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ARCHAEOLOGICAL OBSIDIAN HYDRATION DATING WITH SECONDARY ION MASS SPECTROMETRY: CURRENT STATUS

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ABSTRACT

The dating of obsidian stone tools from the last time were in use by prehistoric man has been approached in 1960, by Friedman and Smith who observed that a freshly exposed surface of obsidian takes on ambient water at a knowable rate that can be used to calculate the time elapsed since exposure and, therefore, the date of an obsidian artifact's production. Subsequently the hydration procedure has been studied further and distinct versions of the so-called obsidian hydration dating (OHD) method has been developed proposing both *empirical rate* and *intrinsic rate* approaches. In the last 20 years, secondary ion mass spectroscopy (SIMS) has been employed to accurately define the hydration profile (water concentration versus depth) in a phenomenological manner. By modelling the hydration profile, the age determination is reached via models describing the diffusion process.

KEYWORDS: diffusion, tools, Fick, chronology, SIMS, hydration, inclusions, artifacts, C-14, modelling

1. INTRODUCTION

Obsidian is a dense volcanic glass that occurs in eruptions is an extrusive igneous rock with a very high silica content composition; the amorphous matrix shows crystallites of various chemical composition, impurities, voids, lattice defects (Liritzis 2006) (Fig.1). Differences in chemical composition, mainly in trace elements, reflects its geological source, such that obsidian artefacts are used for the identification of distribution patterns and early seafaring (Laskaris *et al.* 2011, Simmons 2012). Yet, age calculation is an important piece of information that helps archaeologists place the above distribution patterns in a chronological framework.

The water of environmental humidity in the burial place is absorbed by obsidian's surface leading to the formation of a hydration rim at its interface layer (penetrating a few microns below the surface). It is known that the hydration of obsidian is a complicated, diffusion-based phenomenon, which is strongly affected by temperature, the intrinsic (structural) water of the artefact, water concentration on the glass surface and the glass stoichiometric structure but relative humidity (RH) as well (Mazer et al., 1991-in fact under isothermal conditions, the rate of hydration increased by as much as 25% between 60 and 100% RH). The obsidian hydration dating (OHD) method is based on the modelling of the rate of water diffusion into the natural glass surface, establishing a diffusion coefficient for this process and thereby leading to a calculated duration (in years before present) for this diffusion (Friedman and Smith 1960).

The dating methods in archaeology and cultural heritage is a constant appeal of development. Apart of the obsidian diffusion dating models several other chronological tools are established for inorganic and organic materials (Liritzis et al., 2020). The most important are e.g. the radiocarbon (^{14}C) (Olssen 2009; Cromb et al., 2012; http://calib.org/calib/); and luminescence versions (optical stimulated luminescence, thermoluminescence of burnt stone and sun exposed surfaces; see, Kim et al., 2013; Liritzis et al., 1996; 1997; 2018), preferably when possible application of both on same stratum. The obsidian hydration method has been successfully applied along with OSL surface dating (Liritzis' 1994 novel approach in Comptes Rendus) to date a prehistoric settlement use (Liritzis 2010).

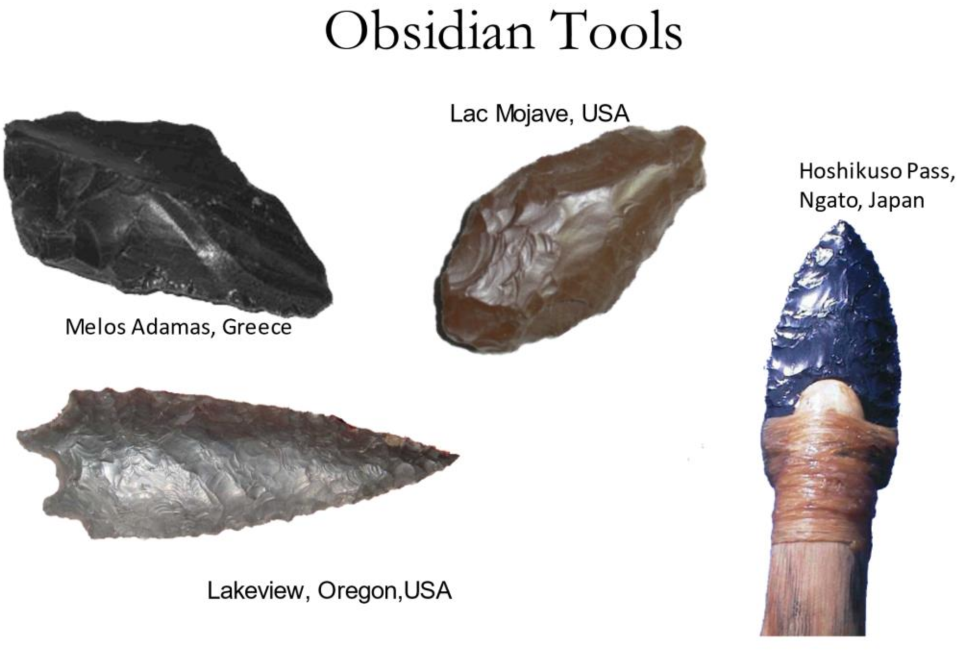

Figure 1 Characteristic images of obsidian tools

2. DIFFUSION MECHANISMS

Friedman and Smith in 1960 assumed that the diffusion rate is constant through time but in later years it was found that the diffusion coefficient is dependent on the concentration of already diffused water (concentration-dependent diffusion) (Drury *et al.* 1962, Lanford and Lanford 1977) Another factor impinging upon diffusion is the variable temperature of the burial environment. All these factors contribute to the final shape of the diffusion profile (concentration vs depth), the sigmoid curve (Fig. 2).

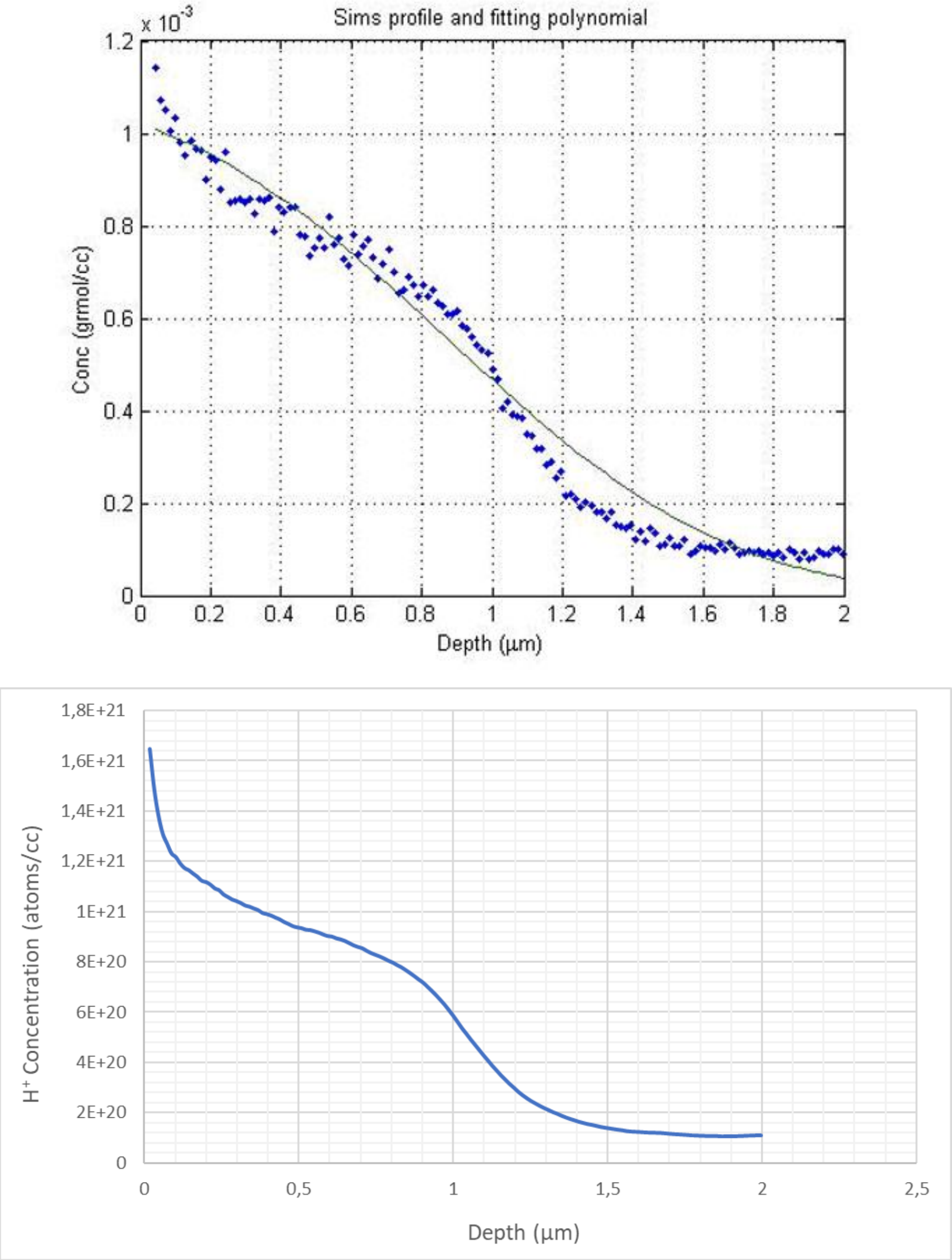

Figure 2. S-shape hydration profile (archaeological obsidian blade from Strofilas, Andros Island, Greece) in two forms; atoms / cc and grmol/cc, and a polynomial fit. SIMS profile was taken by a PHI Model 6300 and 6600 quadrupole-based SIMS (data obtained at Evans East, USA, see Liritzis 2010 and Liritzis et al., 2004

Even now, sixty years after the introduction of the obsidian hydration dating approach, the exact mechanism by which water diffusion occurs in amorphous rhyolitic glass such as obsidian is still subject to research (Doremus 1969, 2000, 2002, Crank 1975, Zhang *et al*. 1991, Nowak and Behrens 1995, Zhang and Behrens 2000, Anovitz *et al*. 2006). In 2000 the late R. H. Doremus (2000) introduced a hypothesis for the diffusion of water, a theoretical model called the "diffusion-reaction model". This proposed model suggests that the water of the burial environment reacts with the Si-O-Si clusters and forms silanol groups (eq. 1).

$$H_2O + Si\text{-}O\text{-}Si \leftrightharpoons 2SiOH \qquad \text{eq. 1}$$

Further analyses (Stevenson *et al.* 2000) showed that the water molecules in the obsidian surface are the principal molecules that are diffused in the obsidian interface and during the diffusion in the bulk matrix the newly formed silanol groups (Si-O-H) remain stable.

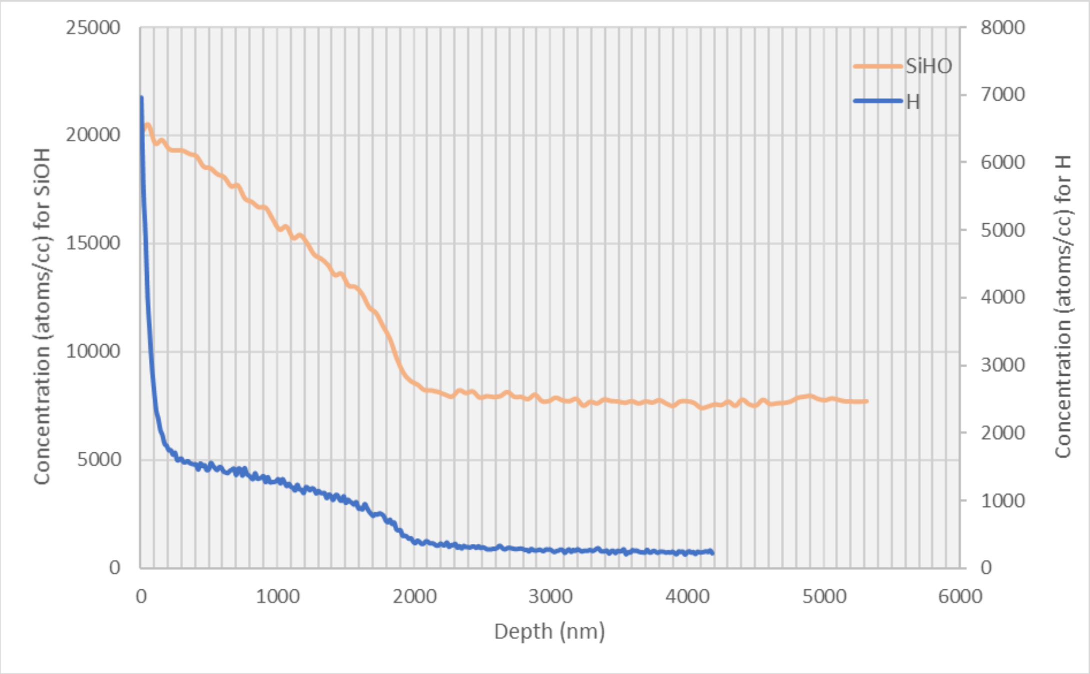

Figure 3. ToF-SIMS depth profiles of hydrogen and silanol (see, Laskaris et al. 2017)

Newer analyses (Laskaris *et al.* 2017) with the ToF-SIMS technique of depth profiling of obsidian artefacts confirmed the simultaneous process of water diffusion and the creation of silanol groups (Fig. 3). In Fig.3, the silanol depth profile follows the same general drop in shape as the hydrogen. At any rate the progressive diffusion and the Si-O-Si bond angle dependence of electronic structure of silicate clusters is a matter of research (Kowada and Ellis 1998). Further investigation of the angle variation along the diffusion area is under way.

Due to the fact that the diffusion mechanism, affected by the environmental temperature and the concentration of already diffused water, provides the hydration profile of sigmoid shape, the diffusion mechanism is called "concentration-dependent diffusion" (Lee *et al*. 1974, Tsong *et al.* 1980, Anovitz *et al.* 1999). In 1979, Lanford *et al.* suggested that the "concentration-dependent diffusion" model depends on a square root of time, but Liritzis and Diakostamatiou in 2002 proposed a more complex exponential dependence of $e^{f(x)}$ with f(x) being a 3rd order polynomial which was theoretically founded and reviewed by Liritzis (2006) (see also Liritzis et al., 2004).

In fact, Liritzis (2006), following the work of Doremus (2002), proposed another mechanism for the diffusion process. In this model, the water molecules randomly choose diffusion paths and the diffusion mechanism is also dependent on the size of the molecules. In this size- dependent diffusion, the water molecules with radius $r_w = 0.15$ nm occupy intermediate positions in the obsidian surface and pass-through doorways of r_D radius, by "jumping" between doorways. The size of these doorways ($r_D = 10$ nm) is derived from an equation of activation energy E which is the elastic energy for the dilatation of a spherical cavity from r_D to r (Frenkel 1946) (eq. 2). Surely, more spectroscopy data regarding the bonding of the various species involved (e.g., OH−, H+, H_2O, O–Si–O or Si-OH) is required to confirm either model. G, the elastic shear modulus for rhyolitic glass, is 30.1 GPa, so that the doorway radius is about 0.10 nm.

$$E = 8\pi G r_D (r - r_D)^2 \qquad \text{eq. 2}$$

Independently from the theoretical approach of how the water enters the obsidian surface forming the hydration layer, the diffusion-reaction model is described approximately by combining phenomenological model (founded though on solid physico-chemical principles of diffusion) introduced by Liritzis (2006) and his team and equation eq. 3:

$$\frac{\partial C}{\partial t} = \frac{\partial\left(D_{eff}\frac{\partial C}{\partial x}\right)}{\partial x} \qquad \text{eq. 3}$$

with $D_{eff} = 2CD/\beta$

Where C is the concentration of total water in obsidian ($H_2O + OH^-$), D_{eff} is the effective diffusion coefficient, 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).

At the onset of the diffusion process, as accelerated hydration experiments have revealed, the diffusion of water is a complex and dynamic process (Anovitz *et al.* 2004; Stevenson and Novak 2011). Thus, as diffusion takes place, hydration exhibits a high surface concentration along with decreasing diffusion coefficient (Liritzis 2014). Following up this Liritzis' method it has been suggested that this change may be due to glass surface relaxation as the stress that builds up in the near surface region is released (Liritzis 2006, 2014).

In 2011, Stevenson and Novak observed that the diffusion rate of molecular environmental water (H_2O_{me}) is getting faster into the obsidian surface going deeper as the concentration of total structural water (H_2O_t) increases. Therefore, following the work of Doremus (2000, 2002) and Liritzis (2006), they suggest that the total structural water H_2O_t shapes a glass structure more open during diffusion that increases the water molecule transportation through gateways in the bulk silica matrix. The presence and percentage of structural water as well as the degree of amorphous state and presence/size of minerals, play a decisive role in the estimation of diffusion rate, reconsidering the motto that higher time the deeper water gets into the obsidian body.

All these experimental results and suggested hypotheses lead to the admission of a difference in the mechanism behind the early stage of water diffusion that differs from the longer-term developmental process. In this case, the proposed mechanism by Liritzis and his students (Liritzis and Diakostamatiou 2002, Liritzis 2006, Laskaris *et al.* 2011, 2017) in which the diffusion process is separated into two sub-processes is reinforced. The first process is about the transport of environmental water to the very first layers of the obsidian surface. The second process is the main diffusion mechanism where the molecular water enters deeper into the obsidian surface. The second process is much slower than the first process, a difference that leads to the formation of a saturation layer (Fig.4). This definition of the upper and lower processes in the approach of Liritzis and colleagues, is the starting point for the main phenomenon of hydration of obsidian in the obsidian-water system in a semi-infinite medium. It sets up the boundary condition (surface saturation layer or SS layer and concentration C_s), in relation to the initial condition where $C = C_o$ (where C_o is the pristine background water concentration).

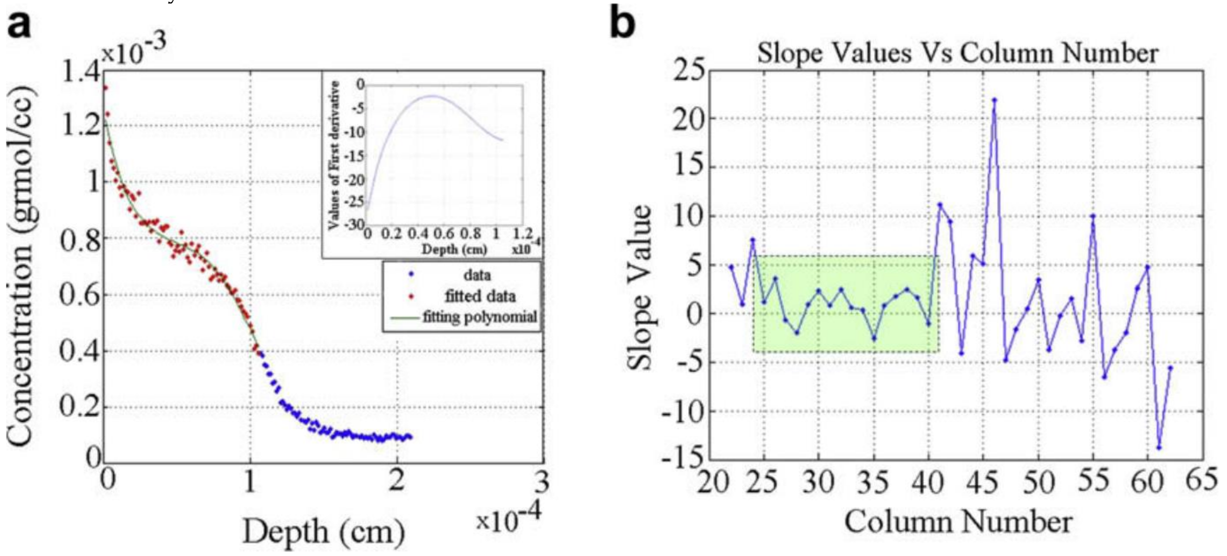

Figure 4. Hydrogen profile, the 2 hydrated regions and the determination of SS layer. The new concept. a) A 3rd order polynomial fitting at the diffused region of the SIMS profile. The 1st derivative of this is shown in the inset, (b) linear regression slopes versus data points. Green square is the saturation layer region.

3. REVIEW OF DATING METHODS WITH SIMS

3.1 Hydration dating basics – the OHD early stages

Obsidian artefacts absorb water, as part of the environmental humidity of the burial context, at a rate that may in principle be calculated. Friedman and Smith in 1960, working on the Obsidian Hydration Dating method, examined thin sections of obsidian artefacts and noted that the hydrated rim is visible under a high magnification microscope. They also observed that its width depends on exposure time, ground (or burial environment's) temperature and glass chemical composition. For dating purposes, they suggested the empirical equation (eq. 4):

$$x^2 = kt \qquad \text{eq. 4}$$

with hydration rate k as eq. 5:

$$k = Ae^{-\frac{E}{RT}} \qquad \text{eq. 5}$$

Where x is the thickness (μm) of the hydration rim, t the age in years, T the absolute temperature (Kelvin) which represents the effective hydration temperature (EHT), A is the diffusion coefficient (μm²/day) as a source-specific constant, E the activation energy (joules per mole) again as a source or burial environment's constant and R the gas constant (joules per degree per mole i.e. 1,987).

Since that first effort in 1960 until the 2000s many inconsistencies were observed when compared with other dating methods resulting in considerable doubts about the reliability of OHD (Ridings 1991, 1996). Thus, several approaches have been suggested to overcome his that are discussed analytically elsewhere (Liritzis and Laskaris 2011, 2012).

In all the approaches, the main question is the determination of the "effective temperature" T which in turn regulates the diffusion rate. This effective hydration (burial) temperature (EHT) (for thermal history and effective temperature, see Smith et al., 2003) is in fact the average temperature of the artefact, that applies to the thermal history during burial time. To overcome this problem two dating strategies were proposed, essentially trying to determine the rate at which water diffuses into glass:

(i) *empirically*, by assessing the relationship between hydration depth (via microscopy or SIMS or something else) and the ^{14}C dates with which the measured obsidian samples are securely stratigraphically correlated context-wise, or

(ii) by *induced hydration* in the laboratory (simulated hydration, aging) (the *intrinsic method*) and calculating a hydration rate (k) of eq.5, based on the activation temperature and Arrhenius equation for reaction kinetics (Friedman and Long 1976, Friedman and Trembour 1983, Anovitz *et al.* 1999, Rogers 2007, Rogers and Duke 2011, Stevenson and Novak 2011, Stevenson and Rogers 2014).

This k value is either estimated from nearby sites of supposedly similar climatic history (Pearson 1995, Stevenson *et al.* 1998, 2001, Rogers 2008) or, in the second approach (*intrinsic rate)*, the k of eq. 4 is experimentally determined and also coupled with accurate measurements of the site's temperature to derive an age (Anovitz *et al.* 1999).

Also worth mentioning is the extended research by Stevenson and his colleagues for the better understanding of diffusion process (Stevenson *et al.* 1998, 2000; Stevenson and Novak 2011, Stevenson and Rogers 2016). In the above-mentioned work of 2011, Stevenson and Novak, by using a combination of infrared photoacoustic spectroscopy (IRPAS) and secondary ion mass spectrometry (SIMS), provide valuable information for the distribution of water (H_2O) and hydroxyl (OH) of several forms (e.g., environmental molecular, total diffused) inside the obsidian matrix. Their conclusion was to propose new approaches for the estimation of the Arrhenius constants (see eq. 5) and thus the hydration rates in ambient temperatures (improving the intrinsic approach).

3.2 OHD with SIMS implementation

In the late 1990s to early 2000s a revival of OHD was made by two leading research groups, one at the Oak Ridge National Laboratory and the University of Tennessee (Anovitz *et al.* 1999, Riciputi *et al.* 2002), and the other at the Laboratory of Archaeometry of the University of the Aegean, Rhodes, Greece under the direction of I.Liritzis (Liritzis and Diakostamatiou 2002; Stevenson *et al*. 2003).

Both groups use the SIMS technique for measuring the hydration profile on the obsidian surface and rely on the modelling of the water concentration profile as a function of hydration depth. The American group at Oak Ridge base their approach on time constraint points via ^{14}C calibration of each site, calling their method ODDSIMS (obsidian diffusion dating by secondary ion mass spectroscopy) method. On the other hand, Liritzis and colleagues, as mentioned earlier, propose the SIMS-SS (secondary ion mass spectroscopy – saturated surface) method where the surface saturated layer (SS layer) is formed in the first 1–3 μm of the obsidian surface through two diffusion mechanisms.

Detailed descriptions of the SIMS technique can be found in Benninghoven, Rudenauer and Werner (2008) and Wilson, Stevie and Magee (1989). As the current authors mention in their review of obsidian hydration dating, "*SIMS technique refers to four categories of apparatus based on the type of operation; static, dynamic, quadrupole, and time-of-flight. Basically, it is a technique with a large resolution in a large number of chemical elements and molecular structures*". (Liritzis and Laskaris 2011)

In 1999 Anovitz *et al*. presented a model which relied solely on compositionally dependent diffusion following numerical solutions with a finite difference approach based on the H^+ profile acquired by SIMS. In 2002 the same research group (Riciputi *et al.* 2002) applied the proposed method to obsidian artefacts from Mount 65 of the Chalco site in Mexico. In this approach, numerical calculations are used to model the formation of the entire hydration profile as a function of time. Assumptions about the behavior of water as it diffused into the glass along with characteristic points of the SIMS H^+ diffusion profile are used, and a finite difference (FD) equations model proposed discussed by Riciputi et al. (2002), where a prerequisite constrained C14 age is involved as explained below.

There, firstly, ''characteristic points'', representative of the hydration depth, can be compared with associated ^{14}C dates for multiple artifacts. The ^{14}C ages and ''characteristic points'' can be regressed using various simple rate equations. If a good fit is obtained using a rate equation, the potential of applying an empirical calibration to use hydration depths as a chronometer can be evaluated. Secondly, the detailed shape of the hydration profiles can be used to investigate actual hydration mechanisms, processes, and rates. This is done by taking fundamental diffusion equations and using finite difference modelling to attempt to reproduce (1) the shape of the hydration profiles, and (2) how the shapes and depths vary as a function of time.

These points are: a) the *half-fall depth,* the depth at which the hydrogen concentration is halfway between the maximum concentration and the baseline concentration, and b) *inflection point*. The inflection point occurs at the depth where the hydration curve changes from being concave downward (exclusive of the near-surface region) to concave upward as the background value is approached. It is a minimum in the first derivative, and a zero in the second derivative of the concentration-versus-depth curve. Subsequently they considered the three models of time dependance of t versus D*t (linear, $t^{1/2}$ and t^n), for age calculation.

On the other hand, their *finite difference method* (FDM) uses a numerical calculation to model the formation of the entire diffusion profile as a function of time, and is fit to the profile as a whole (excluding the near-surface region), which involves solution of Fick's second law. Solution of the equations involves a number of assumptions, including boundary conditions and the nature of the actual diffusion process so that appropriate diffusion equations can be selected. In FDM the calibration condition is that the successful results are obtained using ^{14}C dates from artifacts, and the constraint that hydration depth is zero at time zero, to calibrate the depth-age curve, and then using this curve to derive ages for the other artifacts in the same context.

However, in their SIMS data the saturation level observed in Liritzis' approach is confirmed around 0.5-0.6 μm depth from surface (Fig.5a) and the water content under SIMS S-shape areas in general increases linearly with radiocarbon age (Fig.5b), but with disturbed deviations.

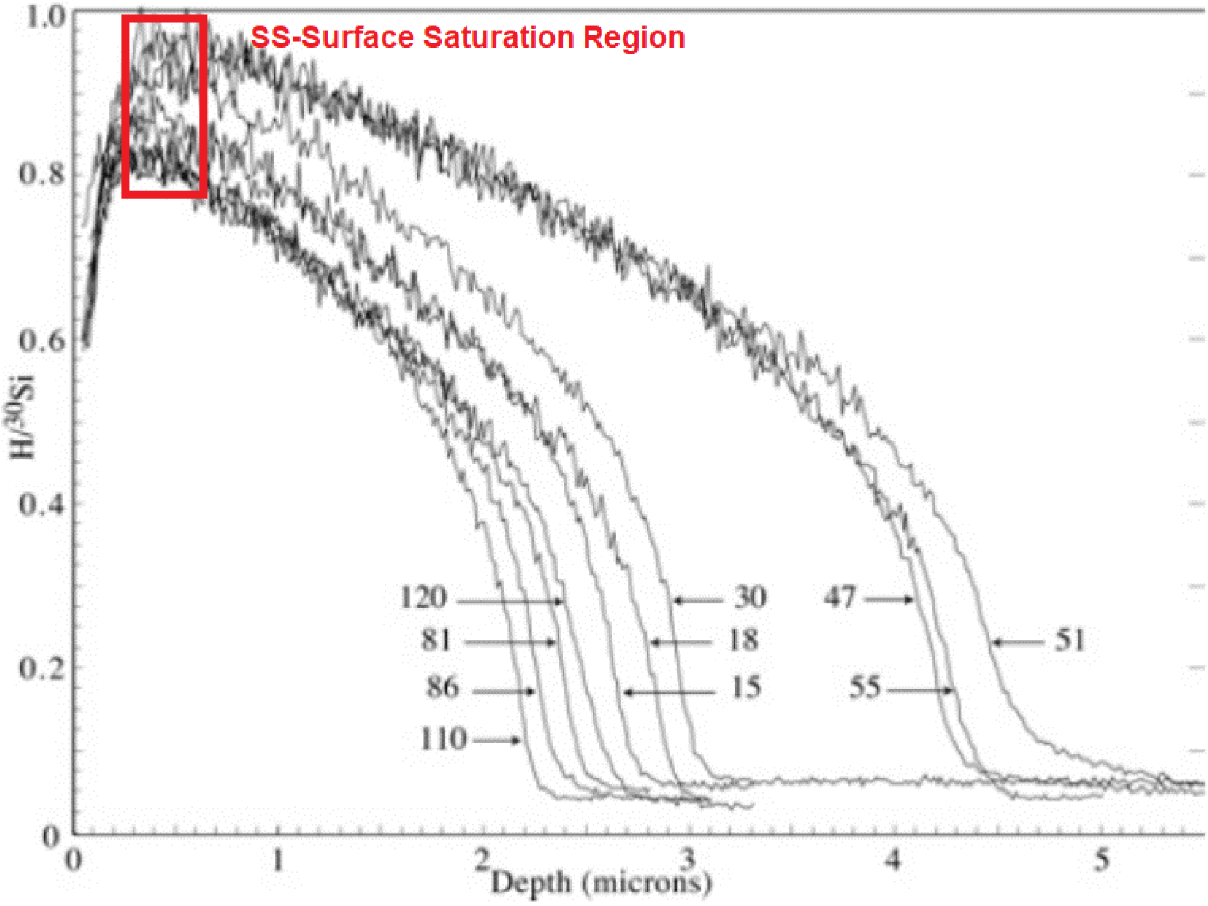

Figure 5 a. Hydrogen depth profiles in all samples from Chalco, Mexico. The H+ profiles are labelled using abbreviated sample numbers (for CHO) (Fig.6, Riciputi et al., 2002). Red rectangular is the region of saturated layer (NB: IL)

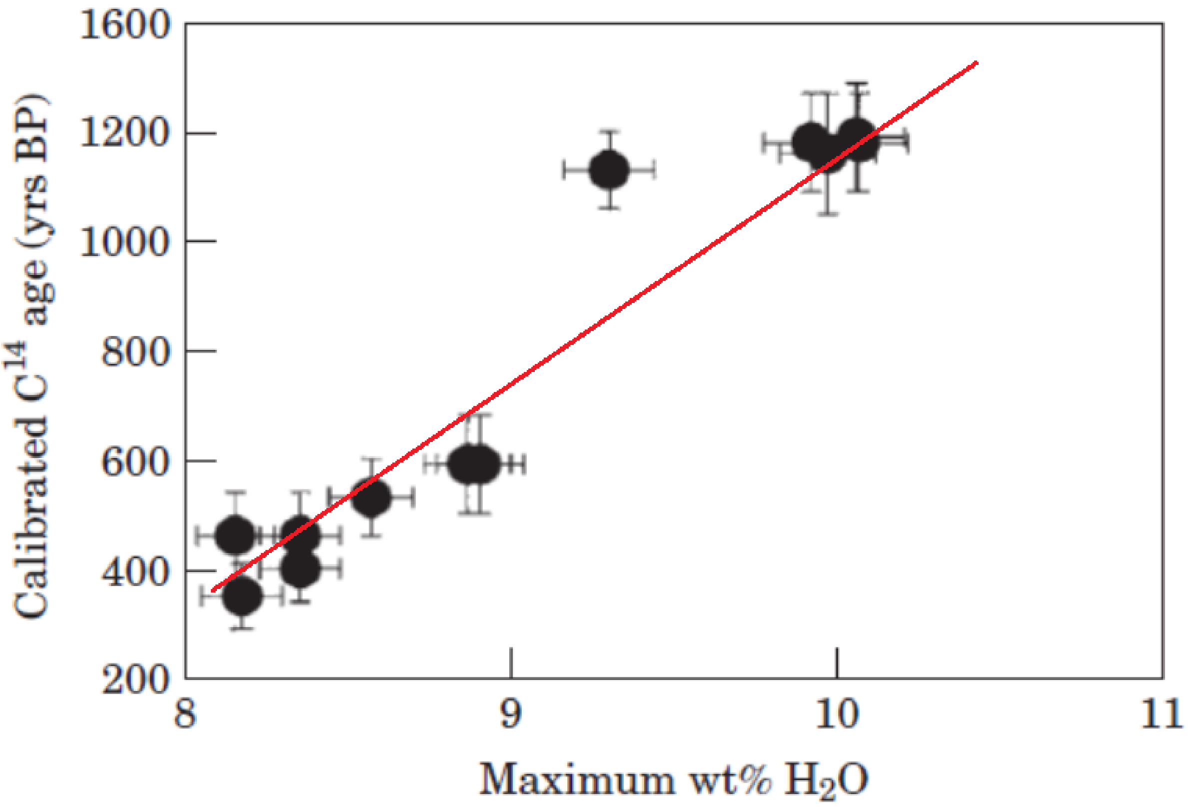

Figure 5 b. Maximum water content obtained in each profile as a function of ^{14}C age. Error bars are 1 standard deviation (fig.7, Riciputi et al., 2002). Red line arbitrary fit by the authors.

In the SIMS-SS method, the dating approach is based on the modelling of the hydration profile with Fick's laws of diffusion and taking into account the formation of a saturation layer (see, Fig.4). This saturation layer, approximately constant, is the key element in the SIMS-SS method as it is formed in the external surface layer and has the role of the boundary condition. Because of the very fast transfer of ambient molecular water into the obsidian surface and the much slower deeper diffusion, the formation period is very short and can be ignored. Therefore, the time required for this is considered equal to zero (t =0).

Recently Nakazawa et al (2020) described a systematic comparison that was done on optical rim thicknesses and hydrogen depths by means of an isotope microscope, which provides micro-imaging with SIMS, though their SIMS hydrogen profile (their Fig.4). x: at surface of obsidian. y: spot where hydrogen diminishes to background, does not convincingly define the onset of glass unaltered point.

Depth profiles of hydrogen were precisely obtained from the spots where optical measurements were taken on the archaeological obsidian flakes from two distinctive cultural horizons (older: Upper Paleolithic, younger: Initial Jomon) in the stratified open-air site of Jozuka in southern Kyushu (Japan). Given the current situation in which both traditional and new diffusion models with corresponding analytical methods (i.e., optical microscopic measurements and SIMS profiling) are juxtapose, the study by Nakazawa et al (2020) introduced the micro-imaging with SIMS, a new method of measurement that can bridge the two measurement methods.

Although a systematic difference between the optical rim thicknesses and hydrogen depths has been reported by Riciputi et al. (2002) and Stevenson et al. (2004), the plots of measurements presented by Nakazawa et al (2020) are more or less equally placed over and under the regression spline. Using the SIMS measurement of hydrogen depth for the Upper Paleolithic specimen J-2445-v-1 that retains the most consistent measurement between the optical hydration rim thickness and hydrogen depth, the hydration date is estimated by the equation: $x^2 = kt$, as $k=6.39\times10^{-3}$ where $x = 12.89$ μm and $t = 26000$ years ago. It is of interest however, to note the apparent difference in hydration rates for the Late Pleistocene and Holocene $k=4.061\times10^{-3}$ ($x = 6.53$ μm and $t = 10500$ years ago), two periods with different mean temperatures. Holocene temperature is higher than the Pleistocene. The lower rate for Holocene is in contradistinction with the anticipated higher. This is explained by factors other than thermal histories, such as intrinsic water content and geochemistry of obsidian. In general, the approach inheres inconsistency and needs reconsideration. We may recall, also, that the early measurements were made using negatively charged oxygen (O^-) bombardment with positive ion detection, while modern instruments using cesium (Cs) bombardment with negative ion detection provide superior backgrounds for H^+ analysis (see, Novak & Stevenson 2012), as well as early attempts on comparisons between Optical measurements with those from SIMS and IRPAS for the determination of the diffused layer (Stevenson et al., 2002; Ambrose & Novak, 2012).

4. THE SIMS-SS DATING METHOD

The rationale of SIMS-SS, the method for obsidian hydration dating, is based on modelling of the diffused water profile, especially along the first ~10 μm.

In the SIMS-SS method, the diffusion process is considered as a one-dimensional phenomenon. In this assumption, the obsidian surface is counted as a semi-infinite medium and the water molecules enter it in a perpendicular direction. The mathematical theory of diffusion in isotropic substances is based on the observation that the rate of transfer of the diffusing substance, through a unit area, is proportional to the concentration gradient measured normal to the section. It is expressed by eq. 6:

$$F_x = -D\frac{\partial C}{\partial x} \qquad \text{eq. 6}$$

where F_x is the rate of transfer of water moles per unit area (kmol m^{-2} s^{-1}) along the x-direction, C the concentration gradient of diffusing substance (mass per unit volume) acting as the driving force, x the distance coordinate measured normal to the section, and the proportionality constant D is called the diffusion coefficient (m^2 s^{-1}) or less commonly as molecular mass diffusivity or just mass diffusivity. The negative sign arises because diffusion occurs in the direction opposite to that of increasing concentration. It is combined with the flux as D = flux/gradient, where the gradient is the ordinary differential dC/dx of the concentration versus depth profile.

In order to use diffusion for dating purposes, it is essential to establish the time that has elapsed since burial. For this reason, a time-dependent analysis is required rather than a simple steady-state. At non-steady state mechanisms (where D depends on C, and C no longer depends linearly on distance through the medium) the equation that defines the rate of transfer is Fick's Second Law. This law, as Brodkey and Liritzis (2004) proposed, could be derived from the conservation law which is given as follows (eq. 7):

input + generation = output + accumulation eq. 7

The variation of concentration in a three-dimensional model of diffusion for a non-steady state and for a semi-finite media is given by eq. 8; if it is assumed that the diffusion phenomenon take place in one dimension, then eq. 8 can be simplified to eq. 3.

$$\frac{dC}{dt} = \frac{\partial\left(D\frac{\partial C}{\partial x}\right)}{\partial x} + \frac{\partial\left(D\frac{\partial C}{\partial y}\right)}{\partial y} + \frac{\partial\left(D\frac{\partial C}{\partial z}\right)}{\partial z} \qquad \text{eq. 8}$$

Furthermore, if the diffusion coefficient is assumed to be constant during diffusion then equation eq. 8 is further simplified as eq. 9, which is another expression of Fick's second law of diffusion.

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \qquad \text{eq. 9}$$

In 1975 Crank proved that eq. 9 has several numerical solutions depending on initial and boundary conditions. For the obsidian-water system Liritzis and colleagues suggested the following conditions (Liritzis and Diakostamatiou 2002, Liritzis *et al.* 2005; Liritzis 2006, 2014):

Initial condition: $C = C_o = C_i$, where C_i is the initial or structural water concentration of the glass; x equals the diffusion depth, where $x > 0$; for a diffusion time, t = 0.

Boundary condition: $C = C_s$ the obsidian surface (saturated) water concentration, for $x = 0$ and $t > 0$.

However, in concentration-dependent diffusion, the diffusion coefficient D is not constant during the hydration process but depends on changes in concentration, C. For this reason, a family of non-dimensional curves that relates concentration with depth (distance from the surface) for an exponential diffusion coefficient during sorption is given, which, through linear interpolation, are based on those given by Crank (1975) (see Fig.6 in Liritzis *et al.* 2004).

In brief, the three principles used for dating with SIMS are:

(i) The comparison of a non-dimensional plot with a family of curves of known exponential diffusion coefficients.
(ii) 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 and its Boltzman's transformation (see Liritzis 2014; Liritzis et al., 2004, 2007; Crank 1975)
(iii) The modelled curve of hydration profile.

Liritzis and colleagues proposed an exponential third order polynomial as the best fitting curve of the real diffusion data (concentration versus depth), as shown in eq. 10 (Liritzis and Diakostamatiou 2002, Liritzis *et al.* 2005, Liritzis 2006; 2014; Liritzis and Laskaris 2012):

$$C = \exp(a + bx + cx^2 + dx^3) \qquad \text{eq. 10}$$

The dating equation that has been proposed which incorporates all the above-mentioned parameters is summarized in eq. 11:

$$T = \frac{(C_i - C_s)^2 \left(\frac{1.128}{1 - \frac{0.177KC_i}{C_s}} \right)^2}{4D_{seff}\left(\frac{dC}{dx}\Big|_{x=0} \right)^2} \qquad \text{eq. 11}$$

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 and K is derived from the family of Crank's curves. The $D_{s,eff}$ represents the effective diffusion coefficient, the average for the whole diffusion time and it is empirically derived from a set of well-known ages and eq. 12 as the effective value of the diffusion coefficient D_s for $C = C_s$,

$$D_{s,eff} = aD_s + b/(10^{22}D_s) \qquad \text{eq. 12}$$

Where $D_s = (1/(dC/dx))*10^{-11}$ assuming a scaling factor of constant flux taken as unity (Liritzis *et al.* 2005, Liritzis 2006, Liritzis and Laskaris 2009). In the calculation of *D*, the multiplication by 10^{-11} has been performed in order to convert the units of *D* from the calculated μm² per 1000 years to cm² per year, which are the units used in SIMS-SS. For $X = X$s, *D*s is computed from equation 13.

$$D\text{s} = (\text{flux}/\text{gradient}) \times 10^{-11} \text{ years} \qquad \text{eq. 13}$$

However, with *D*s the age is far from right. It is well known that the diffusion coefficient is a diffusion constant, which could be derived mostly from the experimental data (Brodkey and Hershey 1988). Therefore, a relationship should be devised relating the coefficient *D*s to an effective coefficient *D*s,eff; that is, *D*s/*D*s,eff versus *D*s × 10^{-11}.

The empirical *D*s,eff is determined for obsidians with a well-known archaeological age (*t*).

Then, the obtained relationship, using the TableCurve 2D statistical package (Version 4 for Windows 95, NT and 3.1), is of the type $y^{-1} = a + b/x^2$; it is constructed from 26 different dated samples and becomes eq. (12), where $a = 8.051 \times 10^{-6}$ and $b = 0.999$ ($r^2 = 0.999$).

5. THE SUITABILITY CRITERIA AND STEPS OF SIMS-SS DATING METHOD

As the Liritzis *et alii* proposed in previous works (Liritzis *et al*. 2008, Liritzis and Laskaris 2009, 2012), the SIMS-SS dating method incorporates a set of suitability criteria along with fixed steps in order to implement SIMS measurement, calculate the duration of the diffusion and, hence, determine the age of an artefact.

First criterion: avoid roughness (Liritzis *et al.* 2008a, 2008b, Liritzis and Laskaris 2009) The surface roughness measured by the atomic force microscopy (AFM) 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 (Liritzis et al., 2008). This correlation highlights the need for appropriate obsidian samples/surfaces selection (especially of the surface area/spot) for the SIMS analysis and therefore for the calculation of the age (Fig.6).

Second Criterion: avoid inclusions (Laskaris 2010, Laskaris *et al*. 2017). Obsidian is a type of fast cooling lava with a rhyolitic composition. The obsidian structure is characterized as amorphous due to the mix of glassy matrix, surrounded by well-defined crystalline phases, such as microliths (feldspars, silica oxide phases, hornblende, biotite and opaque minerals). Therefore, it is of high importance to select a surface area free of inclusions to obtain a SIMS profile (Fig.7).

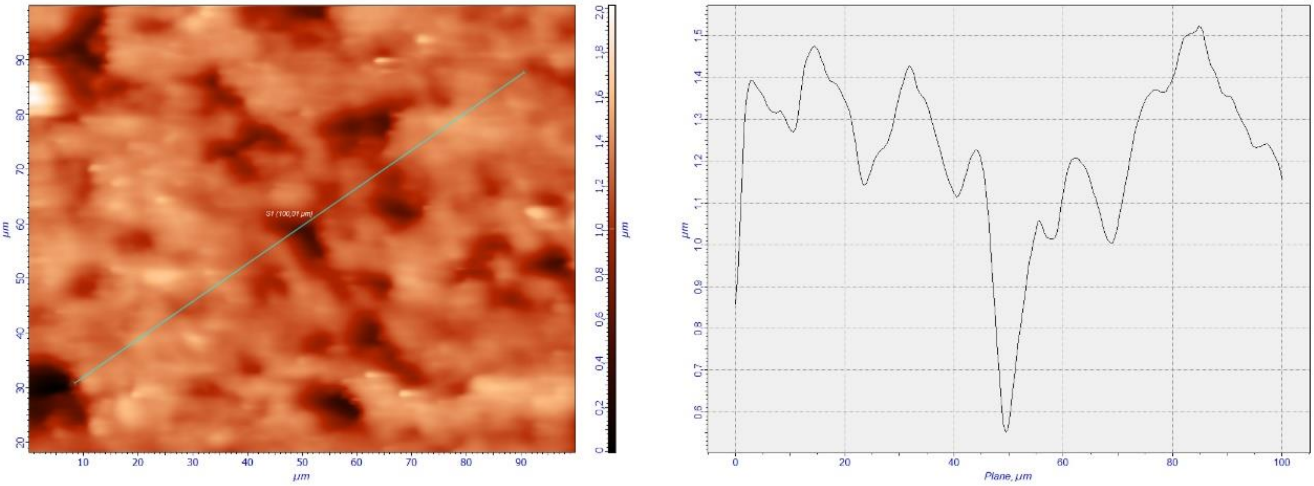

Figure 6. AFM Image of an obsidian surface, left: the scanned image in μm*μm, and right:height profile along the scanned line in left (sample: TAKO4F, Japan made at NCPR Demokritos Athens, by NL).

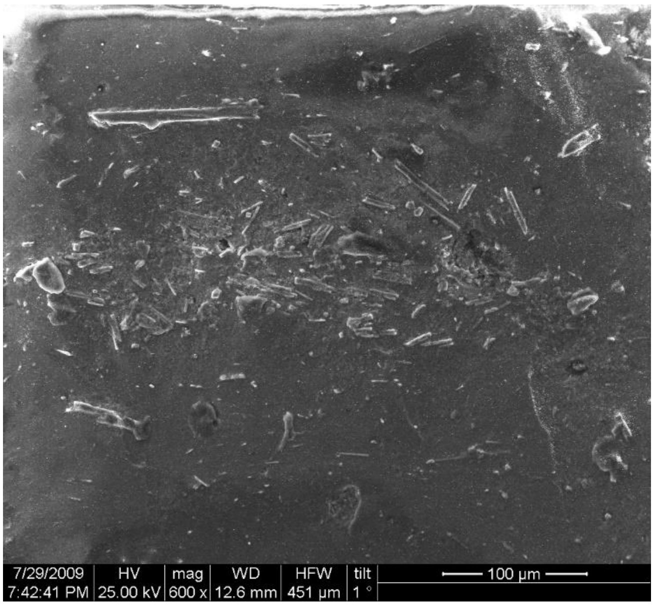

Figure 7. SEM image of an obsidian surface rich in inclusions that should be avoided for best determination of hydration (sample: Desfina Profitis Elias, Desf-10, Greece made at NCPR Demokritos Athens: Laskaris, 2010)

Third Criterion: use other elements as drivers (Laskaris 2010, Laskaris *et al*. 2017). During a SIMS measurement it is important to keep an eye on the distribution over depth of other cations such as carbon (C), magnesium (Mg), fluorine (F) and aluminium (Al). Any disturbance in these profiles implies an area with inclusions and therefore the measurement must be redone in a different spot. Disturbance in C, Mg, F and Al profile, is reflected in the H^+ profile too (Fig.8), implying the presence of some related irregularity such as a microlith. A re-measured profile in a different spot led to an accurate age determination.

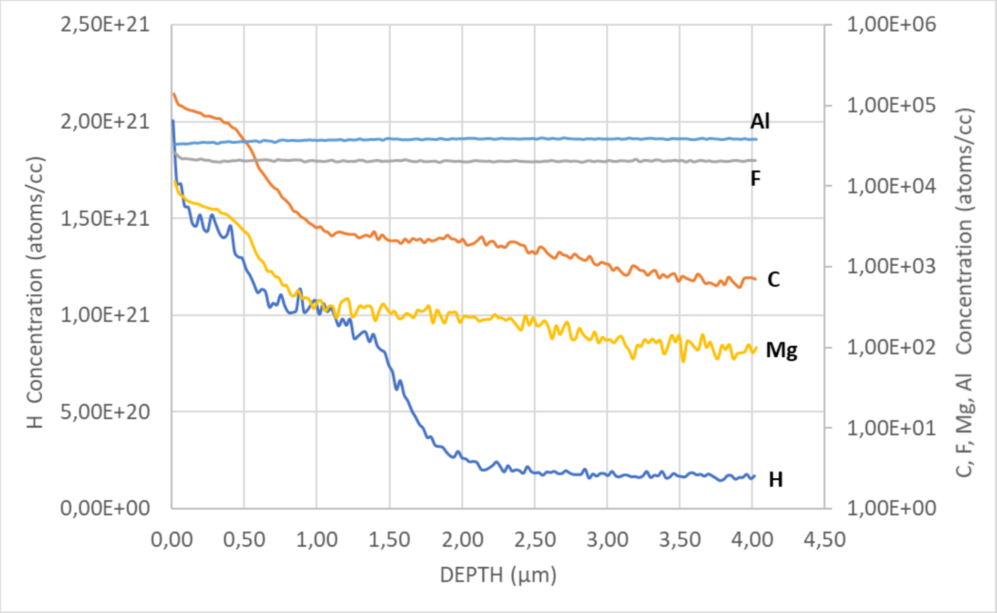

Figure 8. Example of a hydrogen profile with the four cations (C, F, Mg, Al) of a rejected measurement due to the third criterion (sample: Rho-892, Ikaria, Greece: Liritzis & Laskaris, 2012)

Taking into account these criteria for a successful SIMS measurement, the steps for dating with SIMS-SS method are:

1st step: The application of SIMS technique for measuring the H^+ profile.

2nd step: Most of the SIMS instruments, by default, produce results of concentration in atoms/cc, hence, it is important to transform them into g-mols/cc and the depth to cm. This occurs because of the way that the diffusion theory is about the transportation of molecules and not of atoms and all these must be in the scale of centimeters.

3rd step: The application of SIMS for the measurement of the hydration profile produces an S-shaped profile (in fact precisely it is a mirror image of S) that approximates its ideal theoretical curve which also has a sigmoid shape. In the Liritzis' SIMS dating methodology the sigmoid profile of measured data is modelled with a 3rd order polynomial. As aforementioned, in this step a polynomial that best describes the experimental data is produced for the calculation of diffusion coefficient D_s. For this step, the "hyperbola criterion" was introduced, wherein repeated 3rd order polynomial fittings are produced for different sigmoid tail points and the least square deviation R_{sqr} is recorded. In the "hyperbola criterion" the R_{sqr} versus the data at the tail of the SIMS measurement forms a bell-shaped hyperbola (Fig.9). The polynomial where the resulting R_{sqr} gives a maximum peak is taken as the best fit for the experimental data. The hyperbola can also be a reversed bell shape, in which case the minimum peak would be considered the best fit for the experimental data.

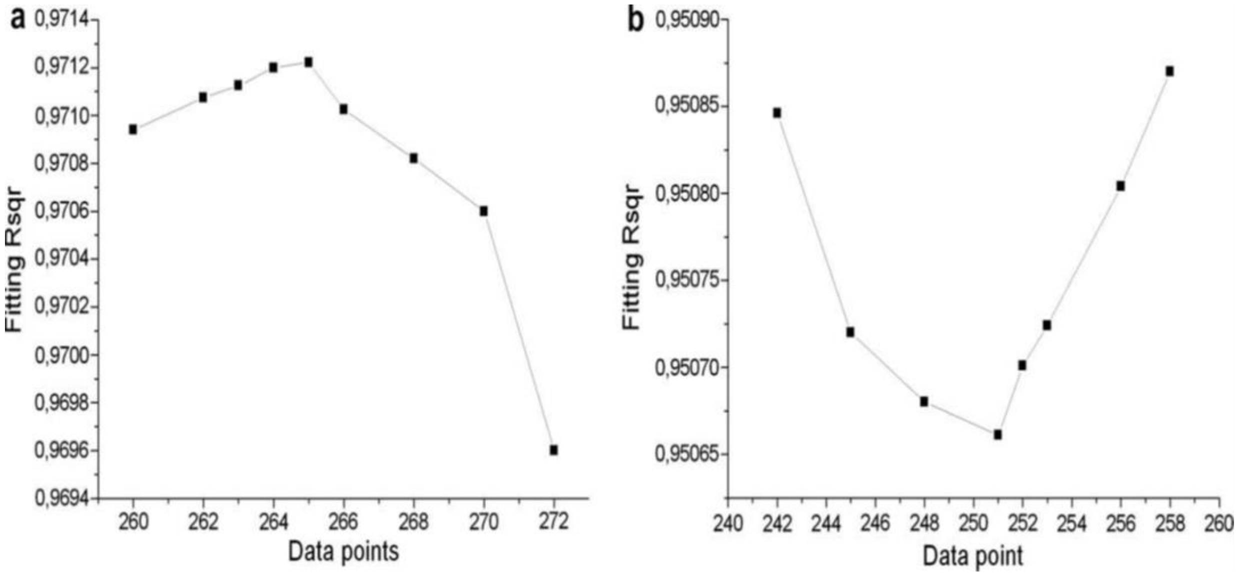

Figure 9. A plot of Rsqr Vs. data point number is constructed which forms a bell-shape curve. This bell-shaped curve, occasionally with a local maximum or a local minimum, in fact, alludes to the suitable polynomial needed for further processing.

4th step: In the two different diffusion mechanisms of the sigmoid curve (with different diffusion rates) and the produced saturation layer in the uppermost layers of the surface, the second mechanism transfers the water molecules from the saturation layer to the interior in the obsidian following Fick's second law of diffusion. Hence, the attributes of the layer (concentration and depth) are very important as initial/boundary conditions. There are several different ways to locate the saturated surface (SS) layer, such as using the first derivative of the best fitting polynomial or the repeated linear regressions of the data points in the diffuse area of the SIMS profile. The present authors proposed a combined method that starts with a cubic spline fitting with Savitziky-Golay algorithm in order to find the inflection point of the profile. The inflection point is the depth at which the chemical reaction takes place, i.e., the diffusion front. After this, repeated polynomial fits from the beginning of the data set up to the inflection point indicate a narrow region of data where the saturation layer is located. Then repeated linear regressions reveal the exact depth and concentration in the saturation level (Laskaris 2010, Liritzis and Laskaris 2012).

5th step: In the age equation we have to calculate a) the *k* value from the comparison of the non-dimensional plot with a set of theoretical curves, b) the D_s and $D_{s,eff}$ from the above mentioned equations, and c) the dC/dx for x=0 which is the simplified form of eq. 10 as *b*exp(a)*.

Finally, all the above values and parameters are incorporated into the age equation (eq. 11) and the age of an artefact is calculated in years before present (yBP).

6. ARCHAEOLOGICAL APPLICATIONS

Through the twenty years of SIMS application in obsidian hydration dating, the validity of the method and its procedures (criteria and steps) is tested through a comparison with independently derived ages. These "archaeological dates" are derived from other archaeological materials dated with methods such as radiocarbon or ceramic association. As the authors mention elsewhere (Liritzis and Laskaris 2009, 2011, Laskaris 2010), samples from all over the world, such as Easter Island (Chile), Mexico, Greece, Japan and Hungary, or artificially hydrated, and covering a time span from a few years up to 30,000 years ago, have been used to establish the success of the method

(Fig.10). The SIMS-SS age estimates fall within the expected age ranges for the archaeological contexts for all samples. A notable instructive example of the significance of obsidian hydration dating with SIMS as an absolute dating method concerns Aegean seafaring in the late Pleistocene/early Holocene (Laskaris *et al.* 2011, Simmons 2012).

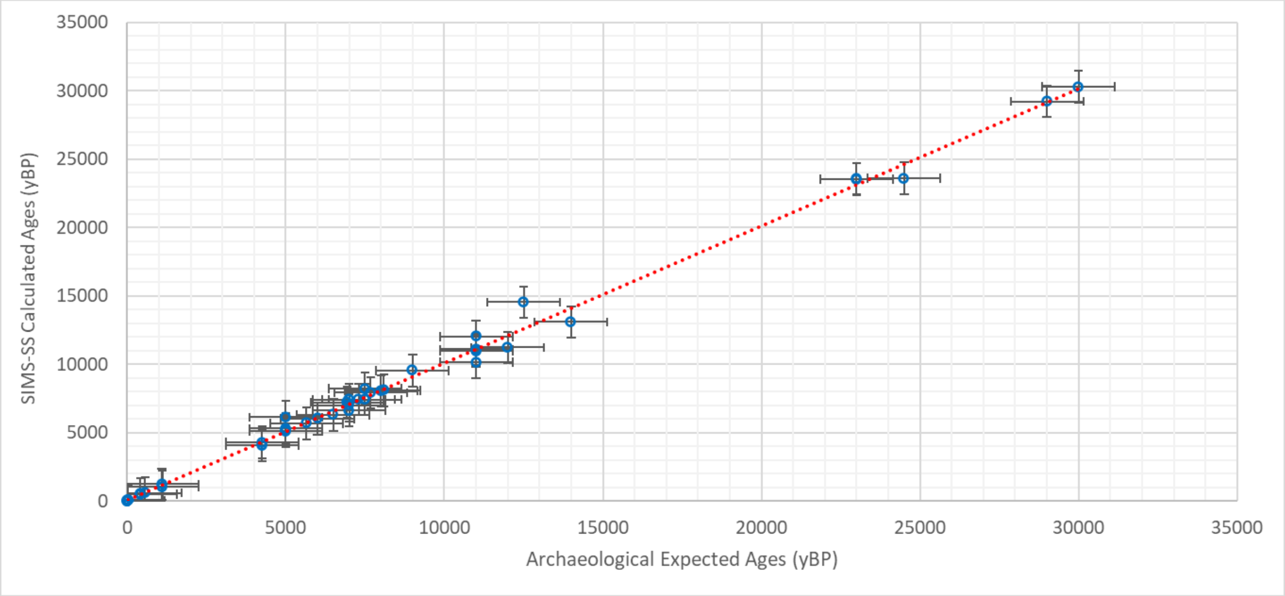

Figure 10. SIMS-SS calculated ages vs ^{14}C/ archaeological expected ages (Rsqr = 0.9958; data source (Liritzis and Laskaris 2011; Laskaris 2010).

7. CURRENT TRENDS IN SIMS DATING

As mentioned above and proved elsewhere (Anovitz *et al.* 2004, Stevenson and Novak 2011), hydration is a complex and dynamic process incorporating a variety of factors that affect the diffusion, such as the temperature, the environmental humidity, the surface roughness and the glassy matrix with the microcrystalline inclusions. Therefore, in the last decade, the aim of research groups (for archaeological or geochemical purposes) has been to study further the surface morphology, size and distribution of phenocrysts (by scanning electron microscopy, SEM) including any imperfections, lattice defects, voids in the matrix (Henderson 2005), and size-dependent inter-atomic configurations (Liritzis 2006, McCloy 2019) and parameters in general that affect the hydration, diffusion and the impact on dating results. For example, the investigation of the obsidian surface with atomic force microscopy (AFM), and relevant investigation of the obsidian surface have shown that the surface roughness is affected by a variety of causes such as weathering (burial conditions) and cleavage during the original manufacture of the tool. The use also has a significant impact on SIMS measurement when this leads to an increased roughness (Liritzis *et al.* 2008a, 2008b, Laskaris *et al.* 2017). Regarding surface morphology and hence the diffusion mechanism, use is made of time-of-flight-SIMS (ToF-SIMS). ToF-SIMS reveals the surface and interface morphology at the nanoscale through 2D and 3D surface mapping and cation profiling (H, C, Mg, Al, F, S, CN, O), as well as the detection of various fragments of organic molecules. Organic compounds, such as fatty acids, lipids, proteins, phenols, acetones, aldehydes and alcohols, detected in natural surface hollows (formed at the cutting of the obsidian tool) may provide clues of the usage of the tool, yet may also overmark the H^+ profile measurement with SIMS (Laskaris *et al.* 2017).

In a recent bibliography, research groups, either for cost effective reasons of a SIMS (Garvey *et al.* 2016), or, as part of their ongoing research, keep working on finding bridges between the SIMS analysis of diffusion profiles and the conventional hydration dating approach of the early 1960s. Representative examples are those of Stevenson and Rogers (2016), Garvey *et al.* (2016), Nakazawa (2016) and Nakazawa *et al.* (2020).

8. CONCLUSION

At the beginning of obsidian hydration dating, the simple square root of time equation produced, under controlled local conditions, some satisfactory dates. This approach, however, was highly questionable and, since then, has been subjected to several re-evaluations and attempts in understanding the parameters involved in glass hydration. The main reason for this problematic of using OHD was the complex phenomenon of hydration and the structural configuration of each obsidian source and archaeological tool. Diffusion of water in an obsidian surface involves chemistry, physics, the micro-/nano- morphology of the surface, along with environmental factors such as the humidity and the temperature.

The application of the SIMS technique to the measurement of obsidian hydration provides a great deal of information about the distribution of water molecules in the near surface of the obsidian and how all the above-mentioned factors affect the diffusion process. In the analytical mathematical approach of H^+ hydration profile (concentration versus depth), values for initial water concentration, boundary conditions, diffusion coefficient and, in general, the fulfilment of Fickian laws are calculated. The obtained profile contains all intrinsic and environmental parameters reflecting the burial history of the artefact. SIMS is generally considered at present to be a promising tool and to offer a more reliable method for diffusion profile measurements.

AUTHOR CONTRIBUTIONS

"Conceptualization, I.L.; methodology, I.L., N.L; software, N.L.; validation, I.L..; formal analysis, I.L., N.L.; investigation, I.L.; data curation, I.L.; writing—original draft preparation, N.L., I.L; writing—review and editing, I.L.; visualization, I.L., N.L; supervision, I.L.; project administration, I.L.

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