechanism for the water molecules, the specific chemical structure of obsidian, as well as the external conditions affecting diffusion (temperature, relative humidity, pressure) (Liritzis and Diakostamatiou 2002; Liritzis 2006; Smith and Van Hess 1987).
4. The diffusing molecules stretch the glass matrix, causing an increase in volume in the hydrated region and a stress between unhydrated and hydrated regions.
5. Increased water concentration progresses into the glass, in time, its rate being a function of the initial openness of the glass, temperature, and the dynamics of the process itself.

*Email: liritzis@rhodes.aegean.gr

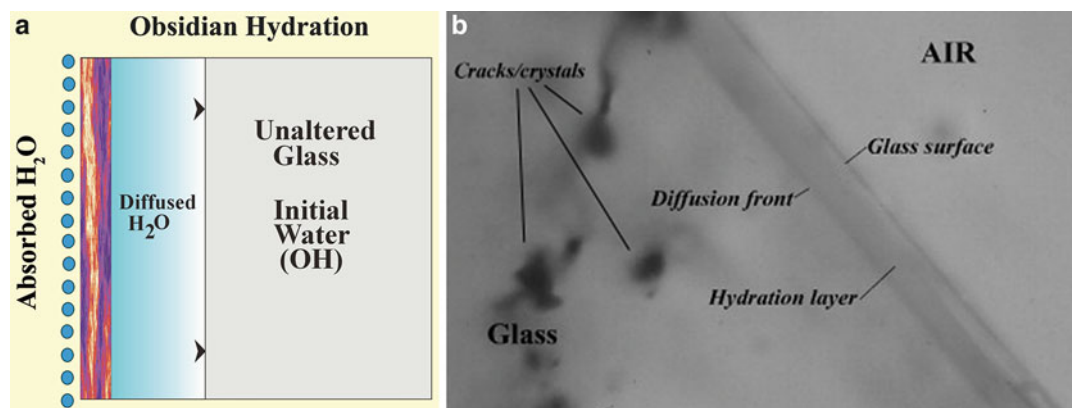


Fig. 1 (a) Schematic diagram of obsidian hydration of diffused water, (b) obsidian hydration rim seen through optical microscopy

6. When the hydrated layer becomes thick enough, typically greater than 20 μm , the accumulated stresses cause the layer to spall off as perlite.

Three general classes of methods have been proposed for measuring obsidian hydration: (a) measurement of water mass uptake or loss versus time by infrared (IR) (Ebert et al. 1991; Stevenson and Novak 2011; Stolper 1982), (b) direct measurement of water profiles versus depth by secondary ion mass spectrometry (SIMS) (Anovitz et al. 1999, 2004, 2008; Liritzis and Diakostamatiou 2002; Riciputi et al. 2002; Liritzis et al. 2004; Stevenson et al. 2004), and (c) observation of the leading edge of the stress zone by optical microscopy (e.g., Friedman and Smith 1960; Friedman and Long 1976; Stevenson et al. 1996).

The environmental water molecules entering obsidian glass depend mainly on (a) environmental temperature, (b) chemical composition, (c) mineralogical structure, and (d) intrinsic water content (see, Silver et al. 1990; Lanford et al. 1979). The deeper the water goes, the greater the time. The higher the environmental temperature in burial sites, the higher the diffusion rate, while for average environmental conditions it is ~ 1 mm/1,000 years (Figs. 1a, b and 2a, b). Attention is exerted on the precise determination of “hydration front,” i.e., the interface layer between unhydrated and hydrated glass. It is a zone of optical contrast when seen under polarized light, due to the phenomenon of “stress birefringence” (Born and Emil 1980, pp. 703–705). Measurement of this layer can be determined to within ± 0.2 μm using digital imagery at higher magnification (800 \times) (Ambrose and Novak 2012). A significant uncertainty can be introduced into the process as a result of poorly defined image quality stemming from improper sample preparation and weakly defined diffusion fronts. It has also been documented that diffused molecular water extends beyond the limits of the optical diffusion front (Stevenson et al. 2001; Tokoyama et al. 2008). Thus, the optical approach does not adequately document the full extent of the diffusion process.

Obsidian Hydration Dating (OHD)

The technique was initiated by Friedman and Smith (1960), where they noted that (a) the exposed surfaces of ancient obsidian artifacts had absorbed water, (b) the hydration birefringent rims were visible under high-power magnification (approximately $\times 500$), and (c) its width was dependent on time, chemical composition (i.e., obsidian quarry), and the temperature. They suggested that

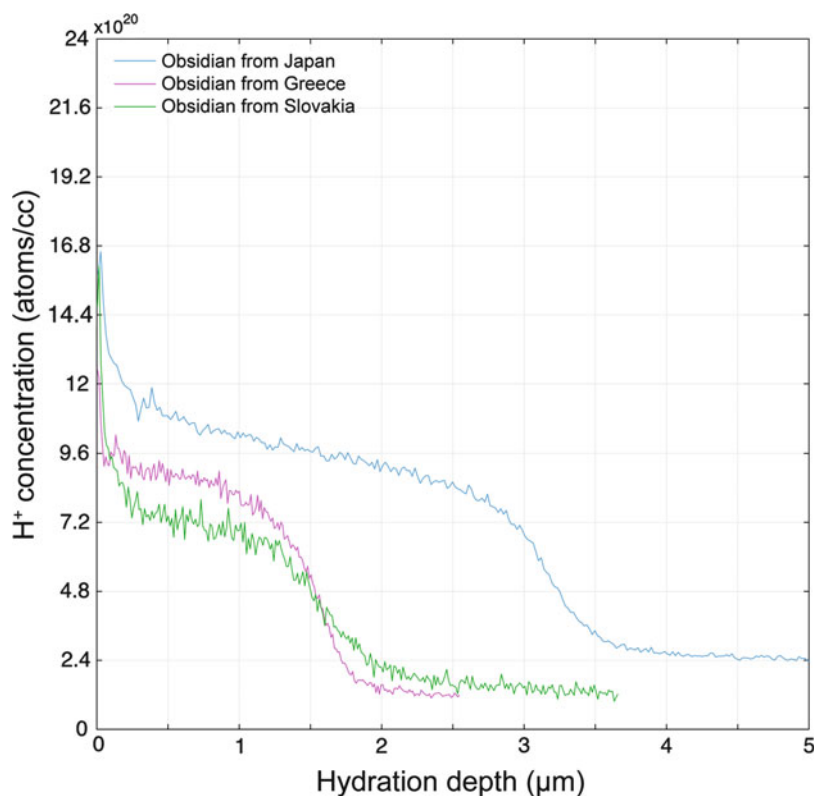


Fig. 2 SIMS H⁺ profiles for three samples from Greece, Japan, and Slovakia

hydration process converts a hydration layer of measured thickness to an absolute date with an established rate for the inward diffusion of molecular water using the empirical Eq. (1):

$$X = (kt)^{1/2} \quad (1)$$

where X is the hydration rim width in microns (μm), k is the hydration rate at a particular temperature/relative humidity, and t is time.

The thickness (X) and the k, which is dependent on the specific archaeological site conditions, are required for age determination.

The hydration rim was initially measured by optical microscopy (Friedman and Smith 1960; Michels, et al. 1983; Stevenson et al. 1989a, b), but inaccuracies in the determination of the end point of the water front (Hull 2001; Stevenson et al. 2002; Anovitz et al. 1999) lead to measurements with other nonoptical techniques, like nuclear reaction analysis, infrared photoacoustic spectroscopy (IR-PAS), and secondary ion mass spectrometry (SIMS) (Stevenson et al. 2000, 2002; Lee et al. 1974; Tsong et al. 1978; Duerden et al. 1982; Liritzis and Diakostamatiou 2002; Anovitz et al. 1999).

The diffusion coefficient was estimated at high temperature (160 °C) and extrapolation to ambient site conditions using the Arrhenius Eq. (3) (Michels et al. 1983; Stevenson et al. 2002; Friedman and Long 1976).

Research subsequent to Friedman and Smith's original presentation has refined the method into two distinct techniques. The simplest referred to as *empirical rate dating* (Meighan et al. 1968; Findlow and Bennett 1978; Meighan 1976; Kimberlin 1976) requires correlating the width to optically measured rims to independent chronometric data, such as ¹⁴C (e.g., Ambrose 1976). The

second more complex and widely applied known as *intrinsic rate dating* requires experimentally determined rate constants and a measure of site temperature (Michels et al. 1983; Friedman and Long 1976; Stevenson and Scheetz 1989; Hull 2001).

The mathematical model utilized in the intrinsic rate OHD was

$$X^2 = A t e^{-E/RT} \quad (2)$$

where X is the depth, A is a source-specific constant, the diffusion coefficient ($\mu\text{m}^2/\text{day}$) is a pre-exponential constant, t is time, and E is the activation energy (calories or Joules per mole), respectively, R is the gas constant (calories per degree per mole, i.e., 1.987), and T is the absolute temperature (Kelvin), in fact the effective hydration temperature (EHT).

Along with this method, the importance of connate water, the compositional indices, and density, in controlling the hydration rate of obsidians, has been demonstrated by several authors (e.g., Ambrose and Stevenson 2004).

Nevertheless, the assumptions made by Eq. (2) are questioned from the sigmoid hydrogen profiles measured by SIMS (Fig. 2).

However, in spite of over 50 years of development and application, of the classical OHD versions has produced consistently reliable results, with the exception of some sites of young age and/or well calibrated to ^{14}C and typology. In some cases, ages have so contradicted other well-established chronometric data that the utility of the obsidian as an independent chronometer had been questioned. The problems with OHD are due to the use of inappropriate analytical techniques, which involved nonsystematic errors arising there from the inherent imprecision of optical measurements, the experimental conditions of estimation of hydration rate, the need for calibration issues, and an improper (empirical) model of the hydration process. The scientific background has illustrated the complexity of the hydration process, and revised working assumptions for OHD have been proposed (Anovitz et al 1999; Friedman and Long 1976; Ambrose 1976; Stevenson et al 2000; Riciputi et al. 2002; Braswell 1992; Hull 2001; Rindings 1996; Liritzis and Laskaris 2012; Liritzis et al. 2004).

An advancement of OHD with a completely new approach – the monitoring of hydrogen profile in obsidian surfaces by SIMS (see below) – suggests that refinement of the OHD technique is possible in a manner which improves both its accuracy and precision and potentially expands the utility by generating chronological as well as palaeoenvironmental and usage data (Liritzis and Laskaris 2011). An earlier attempt of using nuclear reaction to monitor H^+ by depth has not been followed up (Tsong et al. 1981).

Another recent example of progress with classical OHD is based on accurate measurement by IR-PAS and calculation of diffusion rates. The rate of environmental molecular water diffusion depends on the total structural water content of the obsidian found in the bulk glass. As the process of mass uptake is a function of temperature, pressure, and openness of the glass matrix as measured by intrinsic water concentration, mass gain or loss proceeds proportional to t^n , where t is time and n is an exponent lying between approximately 0.5 and 0.6 shown by IR-PAS analysis in a series of 90 °C isothermal laboratory hydration experiments (Stevenson and Novak 2011). Later on, Stevenson et al. (2013) have applied this developed calibration to estimate hydration rates for obsidian based upon the structural water content of the glass as determined by IR-PAS to 53 Rapa Nui, Easter Island, Chile. Here, the Arrhenius constants (i.e., pre-exponential, activation energy) may be estimated from $\text{H}_2\text{O}t$ (see below).

Accuracy of Hydration Rim Measurements

In a satisfactory laboratory technique, accuracy is not limited by resolution of the microscope to $\sim 0.25 \mu\text{m}$, but probably lies in the range of $0.05\text{--}0.1 \mu\text{m}$, which is consistent with data reported. In a practical sense, measurement accuracy is more likely limited by the material properties of the obsidian. In any case, the accuracy of rim measurement is not a large contributor to the error in computed age in OHD (Rogers 2010), who points that computing a hydration rate is *not* a regression problem, however, but a problem of parameter optimization.

However, the apparent rim accuracy thus achieved is not the main factor in age determination. Each data point is a combination of valid data and experimental error, with major errors arising from site formation processes, association with radiocarbon or luminescence dating or the archaeological typology and obsidian, uncertainties in temperature, and fluctuations in the hydration rate which are not accounted for.

OHD Based on SIMS and IR-PAS Methodological Approaches

Initiated by Tsong et al. (1980; 1981), OHD based on SIMS has been followed by dozens of articles on the application of SIMS on obsidian artifacts but most on the determination of hydration layer, the diffusion of cations, and the dating. The direct measurement of the water profile measurement is generally performed by SIMS or the IR-PAS. The principle is to measure the concentration of H^+ ions, as a proxy for water, as a function of depth. The depth of penetration is typically measured by the end point (tail) where the water concentration has fallen to the pristine water concentration value at the surface.

Two teams at Oak Ridge (USA) and Rhodes (Greece) relied on the modeling of the H_2O concentration profile as a function of hydration depth, but following them in different ways. As a result, the ODDSIMS and the SIMS-SS coined versions were produced, respectively (Anovitz et al. 1999, 2004; Liritzis and Diakostamatiou 2002; Liritzis et al 2004; Liritzis and Laskaris 2009, 2011).

In using SIMS, an ion beam (usually Cs) bombards the obsidian surface. (The dating is based on the concentration of H as a proxy for H_2O versus depth) (Fig. 3).

The use of SIMS on obsidian surface investigations, although relatively infrequent, has produced great progress in OHD dating. In essence, it is a technique with a large resolution on a plethora of chemical elements and molecular structures in an essentially nondestructive manner (Liritzis and Laskaris 2011).

Anovitz et al. (1999) presented a model which relied solely on compositionally dependent diffusion, following numerical solutions (finite difference (FD) or finite element) elaborating on the H^+ profile acquired by SIMS. A test of the model followed using results from Mount 65, Chalco in Mexico, by Riciputi et al. (2002). This technique used numerical calculation to model the formation of the entire diffusion profile as a function of time and fitted the derived curve to the hydrogen profile. The FD equations are based on a number of assumptions about the behavior of water as it diffused into the glass and characteristic points of the SIMS H^+ diffusion profile. In fact, the depth of the half-amplitude point of S-like H^+ profile is found to be proportional to t^n , where t is time and n is an exponent lying between approximately 0.6 and 0.7 (Anovitz et al. 1999, 2004; Stevenson and Novak 2011). The half-amplitude measurement is again a function of temperature and openness of the matrix; however, since the measurement is made to a half-amplitude point, i.e., a relative measurement, the technique is not sensitive to the total amount of water present and should not be affected by pressure.

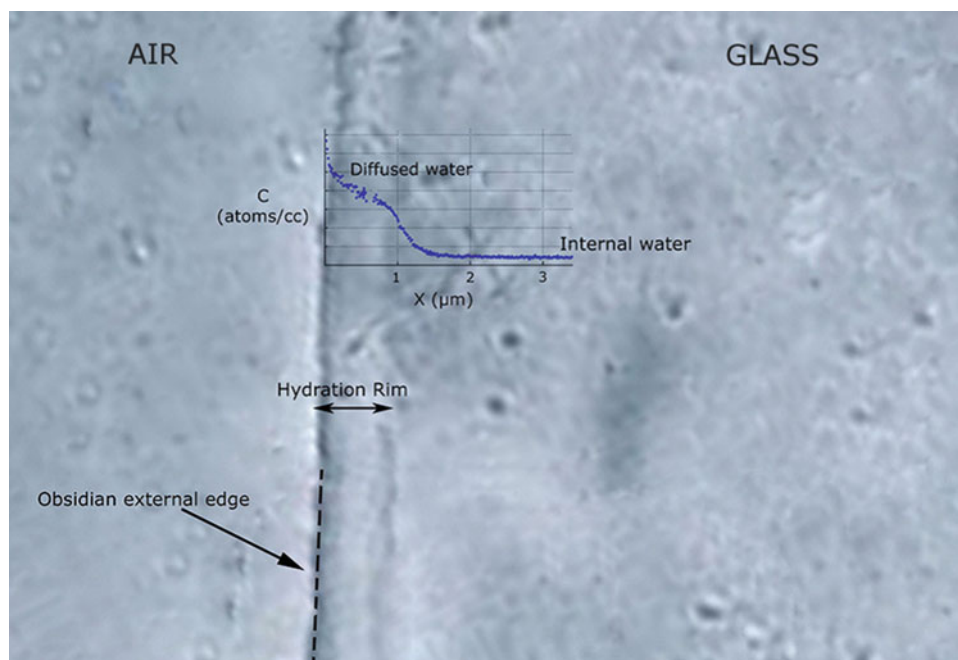


Fig. 3 Overlapping of SIMS H^+ profile in atoms/cc versus depth, on the hydration layer (rim), into the obsidian glass (Liritzis and Laskaris 2011)

In Rhodes, Greece, one dating approach is based on modeling the hydrogen profile, following Fick's diffusion law, and an understanding of the surface saturation layer (surface saturation, SS) and surface topography (Liritzis 2006; Liritzis et al. 2004; Liritzis and Laskaris 2009). The saturation conditions on the surface represent the average conditions of the physical surroundings for the diffusion system during the elapsed time in a particular archaeological context.

It has been shown (Liritzis 2006) that all of the H^+ profiles are broadly similar in form; however, this is their only shared property. Despite the fact that they are derived from the same type of geological material, close inspection of the shape of the profiles suggests that definite differences are present. These which are derived from the significant environmental impact as well as intrinsic effects may alter the form of the SIMS hydrogen profile. It is these slight variations in the profile that are case specific, and this is the important observation that the calculated age by SIMS-SS method relies upon. Therefore, each age calculation is based on this diffusion profile, which is unique for every obsidian sample. There are three advantages to this fully intrinsic procedure: (1) the final shape of the hydrogen profile, properly modeled, incorporates two of the principal external and highly variable environmental parameters, those of temperature and humidity; (2) the use of SIMS instrumentation to measure surface hydration layers results in high precision thickness (depth) values with an error of 0.02–0.05 μm depending upon the degree of surface roughness; and (3) absolute age estimates may be calculated. The currently used two methods, one based on SIMS (namely, SIMS-SS, SS for surface saturation) and the other on IR-PAS, are briefly described below.

The SIMS-SS Method

The water diffusion coefficient at any particular moment is expressed by the first derivative of the hydrogen profile. Its inverse ratio is the apparent hydration rate. The average depth of surface saturation layer X_s and corresponding saturation concentration C_s obtained from the determination of the SS layer gives the overall error attached to the SIMS-SS ages.

Using the end product of diffusion, a phenomenological model has been developed, based on certain initial and boundary conditions and appropriate physicochemical mechanisms that express the H₂O concentration versus depth profile as a diffusion/time equation. The modeling of this diffusion process is a one-dimensional phenomenon, where the H₂O molecules invade a semi-infinite medium in a perpendicular direction to the surface. The model is based on the idea that in the SS layer located near the sample surface, that is, in the first half of the sigmoid curve, the C is assumed as constant along a very short distance. Thereafter, C gradually decreases following the trend of the sigmoid. In brief, the three principles used for dating are (a) the comparison of a nondimensional plot with a family of curves of known exponential diffusion coefficients; (b) the correlation between the rate of transfer (diffusion) from the surface with the diffusion duration, the saturation concentration C_s, the intrinsic (pristine) water concentration C_i, the diffusion coefficient D_s (defined the flux/gradient, where gradient or tangent = dC/dx), and the following Boltzmann's transformation and auxiliary variables; and (c) the modeled curve of diffusion profile (concentration versus depth) of Eq. (3) (see Liritzis et al. 2004; Liritzis and Laskaris 2012).

$$C = e^{a+bx+cx^2+dx^3} \quad (3)$$

The dating in Eq. (4) that has been proposed incorporates all the abovementioned parameters:

$$T = \frac{(C_i - C_s)^2 \left[\frac{1.128}{1 - \frac{0.177kC_i}{C_s}} \right]^2}{4D_{s, \text{eff}} \left(\frac{dC}{dx} \Big|_{x=0} \right)^2} \quad (4)$$

where C_i is the intrinsic concentration of water, C_s the saturation concentration, D_s = dC/dx the diffusion coefficient for depth equal to zero, D_{s,eff} the effective diffusion coefficient empirically derived from a set of well-known ages and Eq. (5) as the effective value of the diffusion coefficient D_s for C = C_s, and k is derived from the family of Crank's curve. It is:

$$D_{s, \text{eff}} = a * D_s + b / (10^{22} * D_s) \quad (5)$$

where D_s = (1/(dC/dx)) * 10⁻¹¹ assuming a constant flux and taken as unity (Liritzis and Laskaris 2009; Liritzis 2006; Brodkey and Liritzis 2004). Equation (5) and assumption of unity are a matter of further investigation.

Often, the obsidian surface at the micro- and nanoscale is not smooth, and this influences the diffusion of water and, as a result, the SIMS profile. Polarized light microscopy (PLM) and atomic force microscopy (AFM) (Fig. 4) have been used to examine the obsidian surface and investigate any correlation between the surface roughness and the SIMS measurements (Liritzis et al. 2007). As proposed by Liritzis et al. (2008a, b), a linear regression fit in the diffused region defines the dispersion which reflects the degree of surface roughness. The smoother the surface, the less pronounced the dispersion of the data points to either side of the trend line and the smoother the SIMS diffusion profile. The surface roughness measured by the AFM instrument is linearly correlated with the standard deviation of the residuals between the data points (H⁺ values of g/mol or atoms/cc) and the linear fit in the diffused region of SIMS. This proportionality aids the selection of appropriate obsidian samples/surfaces for dating and also for the proper choice of the spot where the SIMS analysis is performed. Last, the smooth variation of other monitored cation

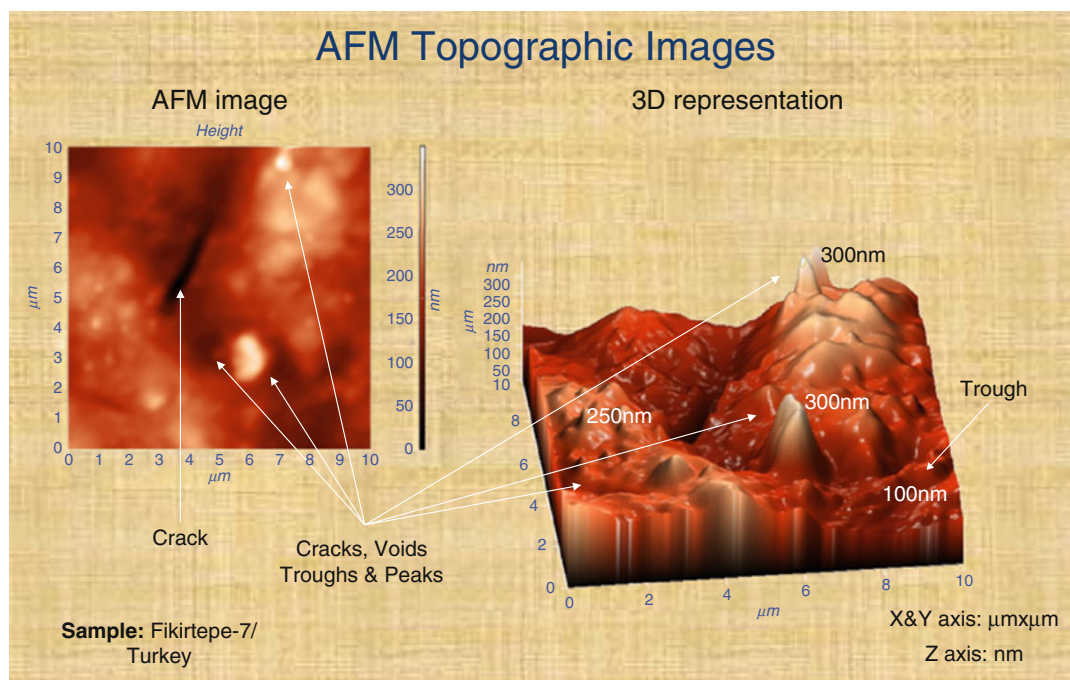


Fig. 4 Atomic force microscopy on obsidian surface indicates surface roughness, most significant parameter for accurate SIMS H⁺ profiling (Liritzis and Laskaris 2009)

profiles (K, Fe, Si, Mg, F, Al) and mapping of ion rastered surface areas act as criteria for acceptable and safe further numerical evaluation of H⁺ profiles.

The validity of these new procedures is tested through a comparison with independently derived age determination. A suite of samples from Easter Island (Chile), Mexico, Greece, Japan, Asia Minor, and Hungary, ranging from few hundreds to 30,000 years ago, have been used, derived from archaeological contexts dated by the radiocarbon method or ceramic associations. Indeed, the convergence between the two dating methods is high (Figs. 5). The SIMS-SS age estimates fall within the expected age ranges for the archaeological contexts for all samples (Liritzis and Laskaris 2009; Liritzis 2010). Table 1 gives an example of two dates by SIMS-SS.

Obsidian Hydration Dating by IR-PAS

The application of IR-PAS (infrared photoacoustic spectroscopy) to the dating of obsidian was proposed as a solution for two central methodological problems associated with OHD using optical microscopy. *First*, optical measurements of hydration layer thickness from prepared thin sections rely upon a visual assessment of hydration layer strain birefringence to establish a depth of penetration. This strain is a secondary effect created by a volume expansion associated with molecular water diffusion that slows the passage of light through the hydrated layer. *Second*, it has been documented in numerous instances that the rate of water diffusion is significantly impacted by the amount of total structural water found within the glass matrix (Karsten and Delaney 1981; Zhang and Behrens 2000; Tomozawa 1985). Calibrations have been developed that correlate the concentration of structural water with laboratory hydration rates at lower temperatures (90 °C) (Stevenson et al. 1998; Stevenson and Novak 2011).

With the IR-PAS method, an absorbance spectrum associated with the vibrational modes of glass functional groups (Si-OH, Al-OH) and water peaks (OH, H₂O) is produced; at 3,570 cm⁻¹, it represents a combination band for OH/H₂O, and the band at 1,630 cm⁻¹ reflects the molecular

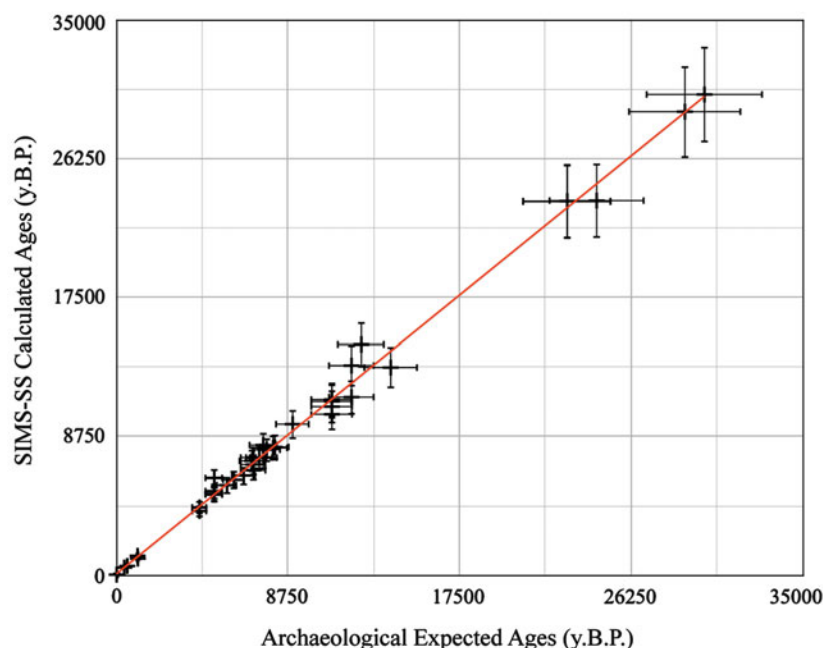


Fig. 5 SIMS-SS versus ^{14}C /archaeological ages for obsidians all over the world (Liritzis and Laskaris 2011)

Table 1 The SIMS-SS dates for two samples from Ikaria Island, Greece (Kerame site), without any other chronological control (From Liritzis and Laskaris 2012)

No.	Lab. No./site	Sampling details	X_s (cm)	C_s (grmol/cc)	C_i (grmol/cc)	e^k	$D_{s,eff}$ (cm ² /year)	Age SIMS-SS (years BP)
1	RHO-891 Kerame, Ikaria	T,C, Spit	$3.1486e-5 \pm 1.87e-6$	$0.00129197 \pm 1.79e-5$	$0.000106014 \pm 6.24e-6$	360	$1.1365e-12$	$11,085 \pm 3,282$
		4 Sq. 5 + 6						
2	RHO-892 Kerame, Ikaria	Trench	$4.90433e-5 \pm 2.24e-5$	$0.0007287 \pm 2.24e-5$	$9.8763e-5 \pm 4.44018e-6$	80	$3.42e-13$	$10,152 \pm 1,643$
		D Spit 4						

concentration of H_2O whether structural molecular or diffused molecular water (Newman et al. 1986), as well as the structural water content of unhydrated region. The method is partially destructive since the artifact or flake must be cut to fit within the sample chamber and the IR-PAS peaks can be impacted by micro-cracks or voids within the glass that trap and retain molecular water. Stevenson et al. (2001) developed a calibration between IR-PAS intensity at $1,630\text{ cm}^{-1}$ and percent molecular water content ($\%\text{H}_2\text{O}_m$), using polished and parallel-sided obsidian samples with a range in total water content from 0.09 % to 1.57 %. The rate constants are then calculated for an archaeological specimen. The $90\text{ }^\circ\text{C}$ diffusion coefficient (D) and activation energy value (E) are estimated from the obsidian total structural water content ($\%\text{H}_2\text{O}_t$) in weight percent concentration. The quantity k in age equation is estimated from the Arrhenius equation:

$$k = D \exp(-E/RT) \quad (6)$$

where D is the diffusion coefficient for H_2O_m at $90\text{ }^\circ\text{C}$, E is the activation energy in J/mol , R is the gas constant (8.314 J/mol K), and T is the hydration temperature (Kelvin). The archaeological site

temperature is determined for this application by direct measurement of soil temperature using cells monitoring T for 1 year. The resulting rate was then used to estimate ages for obsidian artifacts.

Recently, 52 obsidian specimens were measured at two sites of Rapa Nui Easter Island, Chile. Average measurements per parameter and deduced age for the sample 23 of site 15–233, test unit 2 were as follows: temperature as a function of specimen depth (not really an effective hydration temperature), 22.1–23.4 °C; PAS hydrated $1,630 \text{ cm}^{-1}$, 0.1025; %H₂Ome (environmental diffused molecular water) in hydration layer, 0.10 %; $3,570 \text{ cm}^{-1}$ PAS polished, 0.1313; structural %H₂Ot, 0.89; D at 90 °C as %H₂Ome^{0.5}/day, 0.000000118 (exponent 0.5 as in Eq.(1)); E (J/mol), 84.450; diffusion rate estimated (%H₂Ome^{0.5}/year), 0.000027000; and dates, A.D. 1,419 ± 30 to A.D. 1,842 ± 30 years. Ages resulted in an acceptable degree of agreement with radiocarbon ages that those parameters can be used for other obsidian specimens excavated at the island (Stevenson et al. 2013).

However, at Rapa Nui, three problems come into play, which may be applicable to all methods. (i) Handling difficulties and the lack of artifact clarity call for different sampling methods to obtain structural H₂Ot and diffused H₂Ome concentration values.

The amount of damage to an artifact may be substantial when the thick section is removed, and in the worst of cases, small obsidian flakes may be completely destroyed or too small to be processed at all. In addition, opaque obsidians, which constitute a large proportion of the world's natural glasses, may not achieve clarity even after thinning glass thick sections to 0.5 mm. These same issues apply to processing a second subsample in order to measure the hydrated surface. (ii) Laboratory applications of obsidian hydration dating include multiple sources of error that impact the precision of a final age determination. The precision errors cannot simply be added to estimate a total error because the variables are independent of each other with the first associated with a concentration value and the second to a rate coefficient. The latter however seems to coincidentally provide a correct value from hydration experiments at 90 °C, while the used annual results of ambient T need further clarification. (iii) The EHT is a problem that in the above example at Easter Island seems to be overcome due to the short time archaeological intervals involved, since present T measurements are similar for the last say 2–5 hundred of years, but cannot be as such for a few thousand of years BP.

Diffusion Mechanisms in Obsidian

Considerable complexity of phase states has been indicated by a wide range of variability of properties from obsidian sources. The exact mechanism by which water diffusion in such amorphous glasses takes place, by either mechanical transport or molecular interconversion, is still subject to research (Doremus 1969, 2000, 2002; Nowak and Behrens 1997; Zhang et al. 1991; Zhang and Behrens 2000; Crank 1975). In either case, diffusion reaction is described approximately by Eq (7):

$$\partial W / \partial t = \partial (De \partial W / \partial x) / \partial x, \quad (7)$$

where W is concentration of total water, H₂O + OH⁻ (Doremus 2002, pp. 109–110; Zhang and Behrens 2000), and De is the effective diffusion coefficient given by Eq. (8):

$$De = 2WD / \beta, \quad (8)$$

where D is a constant diffusion coefficient characteristic of molecular H_2O and β is a proportionality constant related to the Ostwald solubility of water in obsidian (Doremus 2002, pp. 78, 110). The general solution of Eq. (7) requires numerical techniques and has been a subject of various considerations (Crank 1975), while an elaboration based on Fick's law has led to new age approaches by SIMS (Liritzis et al. 2004; Liritzis and Laskaris 2011; Anovitz et al. 1999).

Accelerated hydration experiments have shown that the diffusion of water is a complex and dynamic process (Anovitz et al. 2004; Stevenson and Novak 2011). The very early stages of hydration exhibit a high surface water concentration, a declining diffusion coefficient, and an advancing diffusion front. This change may be due to glass surface relaxation as the stress that built up in the near surface region is released. However, there may be a difference in the mechanism behind the early stage of water diffusion that differs from the longer-term developmental process.

Following the work of Doremus (2000, 2002) and Liritzis (2006), Stevenson and Novak (2011) hypothesized that H_2O_t creates a more open glass structure which allows water molecules to pass through "gateways" in the silica tetrahedra. It was their observation that the greater the concentration of H_2O_t , the faster the diffusion rate of ambient water (H_2O_m) into the obsidian surface.

Water enters obsidian glass at environmental temperatures as molecular H_2O and as hydroxyl OH formed by reaction with the glass silicate structure. It is believed that the occurrence of greater amounts of Si-OH in the network (silanols, referred to the intrinsic water molecules which may be present as OH- with the siliceous network) may weaken the neighboring Si-O-Si bonds, causing them to easily break, and therefore lower the overall activation energy (Brückner 1970; Ericson et al. 2004). However, the latter view may be revised as silanols seem to follow hydrogen sigmoid profile due to diffused water (see, Fig. 9, Liritzis and Laskaris 2011).

At any rate, as water enters the glass network, the structure is depolymerized and hydrogenated and silanol ions are formed (Si-OH) and allow additional water to enter the glass at a faster rate, while in the course of time, chemical reaction follows Fick's law. This changing diffusion coefficient results in the formation of the characteristic S-shaped concentration-depth profile (Fig. 2).

According to another model, H_2O molecules choose various diffusion paths in a nonhomogeneous way, as the size-dependent mechanism assumes that water molecules of radius $R_w = 0.15$ nm occupy interstitial sites of the obsidian and pass through "doorways" of radius R_D jumping from one doorway to another. The $R_D = 0.1$ nm derives from the equation regarding activation energy E , which is recognized as the elastic energy necessary to dilate a spherical cavity from radius R_D to R (Doremus 2002; Liritzis 2006). The rate at which this process occurs depends upon the intermolecular distance of the host material matrix compared to the size of the diffusing species.

This diffusion process forms an external layer as water leaves the atmosphere and humid sediment and diffuses into the glass structure. In particular, the surface saturated layer (SS layer) is formed in the first 1–3 μm of the obsidian surface through two diffusion mechanisms. The first mechanism transfers the ambient water from the environment into the exterior surface of obsidian, and the second mechanism is responsible for the diffusion process into the interior of the artifact (Liritzis and Diakostamatiou 2002). The mechanism of water diffusion in obsidian and the exponent of time in Eq. (1) are still a matter of investigation.

Discussion of Some Issues Related to Conventional OHD

A variety of strategies have been developed over the years to calibrate the movement of ambient water into a glass, to take into account the composition of the glass, and to model the environmental

history of the artifact context (e.g., temperature, humidity). In essence, the rate of hydration is dependent on the obsidian chemistry, the intrinsic water content of the glass, the temperature and relative humidity, and the chemistry of the diffusing water (Friedman and Long 1976; Ambrose 1984; Mazer et al. 1991; Friedman et al. 1994; Stevenson et al. 1998; Stevenson et al. 2002; Ambrose and Stevenson 2004; Rogers 2008, 2012).

Presently, the exponent of Eq. (1) is being questioned as non-applicable to all environments, and the determination of the diffusion coefficient from extrapolation of laboratory hydrated obsidians down to ambient conditions from the Arrhenius plot is considered as insecure (Anovitz et al. 1999; Stevenson and Novak 2011; Liritzis and Laskaris 2011). Several decades of research illustrated the complexity of the hydration process, and *revised* working assumptions or disillusiones for OHD were proposed (Mazer et al. 1991; Stevenson et al. 1998, 2000; Rogers 2007; Ridings 1996). In spite of many years of development and application, mainly from research groups in the USA and Australia, it appears that neither approach has produced consistently reliable results. In some cases, ages have so contradicted other well-established chronometric and/or typological data that the utility of the obsidian as a chronometer has been questioned (Anovitz et al. 1999; Ridings 1996; Liritzis 2006; Rogers 2008; Eerkens et al. 2008).

Although OHD seemed to give good relative ages in some case studies as in Easter Islands (Stevenson et al. 2000; Stevenson et al. 2013), practitioners of the measurement pointed to significant errors in other cases (Ridings 1996). The problem of determining accurately the hydration thickness is solved with new techniques such as infrared spectroscopy (IR), SIMS. Infrared spectroscopy has been used to measure the bulk water content of obsidian (Newman et al. 1986; Zhang et al. 1996) with the photoacoustic method (IR-PAS) used to quantify the depth of surface water diffusion (Stevenson et al. 2001, 2002; Stevenson and Novak 2011). The latter approach to hydration layer depth assessment has been calibrated relatively to SIMS and shown to have a higher precision and accuracy than obtainable by optical microscopy (Ambrose and Novak 2012).

In certain cases, extensive lab experiments using the same obsidian source, diffusion rate, and average environmental hydration temperature (effective hydration temperature) using temperature cells yielded satisfactory ages. These were controlled by available ^{14}C ages and ceramic typology, e.g., for south coast of Peru, using petrographic microscopic rim measurements (Eerkens et al. 2008), and Hopewell culture (Stevenson et al. 1998, 2004), using rim measurements by SIMS.

To summarize, the early problems with OHD were partly due to inappropriate analytical techniques involving (i) nonsystematic errors arising from the inherent imprecision for optical measurements, (ii) the experimental conditions and data of estimation of hydration rate, and (iii) on a theoretical plan an improper model of the hydration process.

Laboratory-induced hydration does not produce commensurable results with the in situ-induced hydration and/or silica dilution (Morganstein et al. 1999; Bartholomew et al. 1980). This was the case even when using a long-term artificial aging experiment with the obsidian samples from three separate volcanic provinces in Papua New Guinea exposed in normal air and water vapor pressure to controlled temperatures of 10 °C, 20 °C, 30 °C, and 40 °C, for up to 26 years (Ambrose and Novak 2012). Nevertheless, the latter confirm the value of the strategy by providing basic hydration rate constants for obsidian specimens from each of the three major Papua New Guinea sources. But in an archaeological context, these data still require calibration for an optical microscopy hydration measurement. SIMS provides an enhanced measurement system and is combined here with experimentally determined rate constants to independently cross-check radiocarbon dates and site temperature calculation at a ~2,100 BP archaeological site from Papua New Guinea. In fact, Ambrose and Novak (2012) noted that the error figure in age indicates the wide divergence from hydration reading error alone, while additional temperature-based error is even greater than the reading error

by a few hundreds of years and underlines the critical influence of temperature in attempting to derive absolute age values from obsidian hydration dating.

At any rate, the involved age in Eq. (1) is still empirical, surely far apart of the more satisfactory phenomenological approach and certainly not well substantiated by a scientific approach (Brodkey and Liritzis 2004).

Sources of uncertainty in OHD include hydrous and compositional chemistry, humidity, rim measurement, temperature history, diffusion rate variability due to intrinsic water and determination by extrapolation from higher temperature experiments, site formation processes, and age errors from comparative methods (with ^{14}C , archaeological typology) which affect the validity of the age-rim association.

Nevertheless, in spite of rigorous statistical modeling and error propagation, the evaluations of all sources of error impart uncertainties in each variant factor such that the span of uncertainties may sway between extreme percentages of the order of some 10s of a percent. The issue of considering any individual specimen and burial location as a unique case is a rule. Along this direction, calibration models per excavated site are always useful but are cumbersome and timing. A brief evaluation of main factors related and affecting the traditional OHD is described below.

Temperature

Perhaps the biggest problem is temperature, since the hydration process is strongly temperature dependent and the temperature history of an artifact can never be completely known. Past historical temperatures vary over time, both annually and diurnally, and hydration rate of obsidian is temperature dependent. The effect of the varying temperature is coined by the concept of *effective hydration temperature* (EHT), defined as the constant temperature which yields same hydration results as the actual time-varying temperature over the same period of time and can be computed from the time average of D (Rogers 2007). Because of the mathematical form of the dependence of hydration rate on temperature, $\text{EHT} \geq T$ mean. In fact, few degrees in error of EHT in the Arrhenius equation (embedded in Eq. (2)) produce errors of several centuries. For an activation energy (E) of 85 KJ/mol, the error in age for $\pm 1^\circ\text{C}$ is $\pm 11\text{--}13\%$, for $\pm 2^\circ\text{C}$ is $\pm 25\%$, and for $\pm 3^\circ\text{C}$ is around $\pm 37\%$. The well-known modifiers of obsidian hydration rate with temperature (the others being chemical composition and water vapor pressure) may be accounted for, but none is sufficient for precise prediction of hydration rates. For this reason, obsidians still need to be independently assessed for their own specific rate determination. On the other hand, another reported temperature approach using a set of calculated temperature parameters for one site based on a regional temperature scaling analysis contains uncertainties too and can further be corrected for first-order changes in paleotemperature if proxy data are available (Rogers 2010, 2012; Rogers and Yohe 2011; West et al. 2007). Even so, it is unlikely that EHT can be corrected much better than $\pm 1.0^\circ\text{C}$ (Rogers 2007). EHT includes the effects of temperature history in one parameter; furthermore, a change in EHT (Δt_e ; t_e is effective hydration temperature) produces a change in rim value (Δr):

$$\Delta r/r = -\frac{1}{2} (E/RT_e^2) \Delta T_e \quad (9)$$

For $E = 20$ KJ/mol and 90 KJ/mol, Eq. (9) gives 0.0140 and 0.0630, respectively, with a median E value of 0.0007 per KJ/mol. The former leads to a change in rim of about $1\text{--}6\%/^\circ\text{C}$, and the higher holds for nominal conditions. A cautionary note is that the meteorological data are for air temperatures, while obsidian usually is found at a variable depth in the ground where T differs. Alternatively, sensors (e.g., HOBO H8 Family loggers, e.g., Stevenson et al. 2013) are put over a year in situ that record a meaningful annual context meteorological average.

Rim

Typically, the mean and standard deviation of an aggregate of about six individual readings is taken for each hydration rim measurement reported by a laboratory. Standard deviations are nearly always $<0.1 \mu\text{m}$, more often $0.05\text{--}0.01 \mu\text{m}$. A previous analysis (Scheetz and Stevenson 1988) concluded that the accuracy is constrained by the resolution of the microscope system to $\sim 0.25 \mu\text{m}$ or worse; however, the issue here is not resolution but accuracy of coincidence measurement, which is well known to be about two orders of magnitude better than resolution (Jacobs 1943, pp. 86–88), so the error values quoted by obsidian laboratories are reasonable but the precision weak as recent methods have shown. A comparison of optical readings with hydrogen profiles collected by SIMS (Anovitz et al. 1999; Stevenson et al. 2001) and infrared profiling (Yokoyama et al. 2008) show that the depth of water diffusion extends well beyond the optically defined diffusion front. As a result, optical techniques cannot accurately track the diffused species. SIMS has been used to significantly increase precision to $\pm 0.05\text{--}0.1 \mu\text{m}$, but the cost per sample is prohibitive for routine application.

Higher precision of the rim reading is achieved by SIMS profiles or IR-PAS peak integration (Anovitz et al. 1999; Stevenson et al. 2001, 2002).

Diffusion Rate, D

Simulation experiments of hydration rate by laboratory methods (sometimes known as “induced hydration”) have an equivocal history in archaeology, and since it depends on temperature, attempts have been made in the past to measure hydration rate in the laboratory (e.g., Friedman and Long 1976; Stevenson et al. 1998). However, rates measured in the laboratory often have not agreed well with archaeological data (see, e.g., the pointed observations in Hall and Jackson 1989, p. 32), while in other cases agree (e.g., for Rapa Nui Easter Island, Stevenson et al. (2013) and in Topaz Mountain obsidian from Utah, Rogers and Duke (2011)). The hydration rate of obsidian, which is strongly temperature dependent, is allowed to proceed at elevated laboratory temperatures, when measurable hydration rims develop in days rather than years. The temperature dependence of the hydration rate has a well-attested mathematical form, so the principle of laboratory hydration is to hydrate a set of obsidian samples at elevated temperatures, determine the activation energy and diffusion constant, and then compute the hydration rate for temperatures of archaeological interest. Initially, the diffusion rate D was calculated from hydration that was experimentally induced under controlled laboratory experiments for use in the Arrhenius plot, in a high temperature range ($90\text{--}250 \text{ }^\circ\text{C}$) (Stevenson et al. 1998). First, this did not secure safe extrapolation to much lower temperatures, and second, the simulated hydration does not produce the anticipated behavior with obsidian of similar source. Making use of nano-SIMS and simulation experiments, rates are produced at environmental conditions. Such an aging experiment for Papua New Guinea obsidians has shown differing diffusion rates for the same temperature and different storage temperatures of four different sources. There, the SIMS profile depths and regression results for the four hydrated obsidians, namely, Igwageta, Mt Bao, Wekwok, and Umleang, produced diffusion rates that vary by $\sim \times 25$ for a fourfold temperature increase, between $10 \text{ }^\circ\text{C}$ ($0.002\text{--}0.004$) and $40 \text{ }^\circ\text{C}$ ($0.06\text{--}0.10$) for the four different sources, which, however, have no marked chemical composition variation (Ambrose and Novak 2012). From room temperature to $75 \text{ }^\circ\text{C}$, the diffusion coefficient changes by two to three orders of magnitude confirming the well-known sensitivity of the intrinsic dating technique to assumed local temperature (Anovitz et al. 2004).

This had resulted in high measurement error stemming from the use of optical methods; thus, the regression constants also had a large inherent error. But, data have shown a relationship between structural water concentration and D , and an increase in precision is now achieved through the

analysis using infrared measurement of experimentally developed hydration layers (Stevenson et al. 2001).

The errors and their affects have been exhaustively analyzed (Rogers 2010). Hydration rates can be reliably estimated by least squares techniques applied to obsidian-radiocarbon data with errors of about 4–5 %, while rates estimated by least squares techniques applied to time-sensitive artifacts are somewhat worse, with about 8–10 % errors. Rates determined from laboratory techniques (induced hydration) are somewhat more accurate, with about 2–3 % error.

Analytical errors concern (a) the mathematical procedure of a least squares best fit to the logarithmic Arrhenius equation (see Stevenson and Scheetz 1989; Rogers and Duke 2011), especially if data-point weighting is not included (otherwise the activation energy and diffusion constant will be in error); (b) the procedural error that involves laboratory techniques (e.g., erosion rates and rim growth, use of proper hydration environment and temperature); (c) the “scaling” problem, i.e., hydration at high lab temperatures and archaeological temperatures (the scaling is actually a complex function of the both hydration rates (and diffusion constant) and their activation energies and requires knowledge of both for each obsidian source in question); and last, but not least, (d) the role of phenocrysts presence (size and abundance) and obsidian transparency should also be reexamined for they obviate ideal diffusion process.

The Dependence of Time

The dependence of time on the square exponent of x has been questioned (Anovitz et al. 1999, 2004; Liritzis 2006). That is why most reported OHD ages are compared with other dating means (^{14}C , luminescence, ceramic typology), an expected practice for the initial development of the method, though in several cases the square root is valid.

The Surface Loss

The surface loss is identified as an important factor in glass hydration dating (Ambrose 1976, 1994; Liritzis et al. 2008a, b; Morganstein et al. 1999). Once present on an artifact with fissures, the surface dissolution rate of an obsidian artifact can be calculated. Although OHD theoretically is capable of yielding accurate dates in the range 1,000,000 to 200 years B.P. (Michels 1986), the obsidian surface is subjected to environmental flaking, and this limits its range; on the other hand, the nano-SIMS technology at least provides an accurate minimal rim reading that can deal with this issue.

Humidity

Humidity effects are relatively small and are typically ignored in analysis. However, the effect of accelerated hydrations with 100 % Rh on diffusion kinetics has not been adequately studied.

Intrinsic (Pristine or Connate) Water

The remaining variable hydration associated with original fast cooling of lava is an extremely important factor in the diffusion rate. The hydration rate in obsidian at any given temperature is a function of the concentration of water in the glass (Karsten and Delaney 1981; Karsten et al. 1982; Stevenson et al. 1998; Zhang and Behrens 2000; Zhang et al. 1991). Intra-source variability in intrinsic water content has been observed in Coso obsidians from eastern California, USA (Stevenson et al. 1993), and is likely present in others; thus, measurement of intrinsic water content per individual specimen is required as a prerequisite (Stevenson et al. 2001, 2002).

Some Early and Recent OHD Applications and Development

Friedman et al. (1997) provided a substantive review and summarized the problems linked to OHD and referred to case studies including archaeological specimens from New Mexico, central Mexico, Belize, Honduras, and Ohio (the latter imported from Wyoming). Studies of Mexican, Guatemalan, and Sardinian obsidians by Michels and his colleagues however are critiqued therein. The authors cross-dated OHD results with radiocarbon dating, archaeomagnetism, and ceramic phasing. Particular points to take care of included the factors related to hydration rates (as chemical composition of obsidians, their trace elements content, relative humidity, and regional rates), laboratory techniques (preparation of thin sections, optical measurement of hydration rim/rind thickness), and the conversion of hydration rate data to age. In their review, OHD was however promoted as a relatively inexpensive and “simple” scientific technique for determining absolute chronologies, so that the current masterful treatments presented replaced the earlier general assessment.

A series of OHD dates was reported consecutively by the UCLA laboratory (see Meighan and Scalise 1988).

Braswell (1992) pointed out problems concerning laboratory determinations of diffusion rate constants and the estimation of EHT in the field, from a study of the Coner Phase at Copas (Honduras). He concluded that the laboratory-induced rate constants used to determine these dates were of questionable validity and needed to be independently assessed. He showed how an error of but a few Kelvin in estimated EHT can lead to dates that are in error by several centuries. In view of the likelihood of large errors in the Copán obsidian dates, the assertion that the Late Classic Coner phase should be extended beyond 900 A.D. was considered therefore premature (Braswell 1992; Webster and Freter 1990)

Further application in OHD includes the dating of New Zealand obsidians by Stevenson et al. (1996), with a recent age span from 13th to 18th A.D., where hydration rates were calculated on the basis of obsidian water content as estimated from artifact density, while effective hydration temperatures were established from published temperatures derived from thermal cells. The deduced hydration dates have been successfully compared with radiocarbon dates from six archaeological sites in the North Island of New Zealand.

Ambrose (1994) gave a provisional age-depth model for hydration thicknesses for the Pamwak site, Manus Island, Papua New Guinea, spanning from 4 to 13 ka BP, based on internal crack surfaces and compared satisfactorily with ^{14}C age control.

Obsidian hydration dating has served as one of the chronological indicators for the Hopewell Culture earthworks (ca. 200 B.C.–A.D. 500) in central Ohio (Stevenson et al. 2004). This work presented new obsidian hydration dates developed from high precision hydration layer depth profiling using SIMS, and the data suggested that long-distance exchange in obsidian occurred throughout the Hopewell period. From Eq. (2) parameters, diffusion coefficient A and activation energy E were estimated by the density versus OH^- plot; EHT from cell pairs put in the site and Eq. (2) resulted in OHD age estimates that range between 258 and 119 B.C. and A.D. 607–94, and these incorporate the entire Hopewell period, as determined by absolute C-14 dates of the same site.

Based upon the water diffusion in natural glass, Stevenson et al. (2007) introduced the conventional OHD technique to dating high-calcium manufactured glasses with first preliminary results on seventeenth-century North American glass wine bottles manufactured by European settlers, concordant with historical data.

In many cases, intact internal fissures as concealed cracks can be used for OHD, and the rate of surface loss can be calculated from paired readings of these inner surfaces and the outer weathered

(depleted) ones (Ambrose 1998). When secondary rate factors for these fissures were compared to radiocarbon-based rates, a discrepancy was found due to dissolution.

At any rate, since OHD is dependent on processes which have occurred since an artifact was created, it can never be as accurate and reliable as radiocarbon or dendrochronology, and it should be always a secondary source of chronological data. Thus, in this frame, using a radiocarbon assay remains the basis for relative hydration dating; but this raises again the question, for a given site, of the true association of the artifact and the ^{14}C date and, for nearby sites, the remaining uncertainty of the validity of the constancy of environmental characteristics.

The ongoing Easter Island OHD by Stevenson et al. (2011) with more than 800 obsidian specimens analyzed has been advanced with the IR-PAS measurements of D and water, and ages are comparable to ^{14}C ones in the time span of fourteenth to nineteenth century A.D.

SIMS-SS has been applied to obsidians from several parts of the world (e.g., Greece, Chile, Turkey, Japan, Hungary, the USA) with ages from a few hundred to 30,000 years BP (Liritzis and Laskaris 2009, 2012).

Analysis of errors shows that it is unrealistic to expect age errors much less than 15–20 % in obsidian hydration dating (Rogers 2010). With those uncertainties in the computed ages, great caution must be exerted in inferring occupation duration of a site used based on OHD.

Conclusion

The process of hydration in glasses is very complex, involving chemistry, physics, and mathematical modeling. Obsidian hydration has certain weaknesses in terms of a chronometric tool like any other dating method. At any rate, two fundamental equations involved need further experimentation or prior calibration: an age equation of classical OHD and a temperature dependence equation, which is usually of the Arrhenius form and the SIMS-SS. Since the transport parameters being measured differ, the age equations differ slightly as well, in particular the exponent of the time (age) variable. It is likely that the parameters of the Arrhenius equation are slightly different as well, although investigations of this point have not yet been reported. However, it would be unwise to apply, say, an activation energy determined from water mass uptake to the optical (classical OHD) case without careful study or EHT and hydration experiments at ambient conditions.

Despite the fact that the classical OHD is furthest removed from the basic physics of hydration (criticism by advocates of other techniques, e.g., Anovitz et al. 1999; Liritzis and Laskaris 2012), it is still being used since it seems to satisfy coarse chronologies especially of recent centuries, whereas other chronometric data are frequently lacking (Stevenson et al. 2013). The alternative SIMS-SS with the mathematical techniques discussed also offers satisfactory dates for the past 30,000 years (Liritzis and Laskaris 2009, 2011, 2012)

Probably, the greatest needs at present are for (1) a more scientific approach of the age equation; (2) more dates on a “join forces” basis, for the two current approaches, for specimens throughout the world, and comparison with luminescence and C-14; and (3) development of not expensive versions of OHD.

Cross-References

- ▶ [Luminescence, Flints and Stones](#)
- ▶ [Luminescence Dating](#)
- ▶ [Radiocarbon, Plant Materials](#)

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