Review

Fifty years of obsidian hydration dating in archaeology

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ABSTRACT

About fifty years ago Friedman and Smith [1] recognized the obsidian hydration phenomenon and proposed an empirical dating method based on the conversion of the optically measured hydration depth to an absolute age. They and subsequent researchers developed distinct versions of obsidian hydration method consisting of both empirical rate and intrinsic rate development, thus refining the method. However, in spite the accurately measured rinds beyond digital optical microscopy employing infrared spectroscopy and nuclear analysis, the traditional empirical age equation produce occasionally satisfactory results but still fail to produce a reliable chronometer. In the last ten years, secondary ion mass spectrometry (SIMS) has been employed to accurately define the hydration profile. By modeling the profile of the surface hydrogen concentration versus depth the age determination is reached via equations describing the diffusion process. Finite difference modeling and essential assessments of the novel SIMS-SS (surface saturation) phenomenological method produce a sound basis for the new diffusion age equation and provides promising results. This review refers on the development of obsidian hydration dating (OHD) and diffusion process in glass and reckons future directions of SIMS applications in obsidians.

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1. Introduction

The research in the fields of geochemistry and archaeology has developed a useful chronometric technique based on the reaction and diffusion of water in obsidian for dating geological features and aboriginal obsidian artifacts. Correlation of hydration and radiocarbon data indicates that the hydration rates vary among the obsidian sources.

Over the past fifty years the diffusion dating referred to obsidian hydration dating (OHD), essentially a $t^{1/2}$ dependent hydration rim empirical relationship [1], has seen significant advancement, in particular higher resolution techniques in measuring hydration rim and diffusion profile [2–7] (Fig. 1), better approaches in the determination of diffusion rate [8,9a,b], models for effective hydration temperature evaluation [10,11], as well as, studies on diffusion mechanism [12–14].

The purpose of this critical review is to give a brief historical overview of OHD applications and the incurred limitations, on the diffusion processes in obsidians, and to comment on the present status and ongoing research avenues in OHD employing nuclear beams such the secondary ion mass spectrometry (SIMS). The latter has benefited in particular from the many studies of diffusion in glass linked to the nuclear waste long-term storage under vitrified form.

2. Diffusion processes in obsidians

Considerable complexity of phase states is indicated by a wide range of variability of properties from twenty-eight obsidian sources in Western America. The results of thermal expansion, density measurements, Vicker's hardness, chemical durability, electrical properties, Mössbauer and infrared spectra were presented by Ericson et al. [15]. They found that obsidian is a glass of high chemical durability, comparable to Pyrex, and high hardness, comparable with silica glass.

The exact mechanism by which water diffusion in such amorphous glasses takes place, by either mechanical transport or molecular inter-conversion, is still subject to research [9b,13,14,16–20]. In either case, diffusion reaction is described approximately by the Eq. (1):

$$\partial W / \partial t = \partial (De \partial W / \partial x) / \partial x \qquad (1)$$

where, W is concentration of total water, $H_2O + OH-$ [14,17], and De is the effective diffusion coefficient given by Eq. (2):

$$De = 2WD / \beta, \qquad (2)$$

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 [17]. The general solution of Eq. (1) requires numerical techniques [21] and is not treated here, but has been a subject of various considerations [20], while an elaboration has lead to new age approaches by secondary ion mass spectrometry (SIMS) [7,22,23].
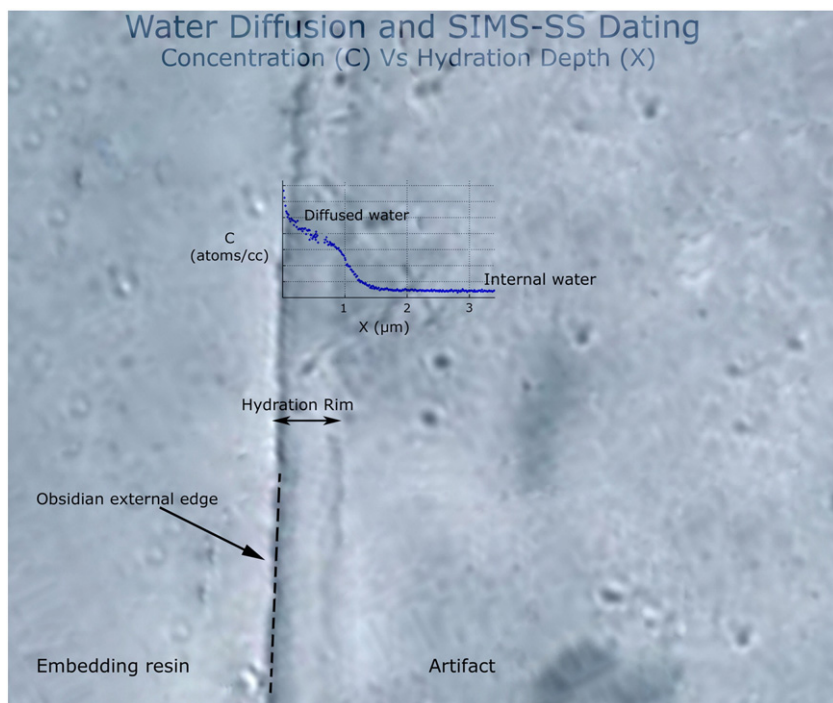
Fig. 1. Optical image of a thin section of obsidian. The hydration layer is visible. A SIMS profile is overlapped.

However, in the archaeological case, temperature variation reflects long-term climatic trends, thus, D is a function of time D(t). It can be shown that, if the constant value of D in Eq. (1) is replaced by a mean value of D(t) over the time period of interest, the diffusion problem can be solved as though D were time-invariant [20]. The latter has been discussed in Brodkey and Liritzis [24]; while in the new modeling approach of SIMS-SS, D is taken equal to the inverse of the slope i.e. the first derivative of diffused water H^+ profile fitted with a 3rd order polynomial. A fully scientific approach to determination of D is still a matter of investigation.

In fact, a significant literature exists regarding the diffusion of water in natural glasses and melts (obsidians, tektites, and glasses) at temperatures near and above the glass transition temperature (i.e. >400 °C) [19,25]. Water enters obsidian glass at these temperatures as molecular H_2O and as hydroxyl OH formed by reaction with the glass silicate structure [14]. It has been demonstrated that structural water is present within unhydrated bulk obsidian as both molecular water (H_2O) and as hydroxyl (OH) [4,26,27]. The sum of both species is referred to as the total water concentration (H_2O). Silver et al. [27] demonstrated the relationship between the two species as a function of total water concentration.

Based upon infrared spectra of the developing obsidian hydration layer [28], it appears that molecular water is the diffusing species that originates on the obsidian surface.

It is also well documented that natural glasses contain structural water concentrations that may range up to several tenths of a percent. This will exponentially increase the diffusion coefficient as concentration rises [14,19,29]. This is believed to occur because the occurrence of greater amounts of SiOH in the network (silanols, referred to the intrinsic water molecules which may be present as OH with the silicious network) may weaken the neighboring Si–O–Si bonds, causing them to easily break, and therefore lower the overall activation energy [30,31]. However the latter view may be revised as silanols seem to follow hydrogen sigmoid profile due to diffused water (see, Section 9, below).

The inter-conversion rate between molecular H_2O and OH is temperature dependent and greatly reduced at temperatures below 400 °C, but basically it takes place at these higher temperatures [18].

The extrapolation to lower temperatures is rather minimal in glasses that hydrate at ambient temperatures (<40 °C), and accelerated experiments of obsidians at ambient temperatures indicate significant differences in rates and kinetics compared to higher temperatures (see Section 3). However, experimental evidence suggests that a different mechanism exists for low temperature water diffusion because diffusion coefficients developed at >400 °C do not accurately extrapolate to coefficients developed on naturally weathered samples [32–35]. Finally, at archaeological temperatures infrared (IR) spectroscopy studies have shown that ambient molecular water is the mobile species that enters the glass surface and that OH concentration within the glass matrix remains constant [33]. The diffusion of water in glasses is also strongly correlated with the concentration of pristine water within the whole obsidian body [2,23,36–38]. This phenomenon is referred to as concentration-dependent diffusion.

Under ambient temperatures (0–40 °C) during the initial stages of hydration the diffusion coefficient does not follow the steady state diffusion process with a constant D and is not mathematically estimated with Fick's second law [20,24].

At any rate, as water enters the glass network the structure is depolymerized, hydrogenated, silanol ions are formed (Si–OH), and allows 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). As a result, alternate modeling procedures are required.

According to another model, H_2O molecules choose various diffusion paths in a non-homogeneous 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 equation regarding activation energy E, which is recognized as the elastic energy necessary to dilate a spherical cavity from radius r_D to r. [17,39]. 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 [39].

This diffusion process forms an external layer as water leaves the atmosphere and humid sediment and diffuses into the glass structure.
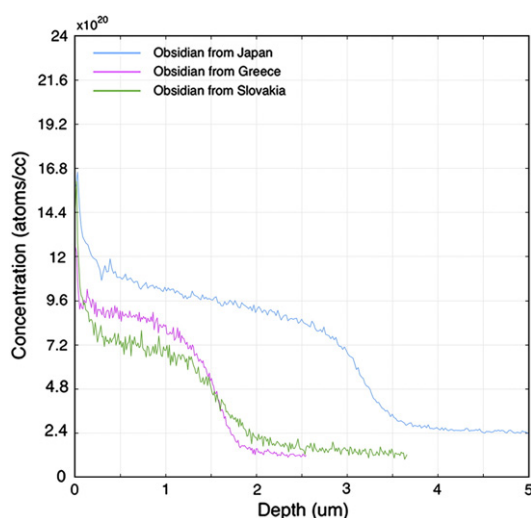
Fig. 2. SIMS H+ profiles for three samples from Greece, Japan and Slovakia.

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.

However, hydrogen profiles on experimental samples at higher than environmental temperatures have shown that the leading edge of the diffusion profile advances into manufactured and natural glasses at the square root of time [5,29,40,41]. This has prompted many researchers to adopt a t1/2 time dependence to describe the diffusion of water into glass surfaces and a basis for estimating archaeological ages [29,42].

3. A brief historical account of OHD

Many types of rocks were used by early men for the making of their tools implements among which obsidian, a glassy volcanic rock rich (>65%) in silica. Although the accurate dating of stone artifacts is of fundamental importance in archaeology, until now this proved to be possible only in the case of obsidian, by fission track dating (FTD) or by obsidian hydration dating (OHD). It was shown from the early days of FTD that the time of the last cooling of an archaeological obsidian from a high (T>500 °C) temperature could be determined [43]. However over the hundreds of artifacts dated so far, only a handful were found to have been heated enough to reset to zero their fission track chronometer [44,45]. To the contrary, during their post-use burial history in soils any obsidian artifact absorbs atmospheric water at a rate that may in principle be calculated. It is on this assumption that Friedman and Smith proposed in 1960 the OHD method. They had noted that in thin section the hydrated rim is visible at a high power microscopic magnification, and that its width depended on exposure time, glass chemical composition and ground temperature. They suggested for dating purposes an empirical equation of the form:

$$x^2 = kt \qquad (3)$$

with

$$k = A\exp\left(-E/RT\right) \qquad (4)$$

for the pre-exponential and activation energy constants for the Arrhenius Eq. (4).

Where, in Eq. (3), x is the thickness (μm) of the obsidian hydration rim, k the hydration rate (μm²/1000 years), and t the age (years), and

in Eq. (4), T is the absolute temperature (Kelvin) in fact the effective hydration temperature (EHT), A is a source-specific constant the diffusion coefficient (μm²/day) and E the activation energy (calories or Joules per mole) respectively, R is the gas constant (calories per degree per mole, i.e. 1.987). Because of the ease of cutting and polishing obsidian and of measuring the hydration rims thicknesses in optical microscopy, a large number of obsidian hydration measurements were performed in the 1970's and until now [46–53]. During the past fifty years, at sites producing obsidian, this needful dating method rivaled radiocarbon dating but many inconsistencies as regards to other dating methods resulted in considerable doubts about its reliability [see e.g. 54,55].

An evident difficulty in OHD from Eqs. (3) and (4) was the determination of the 'effective temperature' T supposed to characterize the thermal history of an obsidian artifact during his ground residence time, hence two dating strategies proposed from the early years of OHD to overcome this problem. In the empirical rate approach, based solely on Eq. (3), the parameter k is determined for a particular site and obsidian composition, from its ¹⁴C calibrated (or otherwise known) numerical age and the mean hydration layer thickness. The k value thus obtained is then considered to be valid for nearby sites of supposedly identical climatic history, though intrinsic water content per individual sample is crucial [11,29,52,56]. However, this procedure was highly questionable and has been subjected to considerable re-evaluations and eagerness in understanding the parameters involved in glass hydration, during 80s and 90s, as well as of the uncertainties linked to the application of averaged environmental data to particular sites [8,12,23,39,57 see also below]. Micro-climatic differences between different localities and even within same source might have drastic effects on k, hence on OHD.

The second, more complex but also widely applied technique known as intrinsic rate requires experimentally determined rate constants and has to be coupled with accurate measurement of site temperature to arrive at a hydration age. Again, the results reported to date were problematic though in cases correct and calibration errors culminated the deficiency of the method to be considered reliable and precise [11,15,29,49,54,58–60].

In effect this approach, using a set of regionally measured/calculated temperature parameters to estimate the effective temperature T for one site may inhere large uncertainties [10,11,61], as, in any case, the temperature history of an artifact can never be completely known. Although mathematical techniques are sometimes used to account for temperature variations, they are still the major source of uncertainty. Whatever the dating approach used, it was therefore a good practice to date as many artifacts as possible for a given site/cultural horizon.

During the last decade, the introduction of new analytical techniques and a re-evaluation of the diffusion processes at work in the hydration of obsidians opened a new era in OHD. Below we draw a short historical account of OHD and emphasize its present status [62].

In any case, a correct equation age for OHD requires a good theoretical understanding of the mechanisms and rates of water diffusion into a natural glass surface and the establishment of a relevant diffusion coefficient for this process. It is accepted that the rate of water diffusion, the diffusion coefficient, is exponentially dependent on temperature and exhibits an Arrhenius type behavior as suggested by laboratory experiments (Fig. 3).

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 modeling the environmental history of the artifact context (e.g., temperature and humidity). In essence the rate of hydration is dependent on the obsidian chemistry, the intrinsic water content of the glass, temperature and relative humidity, and the chemistry of the diffusing water. [29,42,63–67]. Rogers [68] considering that the outcomes are the result of error build-up in the induced hydration protocol especially in EHT determination
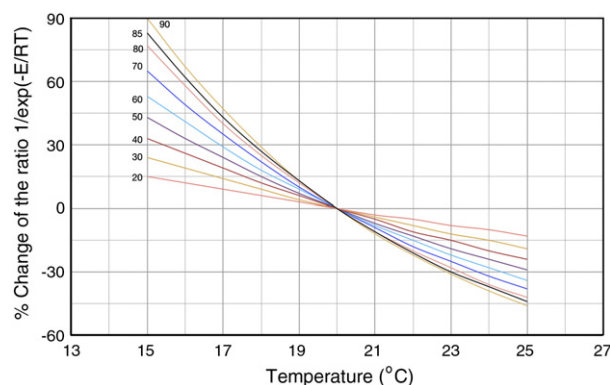
Fig. 3. Percentage error of the ration 1/exp($-$E/RT) for different activation energies from 20 kJ/mol up to 90 kJ/mol and for $\pm$ 5 °C in temperature. EHT is 20 °C.

proposed instead an analysis based on a Monte Carlo simulation of the measurement and analysis process without however including "change of variable" effects, which would have somewhat modified his conclusions. Later, he concludes that obsidian hydration dating, could remain a valid technique for constructing coarse chronologies if using rates determined empirically from radiocarbon associations [11].

Presently, the exponent of Eq. (3) 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 [8,23]. Several decades of research illustrated the complexity of the hydration process and revised working assumptions for OHD were proposed [10,28,29,64]. In spite of many years of development and application, mainly from research groups in 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 [11,23,39,53,55].

Although OHD seemed to give good relative ages in some case studies [28], practitioners of the measurement pointed to significant errors in other cases [55]. One of the major problems seem to be related to the somewhat subjective nature of determining optically the thickness of the hydration layer, the low resolution of the optical microscope and the correlation between the measured thickness and the actual depth of water diffusion [23,58,69]. As these problems were being discovered, newer techniques such as infrared spectroscopy (IR) were being developed to measure the water content of hydrated obsidian. Infrared spectroscopy has been used to measure the bulk water content of obsidian [4,70] with the photoacoustic method (IR-PAS) used to quantify the depth of surface water diffusion [5,66]. 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 [71].

In some cases however with well known and extensive lab experiments with the same obsidian source on diffusion rate and average environmental hydration temperature (EHT) using temperature cells satisfactory ages obtained were always controlled by available C-14 ages and ceramic typology e.g. for south coast of Peru, using petrographic microscopic rim measurements [53] and Hopewell culture [29,72] using rim measurements by SIMS.

To summarize, the problems with OHD were partly due to inappropriate analytical techniques involving (i) non-systematic 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.

Point (i) is now overcome by IRPAS, SIMS and other nuclear analysis techniques. [4,66,70–72], but most old OHD dates are wrong due the imprecise optically assigned rim [23,51], while non-visual

measurement procedure of digital image scanning across strips of the hydration band seems to give an accuracy of $\pm$ 0.05 μm [73]. As early as in the 1970s Tsong et al. [3] demonstrated the use of sputter induced optical emission for obsidian hydration profiling. This technique is similar to SIMS in using an ion beam to sputter the sample; however, the detected signal is the light emitted during the bombardment process. As they pointed out, the ability to sputter the sample with a high current ion beam yields the ability to measure hydration profiles to 10 microns in a reasonable amount of time, making SIMS a versatile technique.

About point (ii) it was shown that unfortunately laboratory induced hydration does not produce commensurable results with the _in situ_ induced hydration and/or silica dilution problems may occur [74,75, unpublished results 76], even using a long-term artificial aging experiments as 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 [71]. 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 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 ~2100 BP archaeological site from Papua New Guinea. In fact, Ambrose and Novak et al. [71] 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 hundred of years and underlines the critical influence of temperature in attempting to derive absolute age values from obsidian hydration dating.

Point (iii) is still debated but at any rate the involved age equation is still empirical, surely far apart of the more satisfactory phenomenological approach and certainly away of a scientific approach [24].

4. Some early OHD applications and development

Since 1960s a vast amount of OHD dates have been published mainly by American and Australian labs, but due to the attached uncertainties only a few still are doing such a work routinely. We could mention a few such efforts that provide a range of outcomes, as any tabular presentation of all dates is cumbersome and finally provides same conclusions briefly drawn below. Thus, a comparison of around 60 estimated chronometric ages based on proposed obsidian hydration rate regression formulas (involving time, temperature and hydration for ^{14}C dated samples) with some calibrated ^{14}C ages have shown apparently significant divergence and a poor correlation coefficient of ~0.5 [52, Fig. 3].

The OHD has been occasionally reviewed in sole articles or as chapters in books. Among those, Friedman et al. [77] 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 are critiqued. 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), the objectification of laboratory techniques (preparation of thin sections and optical measurement of hydration rim/rind thickness) and the conversion of hydration rate data to age. They concluded four directions for future researches: (1) look for an inexpensive method of measuring rinds less than 1.5 microns wide, (2) determine hydration rates for a wider variety of obsidian sources/compositions, (3) develop a non-destructive method of measurement, and (4) standardize laboratory

procedures. In their review OHD was however promoted as a relatively inexpensive and "simple" scientific technique for chronometric dating, so that the current masterful treatments presented replaced earlier general assessment. Since then, points (1) and (3) are already reached, point (2) is ongoing but with drawbacks concerning reinforced (laboratory) hydration as regards to archaeological hydration, and point (4) due to several inherent problems with the method it is not yet realized widely, instead individual group often develop new procedures and there is lack of sufficient interlaboratory comparisons.

The great sensitivity of OHD results concerning laboratory determinations of diffusion rate constants and the estimation of EHT in the field was further pointed out by Braswell [78] from a study of the Coner Phase at Copas (Honduras). He maintained 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 [78,79].

An interesting radiochemical dating development by Lowe et al. [80] concerned the measurement of the amount of water in the hydrated layer on the surface of obsidians exchanging tritiated water (tritium of 20 μl of 5 Ci·ml^{-1} at 90 °C for 10 days) with the water in the layer. The activity of back-exchange water monitored is related to the thickness of hydration rim and to t$^{1/2}$; although it is a non-destructive technique, appears particularly applicable to young glasses where the development of hydrated layers may be inadequate for accurate optical measurement. However there was no follow up of this method.

Following the general rationale of OHD technique it has been extended to basalt flows and bombs that contain remelted rhyolite glass which thus can be dated [81]. No further applications have been reported.

Further application in OHD includes the dating of New Zealand obsidians of last millennium by Stevenson et al. [82], 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. Hydration dates have been satisfactorily but not exact compared with radiocarbon dates from same context, from six archaeological sites in the North Island of New Zealand, though the OHD errors span some 2–3 hundreds of years.

Ambrose [83] gave a provisional age-depth model for hydration thicknesses for the Pamwak site, Manus Island, Papua New Guinea, spanning from 4 ka to 13 ka BP, based on internal crack surfaces and compared with ^{14}C age control. Among other problems weathering and dissolution were readily observed, while the comparison with ^{14}C produced some confusion. In general, some ^{14}C or archaeological dating helped OHD to infer hydration rates for a specific source and location that was subsequently used to date possible tool occurrences at the same site.

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 [72]. 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. (4) 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. (3) resulted in OHD age estimates that range between 258–119 B.C. and A.D. 607–94, that incorporate the entire Hopewell period, controlled however by absolute C-14 dates of the same site.

Based upon the water diffusion in natural glass Stevenson et al. [84] introduced the conventional OHD technique to dating high-calcium manufactured glasses with first preliminary results on 17th century North American glass wine bottles manufactured by European settlers, concordant with historical data.

Lastly, 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 [85]. Secondary rate factors for theses fissures when compared to radiocarbon based rates a discrepancy was found due to dissolution.

International Association of Obsidian Studies (IAOS) Newsletter has published a lot of OHD dates discussed in terms of C-14 and/or archaeological history of case studies (http://www.peak.org/obsidian).

At any rate, the weakness of having an independent and consistent OHD chronometric tool has lead to a decline of applications and lack of confidence to archaeologists. However, the hydration seen as a physico-chemical phenomenon continues to intrigue researchers and exert marvelous efforts that seem promising in revising OHD techniques, surely useful until the mastering of this method. It is along these endeavors that there was a major shift of the OHD rationale moving from measuring hydration depth, the introduction of formulas for monitoring past temperature histories, and the modeling of time dependence on hydration, and others, towards the elaboration of hydrogen profile of concentration variation with depth acquired by SIMS.

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 C-14 date, and for nearby sites, the remaining uncertainty of the validity of the constancy of environmental characteristics.

5. Possible sources of errors for the conventional OHD dating

In spite of the more accurate hydrated rim measurement from nuclear beams and infrared with respect to older optical magnification, there remain uncertain sources of error that any application of the conventional OHD must be treated with due caution.

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, age errors from comparative methods (with C-14, archaeological typology) which affect the validity of the age-rim association.

Radiocarbon measurement errors are typically reported in the range of 50–200 years, with 100 years as a convenient nominal for analysis, though in several time spans drastically oscillating 'Suess Wiggles' are resulting to higher uncertainties. On the other hand typological-stratification age attribution may provide ages within respective cultural phases but verification by archaeologists are often required. Moreover, site disturbances, often met in early strata, create a necessity for independent dating on actual specimen. Nevertheless, in spite of rigorous statistical modeling and error propagation, the evaluations of all sources of error inhere uncertainties in each variant factor that the span of uncertainties may sway between extreme percentages of the order of some 10s%. 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 critical evaluation of main factors related and affecting the traditional OHD is described below:

a) Temperature: a few degrees in error of EHT in the Arrhenious equation (Eq. (4)), produce errors of several centuries. For an activation energy (E) of 85 kJ/mol, the error in age for ±1 °C is ±11–13%, for ±2 °C is ±25%, for ±3 °C is around ±37%. The well-known modifiers of obsidian hydration rate with prominent 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 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. Judgment is required in such type of analysis, because of the variation in weather patterns in different parts of the world, and on evidenced variations on a micro climatic scale, where averages are still insufficient despite the appreciable efforts to produce accurate effective hydration temperatures (EHT) [10,11,61]. 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. There are mathematical techniques to compensate approximately for temperature effects, but they are still a major source of uncertainty. Furthermore, transient heat sources such as forest fires can affect the hydration rim and results of the OHD process at least for T>~200 °C and proximity to fire core of less than ~5 cm [86,87]. It is generally good practice to measure a large number of samples so statistical techniques can be employed.

The effective hydration temperature (EHT) is defined as a constant temperature over a period of time which yields the 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 [10]. If a time-varying temperature history can be modeled numerically [10,11,88], an EHT can be computed which is a rigorous solution to the diffusion problem, the only approximation being the temperature model. Results of this computation have been previously reported, and a practical equation for archaeological use developed [10]. Effective hydration temperature can further be corrected for first-order changes in paleotemperature if proxy data are available [89,90]. Even so, it is unlikely that EHT can be corrected much better than ± 1.0 °C [10]. Effective hydration temperature includes the effects of temperature history in one parameter; furthermore, a change in EHT (ΔTe) produces a change in rim value (Δr):

$$\Delta r / r = -\tfrac{1}{2}\left(E / RT_e^2\right)\Delta Te. \tag{5}$$

For E = 20 kJ/mol and 90 kJ/mol Eq. (5) 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 1–6%/°C, the higher holds for nominal conditions.

Last, the effect of the irregular (diurnal, seasonal, and periodic) variations of temperature in the formation of H profile has not been examined, while the effects of *in situ* differentiation of burial conditions has been seriously considered and discussed in Liritzis [39].

b) 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 μm, more often 0.05–0.01 μm. A previous analysis [59] concluded that the accuracy is constrained by the resolution of the microscope system to ~0.25 μm 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 [91], so the error values quoted by obsidian laboratories are reasonable but the precision is weak as recent methods have shown. A comparison of optical readings with hydrogen profiles collected by secondary ion mass spectrometry (SIMS) [5,23] and infrared profiling [33] 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 +/− 0.05–0.1 μm but the cost per sample is prohibitive for routine application.

Indeed, higher precision of rim reading is achieved by SIMS or IRPAS. Different studies showed that hydrated layer thicknesses

measured using the traditional optical method systematically underestimates the H^+ diffusion depth when compared to SIMS due to sharp decrease in the stress-induced birefringence of the glass that prevents the full extent of the hydrated layer from being optically visible [6]. In contrast to the optical measurements, hydration layer thicknesses measured by SIMS agree well with those measured by IR PAS [5,66]. The excellent linear correlation of the two techniques demonstrates the improved accuracy of both measurements and the wide range of the linear relationship.

c) Diffusion rate: It is calculated from hydration experimentally induced controlled laboratory experiments for use in the Arrhenious plot, in high (with respect to environmental variation) temperature range (90–250 °C). First, this does not secure safe extrapolation to much lower temperatures, and second, the simulated hydration does not produce the anticipated behavior with obsidian of similar source [92]. Making use on nano SIMS and simulation experiments, rates are produced at environmental conditions. Such an aging experiment for Papua New Guinea obsidians has shown rates differing for same temperature and different 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 ~×25 for a 4-fold temperature increase, between 10 °C (0.002–0.004) and the 40 °C (0.06–0.10) for the four different sources, which, however, have no marked chemical composition variation [71]. From room temperature to 75 °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 [9].

Early estimates of D – using Arrhenious plots – were based upon optical measurement of hydration layers developed at elevated temperature (150–180 °C) [29]. 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, while an increase in precision is now achieved through the analysis using infrared measurement of experimentally developed hydration layers [5]. In spite of this improvement in accurate rim measurements the D still would inhere uncertainties, as long as the calculated parameters are not referred to ambient conditions temperatures and kinetics. Further accelerated hydration experiments are needed lasted for a few years, and if possible burying obsidians in sites and using nanoSIMS for H profiling.

It is useful to clarify that the diffusion process of concentration vs depth, ideally, is a step function, but in reality it follows the S-like curve. There are two regions in this sigmoid, the first covers the initial part of the diffusion and the, second, that follows after the drop towards the tail (it includes the FWHM). These are covered by different mechanisms (e.g. see [24]). One should separate these two and consider the diffusion mechanism and partial application of Fick's 2nd law of diffusion.

Last but not least, the role of phenocrysts presence (size and abundance) and transparencies should also be re-examined for they obviate ideal diffusion process.

d) The density versus pristine water % weight does not produce a smooth and narrow variation, instead a strong curving with a high scatter and inflection in densities at around 2.35 [67,82] obviates its use with any meaningful result.

e) The dependence of time (of Eq. (3)) on the purported square exponent of x is questioned and many authors reported other dependence (~t, ~t^n~$t^{0.5}$, etc), found experimentally from a comparison of OHD with other dating technique. [9,23,39]. That is why most reported OHD ages are compared with other dating means (C-14, luminescence, ceramic typology, and archaeomagnetism), an expected practice for the initial development of the method but not in the following years till today. In fact, the rate

dependencies on time exponent has lead to using various exponent models but the linearity between ^{14}C and the measured hydration profile is lacking in several cases and projection of either line to zero time does not result in a half-fall depth of zero. This causes systematic discrepancies between ^{14}C age and predicted hydration age. With the constraint that hydration depth must be zero at time zero the generalized t[n] relationship fitted the data for obsidians from Mount 65, Chalco Mexico with an excellent agreement between the derived half-fall characteristic point calculated dates of the empirical method by SIMS and the [14]C [6]. In the work by Riciputi et al. [6] the coefficient (n = 0.75) is assumed to derive from an average of rates over the time range of the artifacts, but without testing it over a broader time range therefore any extrapolation is unattainable. In a later revisit to this problem the Oak Ridge group deduced that, at but short times, the depth at which a concentration of interest occurs varies from the Eq. (3), with diffusion rate to vary as the square root of time at shorter times but trends toward linear with time at longer times [9a]. However, many archaeologically derived source-specific rate formulas approximate the diffusion equation with an exponent of apparently 0.5 for t. As said already empirical observation seems incompatible with the laboratory findings [9] several factors suggest that results need not be considered mutually exclusive. Taking into account, the non-accurate optical measurements of rim determination in the region of the sigmoid shape where the process takes over, wrongly attributed ^{14}C associations (context and calibrations), and, the laboratory rate formulations that are insensitive to low-end temperatures, as many published source-specific rate derivations would suggest, it is not surprising that this mathematical relationship has not always been embraced by archaeologists [52 and references therein].

f) The surface loss is identified as an important factor in glass hydration dating [60,74,83,92,93]. These issues still intrude on a dating system that initially saw only obsidian chemistry and site temperature as the main determining variables. Once present on same artifact with fissures the positive result from this circumstance is that 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 BP [94], the obsidian surface is subjected to flaking and this limits its range, on the other hand the nanoSIMS technology at least provides accurate minimal rim reading.

g) Humidity effects are relatively small and are typically ignored in analysis. Obsidian artifacts are generally exposed to water via interstitial soil moisture. Relative humidity (Rh) in soils is fairly consistently high, even in deserts [65]. However, the effect of accelerated hydrations with 100% Rh on diffusion kinetics has not been adequately studied, a part of an experiment on Pachuca obsidians that were hydrated for approximately 5 days at 150 °C at relative humidities ranging from 21% to 100%, and the resultant profiles were measured by SIMS. The results suggested that the hydration rate is, indeed, a function of relative humidity, but for the relative humidity levels commonly observed in most soils the effects on hydration dating are expected to be relatively small [9b and related references therein].

h) Intrinsic (pristine) water. The remaining hydration from original fast cooling of lava is an extremely important factor in the diffusion rate. However, a variability of intrinsic water is observed in obsidian that arises from geologic processes when the obsidian was formed. The hydration rate in obsidian at any given temperature is a function of the concentration of water in the glass (see Eq. (4)) [14,19,29,95,96]. Intra-source variability in intrinsic water content has been observed in Coso obsidians from eastern California, USA [97] and is likely present in others, thus measurement of intrinsic water content per each individual specimen is a must pre-requisite. Current methods of measuring intrinsic water in obsidian are micro-densitometry [51,67], mass loss on- ignition [98], and infrared spectrometry [4,5,66].

It is imperative to avoid extrapolations to ambient conditions, as the environmental context of simulated hydration experiments affect diffusion rate estimations.

6. Modern approaches using SIMS

A reviving of OHD was made [62] especially by the two leading groups—Oak Ridge National Laboratory and Tennessee University [6,23], and the Laboratory of Archaeometry of the University of the Aegean, Rhodes, Greece [35,99,100].

It was a turning point for OHD and a revival of obsidian dating studies had emerged [62,101–103]. Near the same time of the American group [6,23], another approach using SIMS initially proposed by Liritzis and Diakostamatiou [35] was based on the surface saturation with diffused water and introduced an alternative approach called SIMS-SS.

Both groups rely on the modeling of the H_2O concentration profile as a function of hydration depth, but following different ways. As a result the ODDSIMS and the SIMS-SS coined versions were produced. The ODDSIMS rely entirely on time constraint points via ^{14}C calibration of each site considered, the SIMS-SS seems independent of such calibration.

Detailed descriptions of the SIMS technique can be found in Benninghoven, Rudenauer and Werner, and Vickerman (editor) [104] and Wilson, Stevie and Magee [105]. A review of SIMS as applied in geochemistry is given by Ireland [106] and Compston and Clement [107] detail the most recent developments in the highly developed SIMS instruments used for isotope ratio measurements. There are two general SIMS modes: static mode and dynamic mode, depending on the primary ion current density, and three different types of mass spectrometers: magnetic sector, quadrupole and time-of-flight (TOF). Any mass-spectrometer can work in static mode (very low ion current, a top mono-atomic layer analysis), and dynamic mode (a high ion current density, in-depth analysis).

Although relatively infrequent the use of SIMS on obsidian surface investigations has produced great progress in OHD dating. SIMS in general refers to four instrumental categories according to their operation; static, dynamic, quadrupole, and time-of-flight, TOF. In essence it is a technique with a large resolution on a plethora of chemical elements and molecular structures in an essentially non destructive manner. Initiated by Tsong et al. [41], 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 of obsidians.

An approach to OHD with a completely new rationale suggests that refinement of the technique is possible in a manner which improves both its accuracy and precision and potentially expands the utility by generating reliable chronological data. Anovitz et al. [29] 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. [6]. 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 Rhodes, Greece, the dating approach is based on modeling the hydrogen profile, following Fick's diffusion law, and an understanding of the surface saturation layer. In fact, the saturation layer on the surface forms up to a certain depth depending 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, and pressure) [108]. Together these factors result in the formation of an approximately constant, boundary concentration value, in the external surface layer.

Within a short period of time after the start of the diffusion process a narrow layer is formed; a layer saturated with water. The time required for this formation is considered equal to $t = 0$. This formation period is very short in comparison to the total diffusion time and can therefore be ignored in the age estimation process. Following this period, the saturated layer increases a greater 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 has been shown [39] that all of the H^+ profiles are 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 derive from the considerable impact of environmental and intrinsic effects may alter the form of the SIMS hydrogen profile. It is these slight variations in the profile that are specific to each case considered and this is the important observation that the calculated age by SIMS-SS method relies upon. Therefore, any 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 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 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.

In comparing SIMS-SS ages with C-14 ones the archaeological context of each example must be discussed with particular attention placed on establishing the integrity of the context and the relationship between the radiocarbon event and the deposition of the obsidian artifact. It is important that both forms of material within the deposit (e.g., carbon and obsidian) reflect, as closely as possible, the same depositional event and depositional history.

7. The SIMS-SS dating method in brief

In order to model the form of the diffusion profile Crank's [20] theoretical diffusion curves were consulted. They derive from the solution of a differential equation that describes the diffusion process based on the modeling of the water distribution into the obsidian surface. A detailed presentation of the mathematics involved is given elsewhere [7,39].

For the non-steady state condition considered here, a collection of sigmoid shaped curves have been produced for non-dimensional distance and concentration. The SIMS profiles are re-plotted as non-dimensional (standardized to 1) diagrams of $C/C_{surface}$ versus $X/X_{surface}$ and are matched to the appropriate profile of our produced curves guided by the end point of C along the x-axis (Fig. 4).

In this way a k-value can be calculated from any particular sigmoid shape. A curve is then fitted to the SIMS data using TABLECURVE 2D software and takes the form of a polynomial with exponential terms. 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 X_s and 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 H_2O concentration versus depth profile as a diffusion/time equation. The modeling of this diffusion process is a one-dimensional phenomenon, whereas the H_2O 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 met near the sample surface, that is, in the first half of the sigmoid curve, the C is assumed as constant along a very short
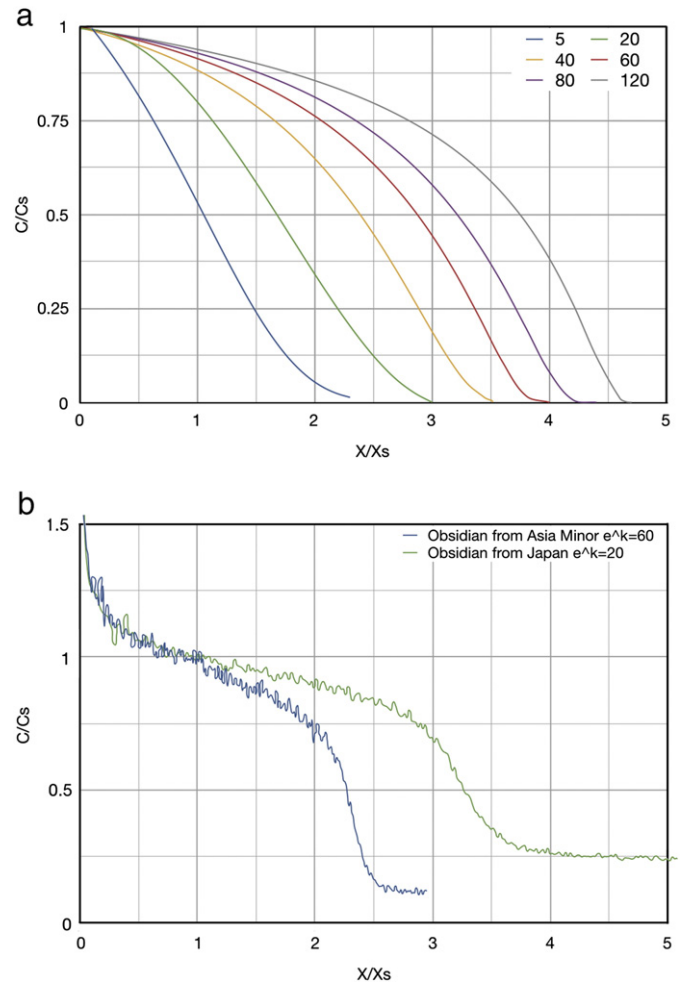

Fig. 4. a) Non dimensional plots of C vs. X. b) Non dimensional plots for two different measured profiles.

distance. Thereafter C gradually decreases following the trend of the sigmoid. In brief, the three principals used for dating are: a) the comparison of a non-dimensional 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 following Boltzmann's transformation and auxiliary variables, and, c) the modeled curve of diffusion profile (Concentration versus Depth) (Eq. (6), Fig. 4) [7].

$$C = \exp\left(a + bx + cx^2 + dx^3\right). \tag{6}$$

The dating equation that has been proposed incorporates all the above mentioned parameters as:

$$T = \frac{(C_i - C_s)^2 \left(\dfrac{1.128}{1 - \dfrac{0.177kC_i}{C_s}}\right)^2}{4Dseff\left(\dfrac{dC}{dx}\big|_{x-0}\right)^2} \tag{7}$$

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. (8) as the effective value of the

diffusion coefficient Ds for C = C$_s$, and k is derived from the family of Crank's curve (Fig. 4). It is:

$$D_{s,eff} = aD_s + b / \left(10^{22}D_s\right) \qquad (8)$$

where $D_s = (1/(dC/dx)) \times 10^{-11}$ assuming a constant flux and taken as unity [24,39,109]. Eq. (8) and assumption of unity is a matter of further investigation.

Very important parameters in the dating process are the calculation of the saturation attributes X$_s$ and C$_s$. Often the obsidian surface at the micro and nano-scale 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) have been used to examine the obsidian surface and investigate any correlation between the surface roughness and the SIMS measurements [92,93]. As proposed by Liritzis et al. [92,93], a linear regression fit in the diffused region (y = a + bx) defines the dispersion which reflects the degree of surface roughness. The smoother the surface, the less the pronounced is 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 gmole 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. A free use of the software is available in the internet (www.rhodes.aegean. gr/tms/sims-ss).

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 (Fig. 5). The SIMS-SS age estimates fall within the expected age ranges for the archaeological contexts for all samples. [109,110].

8. Possible sources of error in the new method of SIMS-SS

Occasionally, SIMS profiles are not properly sigmoid in shape and this affects the dating results. As mentioned above a major problem can arise from the irregular sample surface, but there are instances where the SIMS profile lacks the expected profile shape even though the surface is smooth. In other cases, the SIMS profile seems to be shorter
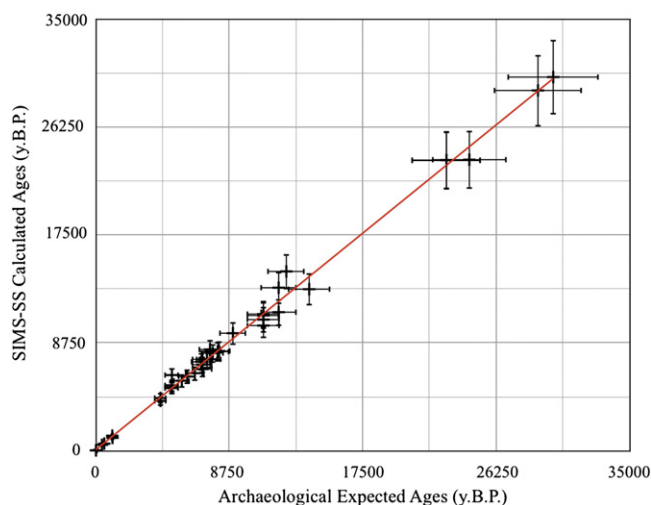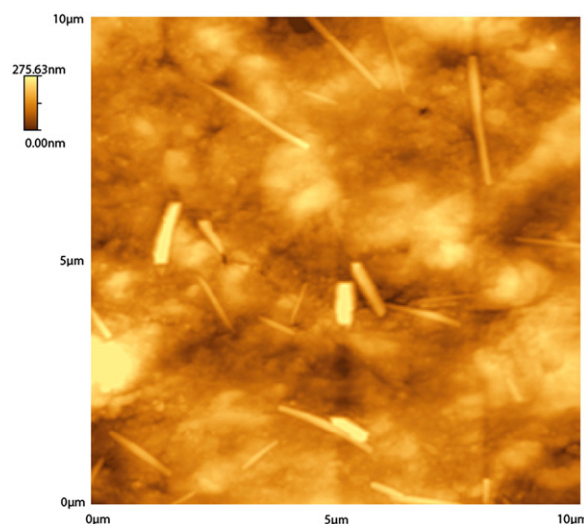

Fig. 6. AFM topographic image of SAR-2 (Sarakinos Cave, Greece) micro-crystallites are visible.

than expected for an archaeological artifact. These unsuitable samples can be grouped to two categories according to their deficiencies.

The first category samples have an eroded (weathered) surface that can be caused by a flaking from an accidental hit or generated by aggressive surface dissolution within alkaline soils. In the majority of these cases such small profiles are not datable. Recent surfaces can be created by the re-processing of an older artifact and this may be expected to occur mostly in areas with no easy access to obsidian sources. Age estimates from the SIMS hydrogen profile can be negatively impacted by corroded surface layers, by natural irregular surfaces and the presence of crystallites in the obsidians. The second category samples have distorted SIMS profiles. A major reason for this irregularity is the existence of crystallites in the obsidian matrix or the irregular surfaces. These samples have not a regular sigmoid shape and the majority of them have disturbed sections the initial profile region and the inflection part of the curve. The preferred analysis for such types of samples is with the aid of other imaging techniques. (e.g., AFM, PLM, and SEM) to guide a re-acquisition of the SIMS hydrogen profile, and hydrogen profiles are then grouped into acceptable and non-acceptable categories [109]. (Figs. 6 and 7).

Regarding age sensitivity to measured parameters, a 10% change in C$_s$ (saturation concentration) produces a 21% change in age, while a 10% change in X$_s$ (saturation depth), C$_i$ and e^K produce 6%, 0.6% and 0.35% error in age, respectively. Age errors are essentially insensitive

Fig. 5. SIMS-SS vs C-14/archaeological ages for obsidians all over the World.
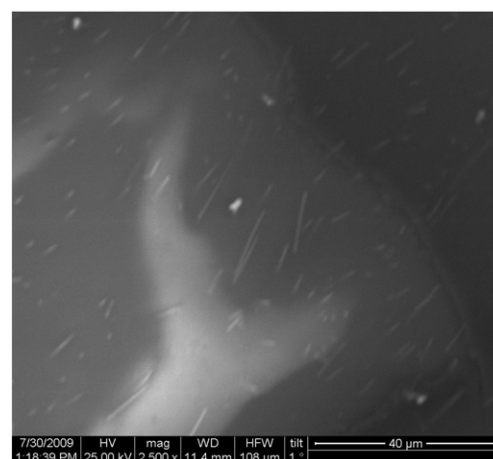

Fig. 7. SEM image of Yal-1 (Yali Island, Greece) (the white shadow is due to charge of the sample surface). A wide spread of micro-crystallites is visible.

to C_i and e^K compared to C_s and X_s [109]. The errors in variables are the standard deviation of X_s, C_s, and C_i. The final age error of Eq. (7) is made from Taylor's error propagation formulae. Once the applied criteria are met the conversion of profiles to ages are guided by the online free software (www.rhodes.aegean.gr/tms/sims-ss).

An example of age evaluation with the SIMS advanced rationale is given for sample YR-2 from the island of Youra, Greece (Section C, layer 3, 1-7-93, A/A8) with expected archaeological age of older than 9000 years BP. Initially, examination of the appropriateness of the sample and usefulness of the sigmoid profile is made by examination of the surface with SEM and AFM for location of a smooth area for the application of SIMS.

The optimum polynomial that describes the sigmoid shape is found through repeated fittings with a 3rd order polynomial. These fittings must follow the recently introduced rule of hyperbola turning [109]. The obtained polynomial coefficients are $a = -6.9926$, $b = -4133$, $c = 2.53e+7$ and $d = -5.9647e+10$. Subsequently, by applying repeatedly successive linear regressions in the hydrated area prior to the inflection of the sigmoid, we locate the length of the saturation layer and record the saturation depth (X_s) and saturation concentration (C_s) as the mean values in this layer. For sample YR-2 the X_s is $7.1699e-5 \pm 1.8396e-6$ cm and C_s is $0.0007738 \pm 1.47e-5$ grmol/cc. The 15–20 last data points of the tail is used, by calculating the average value, for the calculation of the intrinsic concentration (C_i) which for sample YR-2 is $0.0001589 \pm 5.52e-5$ grmol/cc. In all three attributes the $\pm$ error is calculated as the standard deviation of the values. Through a comparison of the SIMS profile with a family of Crank's theoretical diffusion curves [20] we calculate the value of e^k which, for our example, is 220 and therefore k is equal to 5. Finally putting the saturation depth (X_s) in the optimum 3rd order polynomial that models the S-shaped SIMS profile, the diffusion coefficient $D_{s,eff}$ is evaluated. In our example $D_{s,eff}$ is equal to $1.084e-12$ cm^2/year. Considering the depth equal to zero the derivative dc/dx (for $x=0$) parameter for the age equation is found (Eq. (7)). Finally all calculated parameters (C_s, C_i, $D_{s,eff}$ and k) are replaced in the age equation and the result is 11.907 ± 771 years BP. These steps are executed in the online software (www.rhodes.aegean.gr/tms/sims-ss).

9. Future prospects of SIMS in obsidians

Patel et al. [111] investigated depth profiles from diffusion of nitrogen, carbon and other alkalis in obsidian surfaces for dating purposes but without success. Nevertheless, their work was a pioneering initiative about the surface and near surface morphology of obsidians.

Four promising directions of research include, a) detection of organic residues, b) forensic and use-wear research, c) added information on diffusion mechanism and d) monitoring isotopic oxygen ratios, a proxy data for archaeo-palaeo-temperature variations.

In fact, forensic evidence of tool use has long captured the interest of archaeologists. The last forty years in particular have witnessed a remarkable proliferation of approaches and techniques for studying these microscopic attributes of stone tools. However, despite this progress the discipline has established only minimal methodological standards in the context of use-wear analysis. The standardization in use-wear research is a prerequisite for gaining greater insight into and understanding of lithic technologies and their cultural contexts. While the detailed examination of individual tools is important, it is the reconstruction of techno-behavioral relationships between tools, and between assemblages, that is of greatest interest to lithic analysts and archaeology as a whole.

Organic molecules can be traced successfully, while a 3D surface mapping is possible using Cs, Bi and O$_2$ ion beams. This way obsidian ware analysis can be achieved of supreme resolution well beyond optical microscopic inferences; thus use of these tools may be inferred (for hunting, cutting animal or plants).
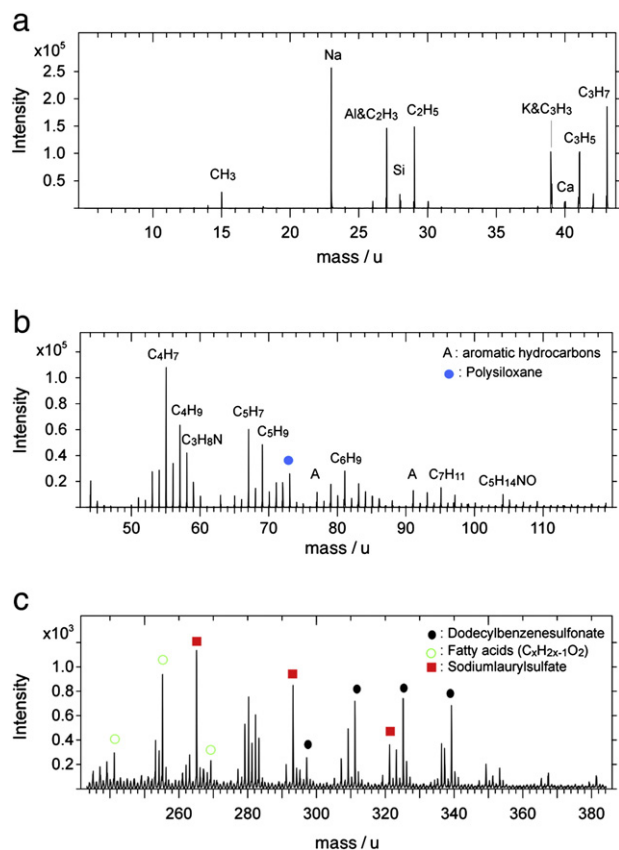

Fig. 8. ToF-SIMS spectrum of organic molecules from sample YR-3. a) and b) are for positive ion detection and c) for negative ion detection.

Detection of organic molecules includes various compounds (Fig. 8). A detailed investigation provides fatty acids, lipids, proteins through C–OH roots but phenoles, acetones, alcohols and haldeids, as well. In one case the chemical compound Oleamide has been found of unknown origin: it may refer to Kemamide U substance a type of amide found in animal brain, from a Mesolithic artifact (Youra Island, Greece), but to plastic bag contamination too. More possible is the origin of this compound to be the plastic bag due to very low fragmentation and high intensity.

These residues are accumulated and detected from within hollows existing at the surface since tool preparation (during skillful cutting of a core and preparing an artifact for appropriate use). Such surface hollows may also affect H profile for SIMS-SS dating, but ways to circumvent this problem are recognized considering the simultaneous variation of profiles of carbon, F, Al and Mg, measured with Quadrupole-SIMS [112].
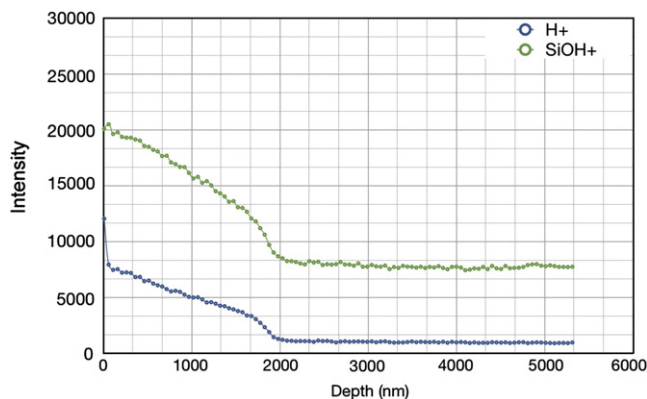

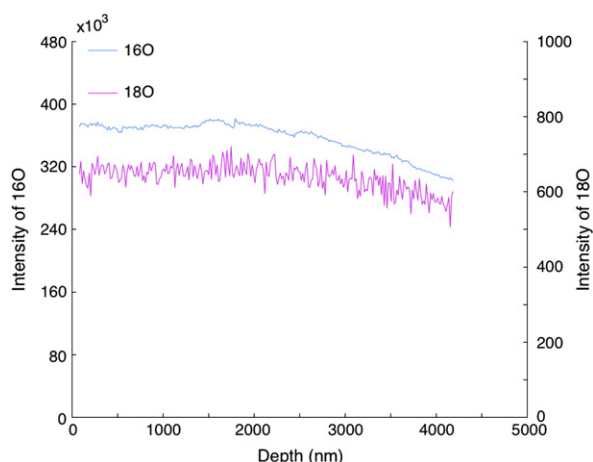Fig. 9. Depth profile of Hydrogen (H) and silanol groups (SiOH).

Fig. 10. Profiles of ^{18}O and ^{16}O. Left axis is intensity of ^{16}O and right axis is intensity of ^{18}O.

The latter cation detection includes also silanol groups monitored by depth that varies much like H+; these may provide implications on the intermolecular conversion and reaction kinetics between water and the amorphous glass. (Fig. 9).

Furthermore, obsidian hydration has been examined as a paleothermometer [113] and once $^{18}O/^{16}O$ ratios are monitored, an extremely useful index that trace past palaeotemperatures can be obtained. Preliminary results are produced in (Fig. 10).

Doremus [114,115] and Ericson et al [116] conclude that during diffusion of water and oxygen in quartz (obsidian and other amorphous oxides) the reversible reaction is occurring, by which ^{18}O carried in $H_2^{18}O$ molecules is exchanged with ^{18}O from the SiO_2 lattice.

These results along with our preliminary results can lead to the hypothesis that the Oxygen profile provides a continuous record of temperatures in the archaeological sites and this may prove soon a tool with many applications [112].

Last, but not least, the application of Obsidian Hydration Dating procedure to hydration profiles of flint and quartz is questioned due to the existence of crystallic network of SiO_2. This SiO_2 lattice has strong impact to the diffusion mechanism through its crystallographic orientation [116]. In Fig. 11 such a SIMS profile is presented. No sigmoid shape occurred. A preliminary investigation has not shown existence of saturation layer or hyperbola turning. If we assume that in flint we have only the second mechanism of diffusion (see Sections 2 and 7) and therefore replace the saturation attributes Cs and Xs with the values of
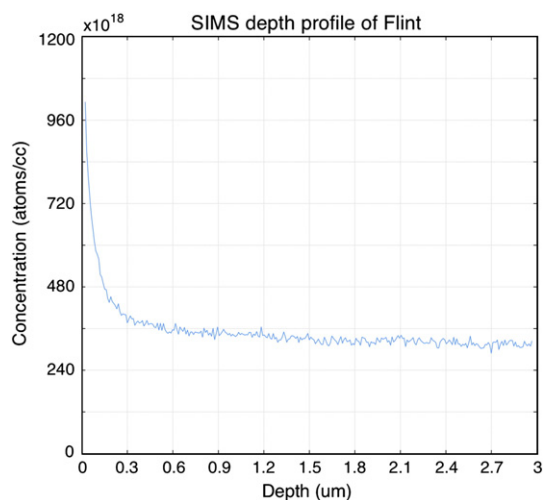
depth and concentration at the initial higher part of the exponentially dropped H + concentration in the hydration layer of flint, the effective diffusion coefficient has values in the same order of magnitude as Ericson's [116]. This effective diffusion coefficient represents the diffusion rate in the predominant crystallographic axis of the SiO_2 lattice and an age could be deduced [117].

10. Conclusions

The OHD based upon the simple squared root of time equation though simple has produced under controlled local conditions some satisfactory dates. The wide application of the method is however not widely approved due to several uncontrolled environmental and variable intrinsic parameters. The development of OHD via SIMS H + profiling has shown that the interesting physical phenomenon of water diffusion in glass offers potential solutions to dating obsidian artifacts. Though a temperature sensitive method, as well as, the lack as yet of a scientific approach to such diffusion, still it makes the method as widely wanted as radiocarbon or luminescence. The recent advances involving modeling of water profile holds at least as a step forward describing a phenomenological model of diffusion. The SIMS-SS method is an intrinsic method that taking into consideration the suitability criteria at present offers a reasonable way to produce so far satisfactory reliable and most important independent of other dating method results. The low cost of the conventional OHD however has not been compensated by the upgraded ones with the high cost of SIMS profiling that makes the method as expensive as C-14. The sigmoid profile of concentration, versus, hydration depth, incorporates all intrinsic and environmental characteristics that reflect the burial history of the artifact. The modeling of the C versus X diffusion profile based on Fick's Laws of diffusion, and auxiliary variables and initial boundary conditions for the non-steady state one dimensional diffusion is expressed with an equation that provides the age for when the artifact was made.

The future of OHD with the new advances looks promising and regains its initial impetus of becoming everyday a self-contained chronometric system, a routinely used absolute dating method in parallel and as complementary to luminescence and radiocarbon methods. Finally, SIMS on obsidian has a multipurpose impact on direct and proxy environmental studies and usage of obsidian tools.

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Fig. 11. Hydration profile of a Flint artifact from Lamia, Greece.

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