

SIMS-SS, A NEW OBSIDIAN HYDRATION DATING METHOD: ANALYSIS AND THEORETICAL PRINCIPLES*

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The water diffusion mechanism in obsidian has been revisited with the advent of a new dating approach employing secondary ion mass spectrometry (SIMS). The water diffusion SIMS(+) profile and the concept of a surface saturation (SS) layer in obsidians both provide a sound basis for the new diffusion age equation (SIMS-SS) and are supported by dated world examples (Liritzis et al. 2004). Here, we present the basic physical–chemical analysis of the mass transport phenomenon on which the new dating method is based. The crucial age parameter of the SIMS-SS dating approach for archaeological obsidians—that is, the surface saturation (SS) layer—is supported by both theoretical and experimental data.

KEYWORDS: DIFFUSION, SIMS, OBSIDIAN, SATURATION, ARCHAEOLOGICAL, CONCENTRATION, DATING, FICK, TRANSPORT

INTRODUCTION

Obsidian is a dense volcanic glass that occurs as a component of eruptions having a rhyolitic composition. Although obsidian is an amorphous natural glass, it may have vesicular and crystalline phases in small proportions. It has a typical major chemical composition of 70–75% SiO₂, 10–15% Al₂O₃, 3–5% Na₂O, 2–5% K₂O and 1–5% total Fe₂O₃ + FeO (see articles in Shackley 1998).

Obsidian was widely used for its sharp cutting edge in prehistoric times in Africa, the Mediterranean and the circum-Pacific regions. Each obsidian artefact will have a chemical composition that reflects its geological source. The potential to identify distribution patterns, and importantly to date the manufacture of an obsidian artefact by hydration dating, has made it a particularly attractive material for archaeological research.

Obsidian hydration dating (OHD) was first introduced by Irving Friedman and Robert Smith (1960). They suggested that

$$x^2 = kt, \quad (1)$$

where x is the thickness of the obsidian hydration rim in μm , k is the hydration rate in μm^2 per 1000 years and t is the age in years.

Riciputi *et al.* (2002) proposed an alternative obsidian hydration dating system based upon the analysis of SIMS profiles. They used ‘characteristic points’ on the hydrogen profile (half-fall depth and inflection point depth) incorporated into evaluated simple hydration rate equations plotted against time constraints provided by associated ¹⁴C dates. They demonstrated that neither the traditional OHD equation for depth (x) as a function of $t^{1/2}$ nor as t^1 fits the data. Using the t^n ($n \sim 0.75$) function, equation (1) provides a satisfactory fit between calibrated

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^{14}C dates and characteristic points that meet the constraint that, at time equal to zero, the depth of the hydration profile must also be zero. However, this may be an average coefficient for the available age range and particular obsidians may vary for other conditions (time range, environmental and structural). They also applied a general and an implicit finite difference (FD) model—one of several numerical approaches to solving diffusion curves (Crank 1975)—and reproduced the detailed shape of the hydrogen concentration versus depth profiles measured in real obsidians. The FD uses numerical calculation to model the formation of the entire diffusion profile as a function of time and is fitted to the profiles as a whole (excluding the near-surface region). Again, here the solution involves a number of assumptions, including boundary conditions and the nature of the actual diffusion process, so that only appropriate diffusion equations could be selected. Moreover, the diffusion coefficient D ($\text{m}^2 \text{s}^{-1}$) was empirically determined (Anovitz *et al.* 1999), but for some combinations of D , time step Δt and depth step Δx , an explicit solution became numerically unstable.

In general, the FD equations are based on a number of assumptions about the behaviour of water as it diffuses into the glass. Therefore, in their report several assumptions and calibration requirements were made, based upon characteristic points of the SIMS H^+ diffusion profile.

At the same time and later, Liritzis and Diakostamatiou (2002) promoted a different concept of obsidian surface saturation with diffused water and introduced the new dating method, SIMS-SS (Diakostamatiou 2003; Brodkey and Liritzis 2004; Liritzis *et al.* 2004, 2006; Liritzis and Ganetsos 2006). There, the hydrogen profile was best fitted by a third-order polynomial, D was taken as the inverse of the first derivative of the S-shape, and varied with an exponential dependence of the concentration (C), and based on Fick's Second Law and Boltzmann's transformation involving auxiliary variables and boundary conditions (see below), the diffusion time (t) that corresponds to the entire profile was found in relation to D and C at the surface saturation (SS) layer.

In our earlier papers, we have presented this new concept and dealt with the entire profile in terms of a concentration-dependent diffusion coefficient, without the detailed description of the SS layer.

Here, we provide a more detailed clarification of the assumptions and concept of the new SIMS-SS approach, emphasizing particularly the surface saturation layer (SS); for example, its thickness, its rate of formation, its dependence on obsidian structure and its phenomenological definition. This was deemed necessary following a recent publication (Anovitz *et al.* 2004), but also from recommendations made by colleagues at the most recent Obsidian Summit in Tokyo (1–7 September 2004, organized by Professor Masao Suzuki).

The arguments structuring the paper refer to: (a) the diffusion phenomenon, supported by experimentally derived hydrogen profiles in obsidians from various parts of the world; (b) the physical meaning of surface saturation by water molecules; and (c) the analytical approach to the shape of the H^+ profile. Although the diffusion phenomenon can be found in textbooks, a brief account is given to aid non-specialists.

THE NEW DATING METHOD (SIMS-SS): DIFFUSION PROFILES

It is common sense to formulate a general rate equation as

$$(\text{rate}) = (\text{driving force})/(\text{resistance}). \quad (2)$$

This equation states that as the driving force increases, the rate (N_A) increases too, while the larger the resistance, the smaller is the rate. Let the molar flux be $(N_A/A)_x$, where the mass (in

moles) of species A is being transferred per unit area per unit time. Experimental observation verifies that the mass flux, at steady state, is proportional to the difference in concentration and inversely proportional to the distance of diffusion. This is the concentration gradient $\partial C_A / \partial x$. If N_A is the rate and ∂C_A is the driving force, and if the resistance is $\partial x / (DA)$ (where D is the proportionality constant, called the diffusion coefficient, and A is the mass of species A), then, according to the descriptive equation (2), Fick in 1855 introduced this parallel empirical process and suggested the following experimental observation at steady state (a state reached in which, after a time, the concentration remains constant at all points of the diffusion medium):

$$(N_A/A)_x = -D(\partial C_A / \partial x). \quad (3)$$

The subscript x denotes mass transfer in the x -direction only. Equation (3) is one of three analogous forms—for heat transfer, mass transfer and momentum transfer. The three equations are quite similar; each involves a flux term, a proportionality constant and a gradient of some measurable parameter. For mass transfer in solids (obsidian), which is the transfer of interest in this study, the analysis is almost identical to that of heat transfer (Brodkey and Liritzis 2004). We must not fail to recognize that each of the transfer operations is totally different; the mechanisms are *not* the same. It is only the mathematics of the simplified equations that is the common factor in the three forms of the proportionality constant.

At non-steady state (where D depends on C , and C no longer depends linearly on distance through the medium) the equation that defines the mass flux, and corresponds to equation (3), is Fick's Second Law. This law could be derived by the general property balance or conservation law, which is given as follows (Brodkey and Liritzis 2004):

$$\text{input} + \text{generation} = \text{output} + \text{accumulation}. \quad (4)$$

Indeed, in a generalized mathematical notion (non-steady state and incompressible), the balance equation is as follows:

$$\partial C_A / \partial t = \partial [D \partial C_A / \partial x] / \partial x = (\partial D / \partial x)(\partial C_A / \partial x) + D \partial^2 C_A / \partial x^2, \quad (5)$$

while for no flow or generation and variable D , it becomes

$$\partial C_A / \partial t = (\partial D \partial C_A / \partial x^2). \quad (6)$$

The SIMS-SS dating method was based and formulated on the solution of the equation that expresses Fick's Second Law (equation (6)). It is generally accepted that this law mainly applies to the description of the diffusion phenomenon, and for non-steady state conditions (Liritzis and Diakostamatiou 2002; Diakostamatiou 2003; Liritzis *et al.* 2004).

Solution of this leads to another equation, which relates the parameters that describe diffusion; that is, concentration C , time t and the diffusion depth x . Essentially, Fick's Law assumes the direction of flow during the diffusion phenomenon towards the lower concentration of the diffusing material. Equation (6) is a second-order differential equation and its solution demands the setting of initial and boundary conditions (Crank 1975; Brodkey and Hershey 1988; Liritzis and Diakostamatiou 2002).

It should be noted that mixing due to the mass transport phenomenon of the liquid phase into the solid (diffusion) is spontaneous. Water diffusion phenomenon takes place in any natural surrounding in which obsidian comes in contact with water vapour (Smith and Van Hess 1987).

The spontaneous nature of this phenomenon is a result of the system's progress for an equilibrium with its surrounding (the spontaneous nature is a result of a reaction producing a condition with a lower energy content). The amount of water spontaneously diffusing into

obsidian is limited even if the contact is continuous. An equilibrium, between the solid–liquid diffusing system and the surrounding medium, determines the limit for the amount of water permitted in the obsidian through spontaneous mixing (Perry and Green 1984; Smith and Van Hess 1987).

This amount of water mass spontaneously diffused into the surface of an obsidian artefact is specific to the physical–chemical properties of the obsidian and the properties of a particular archaeological site; that is, the properties of its surroundings. The diffusion of this specific amount of water mass into the external thin layers of the obsidian and the spontaneous mixing will cease after a short time, and the data processed so far indicate that this time is less than a few years. That is, any more added water, diffused through the obsidian surface, will accumulate but will not diffuse spontaneously within the obsidian external layers.

At any rate, it should be noted that the spontaneous diffusion of more water in the SS layer of obsidian will not occur, because it conflicts with the existing equilibrium. In fact, as the diffusion proceeds as a dynamic process in which transport occurs, equilibrium is not set. Once an initial thin SS layer is formed within a short time, the water concentration throughout the SS layer remains constant, despite the fact that the diffusion front proceeds as the water diffuses further into the obsidian mass. That is, the SS is in a steady state. Since at the SS layer $dC/dx = 0$, the flux must be zero. There can be no mass transfer (diffusion) across the SS layer. Thus, it is in equilibrium. Irreversible thermodynamics tries to address this by looking at conditions just a small distance from equilibrium.

Initially, the water from the external surroundings diffuses through the surface of the obsidian. The mass transport from the surrounding medium into obsidian is achieved through two mechanisms:

- The *first* mechanism is through the external surface of the obsidian, which is in direct contact with its surroundings. This mechanism is defined as the initial mass transport between a layer of resistance on the surface, from the surroundings to the external surface.
- The *second* mechanism is the transport of the water into the obsidian mass, in other words, the diffusion of water in obsidian.

It should be stated that the first mechanism is the mass transport through a film on the surface. The mass transport in this surface film is much faster than the mass transport in the solid body. This phenomenon is due to the fact that, in the first case, the humidity transport from the surrounding is made through the air layer that exists between the surroundings and the obsidian. This air layer exerts a much smaller resistance to water diffusion than the solid obsidian.

The mass transport essentially takes place once the molecules of the diffusing material are transported into the mass structure of the material. The ability for this transport—that is, the existing resistance to the diffusion—depends upon the intermolecular distance of this material compared to the size of the molecules of the diffusing material. Since the diffusing compound is the same, the rate for the transport of the diffusing material differs considerably for the transport within the solid, compared with that within the liquid or gas medium. Therefore, the transport rates are much faster within the air medium than the liquid, and much more than in the solid (Brodkey and Hershey 1988). The size-dependent mechanism may work as follows.

In the case of hydration dating, the reaction of water with silicates has been suggested (Ladram *et al.* 1997; Doremus 1999). Here the diffusion of water in these oxides influences properties such as viscosity, strength, chemical durability and optical absorption. The motion of network hydrogen and oxygen ions is often proposed as the mechanism of diffusion, while the suggested diffusion of dissociated water versus molecular water versus hydronium has also

been put forward for years (Doremus 1982; see also the review of references in the discussion section of Anovitz *et al.* 2004).

The size-dependent mechanism relevant to our model assumes that water molecules of radius r_w ($= 0.15$ nm) occupy the interstitial sites of the obsidian and pass through ‘doorways’ of radius r_D , jumping from one ‘doorway’ to another. In terms of the activation energy E of diffusion for molecules in a glass, equation (7) has been proposed (see Doremus 1994):

$$E = 8\pi G r_D (r - r_D)^2, \quad (7)$$

where E for water in rhyolitic glass is 84 kJ mol^{-1} (at well below the glass transition temperature of 600°C); however, ageing hydration experiments on Melos obsidians at $60\text{--}90^\circ\text{C}$ for 103 days and 100% humidity have shown E values of 78 kJ mol^{-1} instead of the $\sim 85 \text{ kJ mol}^{-1}$ found in earlier experiments conducted at $150\text{--}180^\circ\text{C}$ and on other obsidians with an equivalent water content of around 0.10% (Stevenson *et al.* 2003). G , the elastic shear modulus for rhyolitic glass, is 30.1 GPa, so that the doorway radius is about 0.10 nm. Actually E is the elastic energy to dilate a spherical cavity from radius r_D to r (Frenkel 1946). Surely, more spectroscopy data regarding the bonding of the various species involved (e.g., OH^- , H^+ , H_2O , O-Si-O or SiOH) is required to confirm either model.

The study of water diffusion in obsidian is based on the assumption that the diffusion goes forward in only one direction, the x -direction, which is perpendicular to the external surface of the obsidian sample (Liritzis and Diakostamatiou 2002). It is considered that the water-obsidian diffusion system is semi-infinite. This is justified by the fact that on one side of the system (the external surface) there is the specified surface concentration of the saturated layer (Friedman and Long 1976), while on the other side is the solid mass of obsidian that represents the infinite direction. The diffusion process is shown in Figure 1.

Consequently, as the diffusion of the water from the surroundings to the external surface of obsidian is much faster than the diffusion of water within its mass, an external surface layer of obsidian becomes saturated in water within a short period of time (Brodkey and Liritzis 2004; Minoru Tomozawa, pers. comm., 2005). As the water diffuses further into the obsidian, the profile of the water concentration C versus the diffusion distance x has a sigmoid (S-like) shape (Lee *et al.* 1974; Tsong *et al.* 1978; Anovitz *et al.* 1999; Stevenson *et al.* 2002a,b).

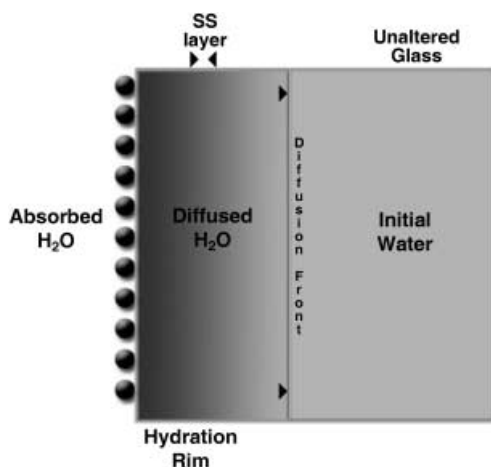


Figure 1 A schematic representation of water diffusion in obsidians.

The combined factors of the faster diffusion rate of water in the obsidian surface, together with the kinetics of the diffusion mechanism for the water molecules and the specific stereochemical structure of obsidian, as well as the external conditions for the diffusion (temperature, relative humidity and pressure; Smith and Van Hess 1987), all result in the formation of an approximately constant boundary concentration value in the external surface layers. This is the surface saturated layer (the SS layer).

The saturation layer on the surface forms up to a certain depth, depending on the above-mentioned parameters. Within a short time of the start of the diffusion process, a narrow elementary layer is formed, saturated with water. The time required for this formation is considered to be equal to $t = 0$. This assumption can be made as this time is very short compared to the total diffusion time and can therefore be ignored. This means that it could be assumed to be the elementary saturated layer that has existed since the beginning of the diffusion process. The saturated layer front progresses over time to greater depth. The saturation conditions on the surface are the average conditions of the physical surroundings for the diffusion system during all the elapsed time in the particular archaeological region.

The following initial and boundary conditions are recommended for the diffusion of water in obsidian:

- *Initial condition:* $C = C_0$, where C_0 is the assumed homogeneous initial concentration; that is, the concentration of the intrinsic water in obsidian for $x > 0$ (where x is the depth in the mass structure of the obsidian sample) if the diffusion time $t = 0$.
- *Boundary condition:* $C = C_s$, where C_s is the concentration of water in the saturated surface of obsidian, for $x = 0$ and $t > 0$.

Figures 2 and 3 show the hydrogen diffusion profiles in obsidian by secondary ion mass spectrometry (SIMS) for Aegean obsidians dated by the secondary ion mass spectrometry–surface saturation (SIMS-SS) dating method (Liritzis *et al.* 2004).

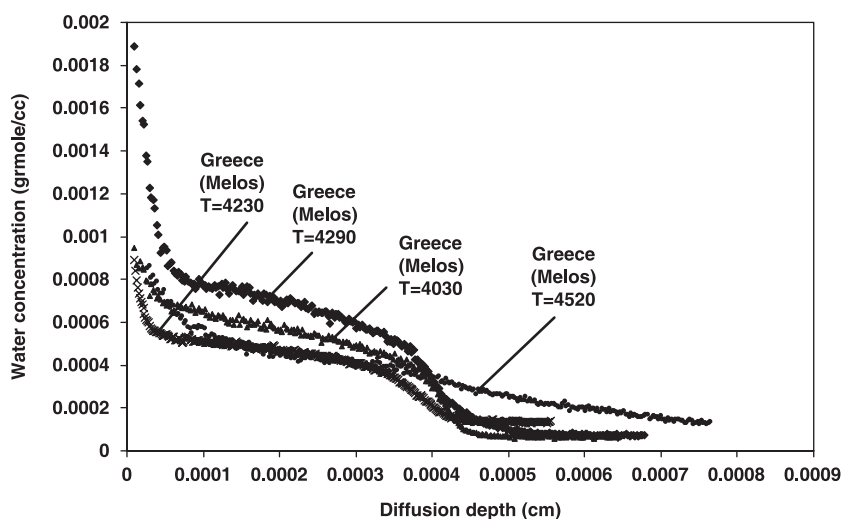


Figure 2 Diffusion profiles in obsidians from the Phylakopi Bronze Age settlement on the island of Melos. The obsidians were derived from Melos sources. The SIMS-SS ages of the various samples (code numbers in parentheses), are in years BP: \times , $T = 4230$ BP (DL 2000-147, Liritzis and Diakostamatiou 2002); \bullet , $T = 4520$ BP (DL 2000-146, Liritzis and Diakostamatiou 2002); \blacktriangle , $T = 4030$ BP (DL 2000-145, Liritzis and Diakostamatiou 2002); \blacklozenge , $T = 4290$ BP (DL 2000-144). Age errors are less than 3% (Stevenson *et al.* 2002b).

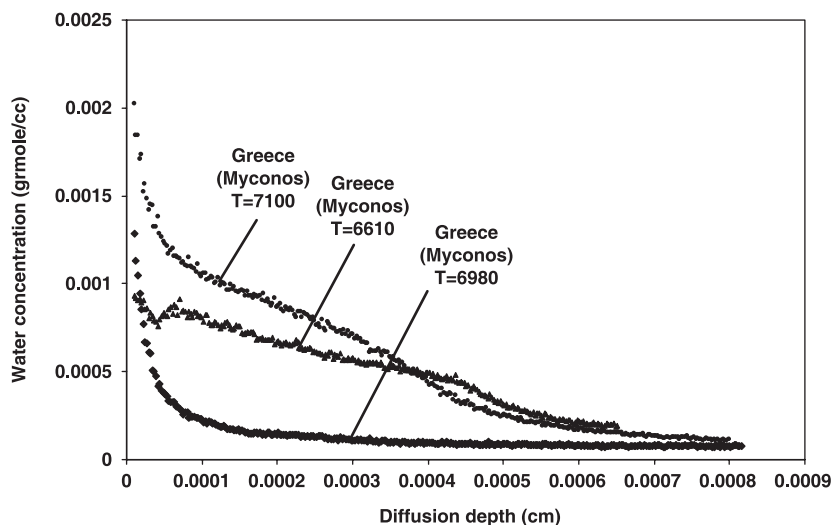


Figure 3 Diffusion profiles in obsidians from the Ftelia settlement on the island of Mykonos. The obsidians were derived from Melos sources. The SIMS-SS ages of the various samples (code numbers in parentheses) are in years BP: \blacklozenge , $T = 6980$ BP (DL 2000-150); \blacktriangle , $T = 6610$ BP (DL 2000-149); \bullet , $T = 7100$ BP (DL 2000-148) (Liritzis et al. 2002, 2004; Stevenson et al. 2002b).

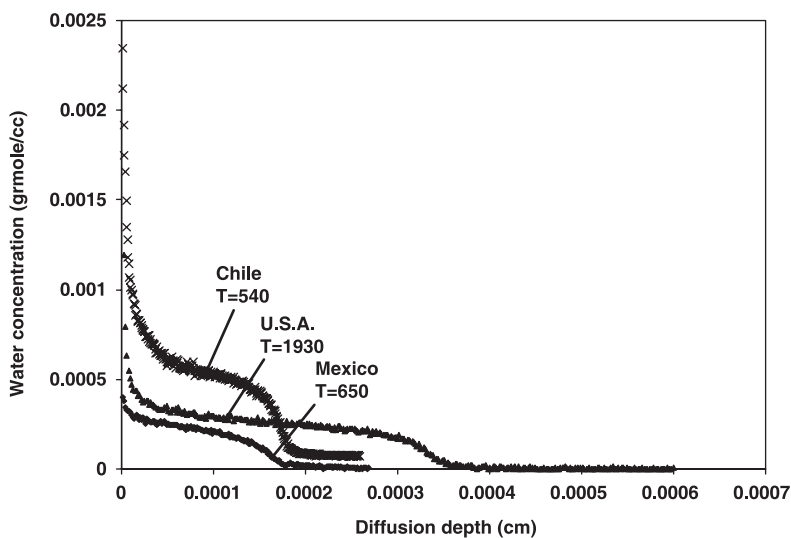


Figure 4 Diffusion profiles in obsidians from three different regions of the world, with corresponding SIMS-SS ages in years BP (the respective sample code numbers are in parentheses): \blacklozenge , $T = 650$ BP (DL 1993-184, Stevenson et al. 2000); \blacktriangle , $T = 1930$ BP (DL 1983-99, Liritzis and Diakostamatiou 2002); \times , $T = 540$ BP (DL 1993-74). Associated errors less than 3% (Stevenson et al. 2000).

The diffusion profiles for obsidians from other parts of the world (Mexico, Ohio and Easter Island) are shown in Figure 4.

The following important observation can be drawn from these profiles: although they are broadly quite similar, this is their only shared property, because despite the fact that they are

derived from the same source and are of adjacent age, close inspection of the shape of the corresponding profiles suggests definite differences. The above remark derives from the considerable impact that environmental and intrinsic effects may have on the obtained form of the SIMS hydrogen (H^+) profile.

It is due to these effects that apparent variations in the obtained profile are specific to the particular case considered. This is an important observation, upon which the method of calculating the age by SIMS-SS relies. Therefore, any age calculation is based on this diffusion profile, and is unique for each obsidian sample.

DETERMINATION OF THE SURFACE SATURATED LAYER (SS)

With the advent of SIMS-SS, it was assumed that the identification of the saturated layer referred to the surface region, where the water concentration is assumed to be constant (Liritzis and Diakostamatiou 2002). Eventually, it became clear that the diffusion profile should be studied analytically, before any attempt is made to identify and locate the SS segment. The external surrounding conditions would certainly cause deviations in the profile, especially near the surface, as observed, for example, in the profiles of Figures 2–4. In the first points of the profiles, there are deviations due to saturation conditions of the surface, which become more distinct a little deeper from the surface.

A basic presumption for the formation of the saturated layer is that it appears within a short distance from the surface. However, if the SS is very near to the initial experimental points, it could easily be affected by variations in the external surrounding conditions (Diakostamatiou 2003).

The ‘almost’ constant water concentration in the saturated surface should be clarified, since it is known that, in the microscale, obsidians are not completely homogeneous in composition and amorphous texture. Therefore, it is not certain that at every point of the surface, the same amount of water would be demanded for saturation (due to the presence of cracks, phenocrysts, voids, foreign ions and external effects affecting near-surface water loci sites, as scanning electron microscopy (SEM) photographs have shown; Liritzis *et al.* 2006b). As the water diffuses deeper into the obsidian, the effects of the external surroundings diminish in importance. This happens mainly because the diffusion phenomenon takes place in a solid material.

It should be remarked that the alterations due to environmental conditions (temperature, humidity, pressure, exposure and contact with sediment) are not between extreme values and they are not abrupt. Nevertheless, even if there is an abrupt external alteration for some reason, this alteration will not last for long. To produce any measurable effect on the shape of the diffusion profile in obsidian, such possible alteration should be long-lasting and should be very different to values within the natural environmental parameters. However, it is accepted that the variations due to the conditions of the physical surroundings on the whole refer to normal environmental values. As a result, the surrounding environmental conditions for water diffusion in obsidian support the formation of a ‘normal’ diffusion profile in the deeper parts of the obsidian. This profile depends on the total environmental conditions in the excavation region.

Taking into account the above-mentioned diffusion phenomenon of water in obsidian and solving equation (6), the following dating equation is obtained for the diffusion time t (= age):

$$t = \frac{(C_0 - C_s)^2 \left(\frac{1.128}{1 - \frac{0.177 k C_0}{C_s}} \right)^2}{4D_{s,eff}(be^a)^2}, \quad (8)$$

where C_0 is the initial concentration of the intrinsic water in obsidian; C_s is the constant surface concentration of water in the saturated layer; k is the constant factor that corresponds to the non-dimensional X/X_s versus C/C_s curve that characterizes the particular diffusion profile, according to Crank (1975), where k -values, presented as e^k , are derived from a family of curves of e^k versus X/X_s for certain C/C_s ; and

$$D = D_s \exp(kC/C_s). \quad (9)$$

$D_{s,\text{eff}}$ is the active (effective) diffusion coefficient of water in the saturated surface layer; and a and b are the coefficients of the fitting curve for the diffusion profile. X_s is used in the calculations of the gradient dC/dx of the C versus X profile. For $C = C_s$ and $X = X_s$, we set diffusion coefficient $D = D_s$. According to Fick's First Law, D_s is the inverse of gradient; thus it is

$$(\partial C / \partial x)_{x=0} = b \exp(a) \quad (10)$$

and

$$D_s = (\text{flux/gradient}) \times 10^{-11} \text{ years}. \quad (11)$$

In the calculation of D , the multiplication by 10^{-11} has been performed in order to convert the units of D from the calculated μm^2 per 1000 years to cm^2 per year, which are the units used in SIMS-SS. For $X = X_s$, D_s is computed from equation (11).

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 $D_{s,\text{eff}}$; that is, $D_s/D_{s,\text{eff}}$ versus $D_s \times 10^{-11}$.

The empirical $D_{s,\text{eff}}$ 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

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

where $a = 8.051 \times 10^{-6}$ and $b = 0.999$ ($r^2 = 0.999$).

The derivation of equation (8) is given elsewhere (Liritzis *et al.* 2004). Equation (8) gives the diffusion time, which includes the time required for the formation of the saturated layer, the depth X_s and the concentration C_s . Needless to say, the SS layer formed with the highest concentration and with a progressing front during the diffusion time is defined by C_s and X_s .

The determination of SS is explained below, with two cases of Aegean obsidian from the prehistoric settlement of Ftelia, Myconos (Figs 5 and 6). On each plot, points A, B, C, D and E explain the chosen locations of the saturated layer.

For the initial (sigmoid-shaped) part of the diffusion profile, points A, B and C help to clarify the SS layer according to the following comments. Although the Fickian law explains the ideal S-shape, some factors affect this theoretical model:

(1) In the first $0.5 \mu\text{m}$ up to point A, any definite spectral alteration is caused by SIMS sputtering effects (an expected effect that appears in SIMS profiles), as well as being due to drastic impacts of the external surroundings. Thus, A is limited by the lack of expected C stability in this initial depth.

(2) From point A to point B, there is no possible stability that would make this belong to the saturated surface layer. The curve has a constant negative or positive slope and, similarly, point B is very close to the external surface of the obsidian ($\sim 1\text{--}3 \mu\text{m}$), and it could be

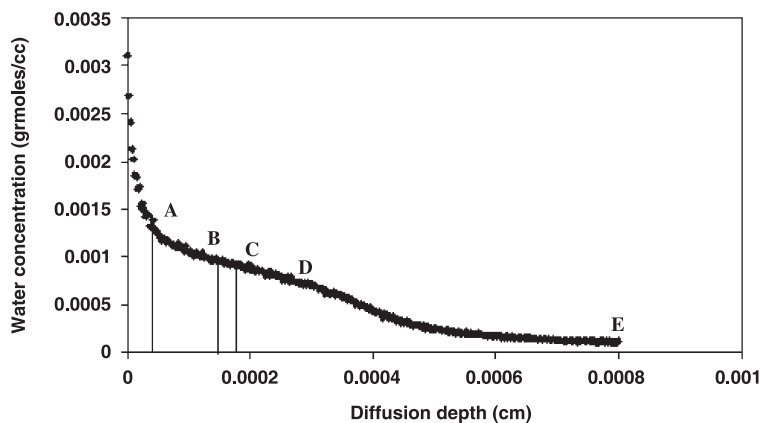


Figure 5 A water diffusion profile in an obsidian blade (sample DL-2000-148) from Ftelia, Mykonos. Points A, B and C define the initial part of the sigmoid curve, and D and E the latter part. Both parts aid discussion of the determination of the saturated layer (see the text).

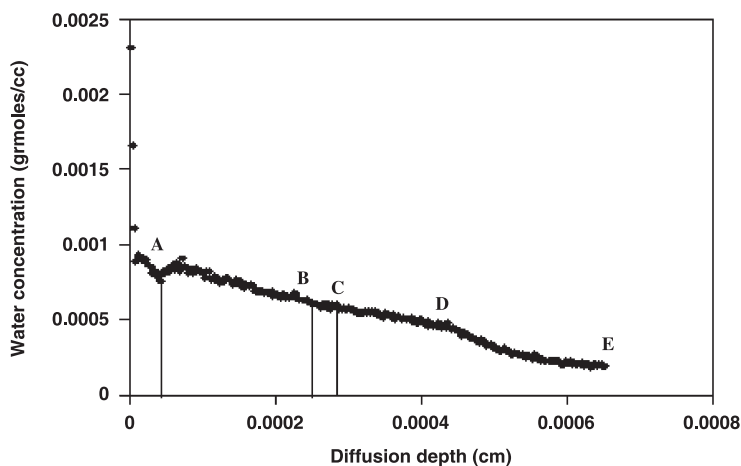


Figure 6 As per Figure 5: a water diffusion profile from another obsidian tool (sample DL-2000-149) from Ftelia, Mykonos. Points A, B and C define the initial part of the sigmoid curve, and D and E the latter part. Both parts aid discussion of the determination of the saturated layer (see the text).

assumed that this spectral part is also the result of the effect of the external surroundings. This effect might cause diminution or accumulation of water mass in the first few micrometres. Thus in Figure 5 there is an accumulation of water in the first few micrometres. In contrast, in Figure 6 there is an initial drop in water, followed by an accumulation. In spite of these initial low–high water values, the remaining part of the diffusion curve is not affected, and it is this later part of the sigmoid curve that is essentially controlled by the final part of the saturated layer; that is, from point B to point C.

(3) From the point B to point C part of the diffusion curve, a layer exists that could be considered as the end of the saturated layer. This assumption is augmented by three arguments: (a) that this part of the curve is some distance from the external surroundings, and any effects on the diffusion profile, from point A to B, become unimportant; (b) that this is the first part

of the curve on which the assumption of constant concentration is valid, and therefore it is this part of the curve that satisfies the necessary condition for the constant concentration of the saturated layer; and (c) that this particular sigmoid shape of the total diffusion profile is also a result of the stereochemical structure of each particular obsidian sample. This means that the diffusion curve starts with the saturated layer and shifts to deeper layers with the rest of the diffusion profile.

The SS layer is a phenomenological convenience: thus, at present it is not possible to define it in terms of the basic structure of obsidian. With a possible full numerical approach, we may learn more about it. However, at present we may say that it consists of packed water molecules filling in interstitial sites in the Si network. Its thickness varies depending on the particular obsidian structure, and from the data obtained so far it lies between 0.15 and 0.30 μm . The rate of formation depends on structure and bulk composition; that is, on cracks, porosity, density, crystallization and so on.

The latter claim can be supported by the following facts: it has been shown (Stevenson *et al.* 1996; Ambrose and Stevenson 2004) that the density in 31 obsidians is correlated (r^2) with several chemical elements of major oxides such as Al_2O_3 (0.11), SiO_2 (−0.84), FeO (0.75), TiO_2 (0.76), Cl (0.73), CaO (0.39), K_2O (−0.29) and Na_2O (0.64), with confidence levels between 11% and 84%. Apart from silica, which correlates inversely with density, the other major elements with significant correlations are additive in increasing obsidian density. The relationship of connate water (intrinsic to the lattice since formation from magma) with silica and iron provides a two-phase correlation, with a major change around 76%, while FeO shows the same effect in reverse at around 1.5%, which indicates that density has a generally linear relationship. In the case of silica and iron, the relationship between these elements and water is more complex; that is, in their major influence on density, these elements also influence the connate water accommodation in obsidians. The additive effect of Ca, Na and Ti reinforces the density figure but, overall, silica maintains its strong correlation with the final density value. From this, it appears that a more open structure of the obsidian aluminosilicate glass can accommodate an increasing volume of water with an increasing silicate content above ~76% SiO_2 .

The relationship between density and water content shows a two-component curve, with an inflection at a density of about 2.35 and a water content of around 0.15% (Stevenson *et al.* 1996; Ambrose and Stevenson 2004). The ‘dry’ obsidians that are denser than 2.35 have a very low water to density ratio, while those less dense than 2.35 have a high water to density ratio and can be typified as ‘wet’. The relationship between water content and density appears in other reports, where it is generally seen as an accommodation of the silicate structure to the depolymerizing effect of hydroxyl in silicate glasses (Heatherington and Jack 1962, 131).

Furthermore, we have correlated the density with more than one chemical oxide of the same 31 obsidian data above and found that density correlates (a) with Fe and Ti at a 91.4% level, (b) with Al, Fe and water at a 96.8% level, (c) with Fe, Cl, Si and Ti at a 95.6% level and (d) with Fe, water and Ti at a 92.8% level. As with the simple systems, the diffusion coefficient depends on the material’s composition and on the physical nature of the material (e.g., pores etc.); here also, the obsidian structure reflected in the density depends on the bulk composition and the connate water content, and the water diffusivity depends on these factors.

The SS layer is visualized as the divider between the two regions A–B and D–E. Therefore, we have a first region, the first part of the profile A–B, which does not look like moisture-driven diffusion through glass. Here, a thin-film concept may work better than the use of a Fickian law. In this case, a concentration difference, $\Delta C = C_1 - C_2$, and a transfer coefficient, k_t ,

are used to replace the more fundamental transport equations such as Fick's Law. This needs further consideration. Then, the dividing region of no mass transfer (the SS layer) corresponds to B–C, and following that lies the Fickian diffusion region (D–E) (Figs 5 and 6).

For these reasons, the boundary condition that is used for the solution of equation (6) in order to derive equation (8) is justified. The inner part of the diffusion profile is defined at the start of this saturated layer since, according to equation (5), the mass transport is a result of the differential difference in the concentration between neighbouring points. It is specified that the diffusion coefficient in the obsidian–water diffusion system depends upon the water concentration at each profile point (Diakostamatiou 2003).

On the whole, the spectral deviations in the first experimental points of the profile do not have any effect on the rest of the diffusion profile. It is a reasonable assumption that the saturated layer has certainly started to emerge right from the first point of the profile; it progresses increasingly and within a short time reaches the SS layer at point C, thereafter moving deeper into the obsidian, following the diffused water front. The almost constant concentration value for the interval B–C—and therefore the location of C—can be computed from the slopes of the regression lines (the method of successive linear regressions; Liritzis *et al.* 2004) connecting the points from A up to the inflection part of the S-curve (Table 1), and by applying a least-squares test on successively increasing segments the respective slopes were evaluated. Some of these straight lines have a slope value near zero. This implies that they are almost parallel to the x -axes, and that the C values are constant. Alternatively, the SS is defined from three derivatives of the best third-order polynomial fit (or on the raw data) of the profile not necessarily coupled with successive linear regressions (Liritzis *et al.* 2005).

The above-mentioned remarks make clear the importance and clarify the meaning of the saturated layer of water in obsidian. The meaning of the saturated layer is one of the basic principles upon which the SIMS-SS obsidian hydration dating method relies.

The above analysis explains some specific terminology for the non-specialist, and at the same time elucidates misunderstanding (e.g., by Anovitz *et al.* 2004) of our earlier papers about SIMS-SS and the basic scientific background. Anovitz *et al.* have had a misconception regarding the surface saturation layer, indicating prolonged increase of C over time. Contrary to their conclusion, their data profiles for Pachuca obsidian samples experimentally hydrated at 75°C instead support the short time interval of the occurrence of saturation. Likewise, the natural Chalco samples (their fig. 7), within the large errors involved, imply that the chosen Boltzmann–Matano model is not applicable. On the other hand, referenced comparisons with other experiments are incompatible due to essential differences in all conditions (pressure, temperature and environmental surroundings).

CONCLUSIONS

The new SIMS-SS obsidian dating method is based on Fick's Law of Diffusion, and a solution of the concentration to hydration distance curves. It is based upon the surface saturation layer and the analytical mathematical solution describes the diffusion time. The diffusion coefficient is assumed to vary exponentially and derives from the first derivative of the diffusion profile. The approach is phenomenological, but is founded on solid physico-chemical principles of diffusion.

The most representative equation to describe the variation of concentration of the material that diffuses, as a function of time and distance, is equation (6) for the mass transport in one direction, which is applied to diffusion phenomena at a non-steady state. Equation (6) derives

Table 1 The determination of the saturated layer for Evans East sample DL-2000-149 from calculation of the successive linear regressions. The slopes in bold mark a change to steadily negative values. X_s and C_s are the average values of the last 10 slopes around the end point of SS, which correspond, respectively, to X and C

Diffusion depth (cm)	Water concentration (g·mol cm ⁻³)											Depth (cm)	Water concentration (g·mol cm ⁻³)															
0.0002158	0.000657											0.0002836	0.0006027															
0.0002182	0.000649											0.0002836	0.0006027															
0.0002207	0.000658											0.0002836	0.0006027															
0.0002231	0.000660											0.0002836	0.0006027															
0.0002255	0.000679											0.0002836	0.0006027															
0.0002279	0.000671											0.0002836	0.0006027															
0.0002303	0.000633											0.0002836	0.0006027															
0.0002328	0.000635											0.0002715	0.00060927															
0.0002352	0.000626											0.0002715	0.00060927															
0.0002376	0.000628	1										0.0002715	0.00060927															
0.0002400	0.000630	1.1616	2									0.0002715	0.00060927															
0.0002424	0.000637	1.9785	2.7953	3								Mean	0.0002787	0.00060533														
0.0002449	0.000629	0.5010	-0.2116	-3.2186	4							Standard deviation	5.9280 × 10 ⁻⁶	3.2192 × 10 ⁻⁶														
0.0002473	0.000612	-1.3301	-2.6020	-5.1980	-7.1173	5																						
0.0002497	0.000615	1.3616	-2.2874	1.3616	-2.9079	1.3616	6																					
0.0002521	0.000609	-1.6241	-2.2217	-0.5475	-2.3455	-0.5475	-2.4566	7																				
0.0002545	0.000604	-1.7342	-2.1924	-1.2246	-2.1976	-1.2246	-2.3123	-2.1681	8																			
0.0002570	0.000603	-1.6997	-2.0348	-1.2043	-1.9051	-1.2043	-1.7381	-1.3072	-0.4463	9																		
0.0002594	0.000596	-1.7540	-2.0267	-1.4576	-1.9199	-1.4576	-1.8792	-1.7342	-1.7320	-3.0177	10																	
0.0002618	0.000577	-2.0497	-2.3270	-2.2069	-2.3999	-2.2069	-2.7377	-2.9942	-3.6231	-5.3123	-7.6070	11																
0.0002642	0.000597	7.9984	-2.0214	-1.6687	-1.9308	-1.6687	-1.8941	-1.7838	-1.6770	-1.5486	0.1957	7.9984	12															
0.0002666	0.000593	3.2689	-1.8236	-1.4036	-1.6663	-1.4036	-1.5064	-1.3169	-1.0901	-0.7782	0.4791	3.2689	-1.46	13														
0.0002691	0.000610	3.9228	-1.4123	-0.8090	-1.1269	-0.8090	-0.7567	-0.4272	-0.0109	0.5566	1.8450	3.9228	2.782	7.025	14													
0.0002715	0.000609	3.2027	-1.1230	-0.4630	-0.7853	-0.4630	-0.3520	-0.0058	0.4118	0.9380	1.9241	3.2027	2.272	3.347	-0.3337	15												
0.0002739	0.000572	0.3483	-1.2902	-0.8354	-1.0585	-0.8354	-0.8123	-0.6274	-0.4408	-0.2592	0.1030	0.3483	-1.35	-2.627	-7.8367	-15.3360	16											
0.0002763	0.000598	0.4393	-1.1374	-0.6798	-0.8939	-0.6798	-0.6347	-0.4511	-0.2665	-0.0866	0.2283	0.4393	-0.66	-1.154	-3.0212	-2.3121	10.711282	17										
0.0002787	0.000589	0.1281	-1.0837	-0.6698	-0.8583	-0.6698	-0.6300	-0.4762	-0.3297	-0.1985	0.0216	0.1281	-0.75	-1.103	-2.2040	-1.4409	3.4809916	-3.7492985	18									
0.0002812	0.000584	-0.1661	-1.0640	-0.6991	-0.8620	-0.6991	-0.6692	-0.5451	-0.4346	-0.3462	-0.2000	-0.1661	-0.90	-1.193	-1.9566	-1.3999	1.081656	-2.9279978	-2.11	19								
0.0002836	0.000603	0.1168	-0.9105	-0.5321	-0.6954	-0.5321	-0.4839	-0.3510	-0.2276	-0.1195	0.0416	0.1168	-0.39	-0.484	-0.8266	-0.0789	1.938444	0.3620111	2.829	7.765	20							
0.0002860	0.000563	0.4835	-1.0211	-0.7302	-0.8555	-0.7302	-0.7128	-0.6282	-0.5620	-0.5219	-0.4550	-0.4835	-1.01	-1.220	-1.6605	-1.3646	-0.448295	-2.3488508	-2.47	-4.359	-16.482							
0.0002884	0.000575	-0.6202	-1.0252	-0.7693	-0.8781	-0.7693	-0.7585	-0.0690	-0.6411	-0.6181	-0.5760	-0.6202	-1.07	-1.257	-1.6078	-1.3728	-0.72059	-2.0783916	-2.04	-2.774	-5.7581							
0.0002908	0.000565	-0.8159	-1.0642	-0.8490	-0.9400	-0.8490	-0.8484	-0.7986	-0.7692	-0.7664	-0.7520	-0.8159	-1.23	-1.404	-1.7143	-1.5551	-1.111526	-2.1930801	-2.21	-2.712	-4.1734							
0.0002933	0.000580	-0.7334	-1.0129	-0.8039	-0.8907	-0.8039	-0.7986	-0.7488	-0.7170	-0.7080	-0.6870	-0.7334	-1.07	-1.189	-1.4045	-1.2152	-0.79464	-1.5265849	-1.35	-1.396	-1.7461							
0.0002957	0.000568	-0.7868	-1.0135	-0.8252	-0.9026	-0.8252	-0.8225	-0.7805	-0.7558	-0.7524	-0.7400	-0.7868	-1.08	-1.186	-1.3646	-1.2052	-0.86353	-1.4481288	-1.29	-1.313	-1.5196							

from the principle of mass conservation in the diffusing system. This principle is valid in the specific diffusion phenomenon, since it takes place in the natural surrounding conditions, and there is no chemical reaction or production of mass. The boundary condition used for the solution of equation (6) is the result of local equilibrium conditions on the obsidian surface.

The SS layer is formed within a short period of time and there is no true time-dependence of the 'surface concentration', as wrongly stated by Anovitz *et al.* (2004).

The excellent agreement between SIMS-SS ages and well-known archaeological age obsidians from other parts of the world (Diakostamatiou 2003; Liritzis *et al.* 2004, 2005, 2006a) reinforces the validity of the method.

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