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TOWARDS A NEW METHOD OF OBSIDIAN HYDRATION DATING WITH SECONDARY ION MASS SPECTROMETRY VIA A SURFACE SATURATION LAYER APPROACH

IOANNIS LIRITZIS*
MARIA DIAKOSTAMATIOU

University of the Aegean
Department of Mediterranean Studies
Laboratory of Archaeometry
1 Demokratias Ave., Rhodes 85100, Greece

**to whom all correspondence should be addressed*
e-mail: liritzis@rhodes.aegean.gr

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ABSTRACT

The obsidian hydration dating (OHD) has undergone a considerable evolution, especially with the use of nuclear analysis techniques to accurately determine the hydration rim. We develop a novel approach to the OHD employing certain mathematics of diffusion and making use of available secondary ion mass spectrometry (SIMS) data on obsidians. Our model is based on the non-steady state concentration-dependent diffusion for semi-infinite medium, where diffusion coefficient varies exponentially during diffusion, and for certain initial and boundary conditions the age equation of the obsidian diffusion dating employing SIMS derives from a differential equation that describes diffusion. An essential factor addressing our model is the surface saturation (SS) plateau level at certain depth, which is the result of the diffusion mechanism in the first 1-2 um, the physicochemical factors that address the formation of a surface saturation plateau, the stereochemical structure of obsidian, and certain environmental parameters, naming the method as the obsidian diffusion dating by SIMS (ODDSIMS) - SS approach. The measured data points derive from the H^+ concentration-depth profile by SIMS. Application of the present model on available data of well-dated obsidians from the Aegean (Greece), Mexico and USA, provided satisfactory results.

KEYWORDS: SIMS, obsidian, dating, diffusion, hydration, Mykonos, Mexico

INTRODUCTION

Obsidian hydration dating has not proven useful method to archaeologists, though occasionally it may produce a satisfactory result. The reason for this uncertainty relies on several factors, most important, a) the lack of our understanding of the water diffusion mechanism within the obsidian glass, and b) the unknown temperature / humidity dependent hydration rate variation, throughout the archaeological age.

Obsidian hydration dating (OHD) relies upon measuring the depth to which water has diffused into rhyolitic glass surface and converting the thickness to an age using experimentally derived diffusion coefficients. This diffusion coefficient in amorphous silicates is strongly correlated with the concentration of water within the surface hydration layer, and is referred to as concentration-dependent diffusion (Drury and Roberts 1963; Lanford 1977; Nogami and Tomozawa 1984). The anhydrous component of the glass has little influence on the mobility of water within a narrow compositional range (Behrens and Nowak 1997). As molecular water enters the glass it results in the formation of a sigmoid (S-shaped curve) concentration versus depth profile (Crank 1975; Tsong *et al.* 1980; Lee *et al.* 1974; Anovitz *et al.* 1999; Stevenson *et al.* 2001, 2002).

The experimental data have repeatedly documented that hydration proceeds with the square root of time and this supports the traditional age equation given by $x^2=K.t$, where x is the hydration depth or hydrated rim, (K) is the diffusion rate (in um^2/ka, 1 ka=1,000 years, distinct from diffusion coefficient i.e. diffused water mass/unit of time), and (t) is time (Friedman and Smith 1960).

However, the diffusion rate controlling parameters are still poorly understood and impact our understanding of obsidian hydration (Anovitz *et al.* 1999; Stevenson *et al.* 2000). Moreover, the determination of the hydration rim by optical microscopy means has been proved inadequate due to various reasons (Stevenson *et al.* 2002, 2001a, 2001b; Anovitz *et al.* 1999). Alternative successful attempts were made to determine rim by infrared photoacoustic spectroscopy (IR-PAS) and SIMS (Stevenson *et al.* 2002, 2001).

The archaeological hydration rates at ambient conditions are estimated through ageing experiments at elevated temperatures extrapolated down to these conditions, with the Arrhenius equation (Michels *et al.* 1983), a rather unsecured procedure.

On the other hand, a strong dependence between the structural water content (OH) of the glass with the archaeological hydration rates is reported (Mazer *et al.* 1991; Stevenson *et al.* 1998).

Several controlling parameters have been considered to estimate hydration rate in obsidian glass (e.g. soil and obsidian chemical composition, obsidian's structural water and density, associated cations).

Nevertheless, whatever the efforts made are, the past climatological and environmental factors significantly influence the rate of obsidian hydration.

In this note we present evidence of alternative solution of the OHD age equation, based upon the concentration-dependent diffusion of water profile – concentration to distance sigmoid shape (Doremus 1979) – determined by SIMS (secondary ion mass spectrometry nuclear analysis method), a work developed during the last three years (Liritzis and Diakostamatiou 2002). In this approach the age modeling is independent of the former unknown factors, being a purely intrinsic method.

SIMS can resolve variations in concentration occurring within a few nanometers for a large range of chemical elements, over depths ranging from tens of nanometers to several microns (Gillen *et al.* 1998, Valley *et al.* 1998), and has been used in earlier studies of glass (Bach and Baucke 1982; Smets and Lommen 1985).

This analytical method is based on the spectroscopic analysis of (secondary) ions ejected from a sample during the bombardment by a focused beam of primary ions accelerated at 2-20 KeV (Benninghoven *et al.* 1987).

The type and composition of these secondary ions represents the type and composition of the sputtered sample surface, so that the mass spectrometric analysis of these ions can provide a quantitative elemental or isotopic analysis of the sputtered volume.

In fact in SIMS analysis, as secondary ions are only removed from the upper few atom layers of the material, it is possible to obtain highly resolved depth profiles, by taking repeated measurements of the elements of interest while steadily sputtering into the sample.

The typical resolution of depth (penetration depth or distance from surface) determination for obsidian is 0.02-0.04 um. The depth profile is determined by measuring the depth profile with a profilometer with a precision better than 5% (Anovitz *et al.* 1999).

The water concentration is given either as H^+ atoms / cc or as ratios H^+/Si^+. The overall analytical precision is estimated to be 1-5% for H^+ concentration. The first few high data points of H^+ are thought to be due to sputter equilibration (Anovitz *et al.* 1999).

The best way at present to obtain H^+ depth profiles is using SIMS, the data from which are more detailed, though in some cases of comparable precision, than earlier attempts employing, a) ^{19}F nuclear resonance in the nuclear reaction $^1H(^{19}F, \alpha\gamma)^{16}O$ (Lee *et al.* 1974), b) sputter-induced optical emission produced by the bombardment of 18 keV Ar^+ ions (Tsong *et al.* 1978), c) the ^{15}N hydrogen profiling technique using the narrow isolated resonance (0.4 KeV) in the nuclear reaction: $^{15}N + {}^1H \rightarrow {}^{12}C + {}^4He + 4.43$ MeV γ-ray, (Lanford 1978), d) Rutherford backscattering and heavy ion implantation (Perera and Doremus 1991).

ODDSIMS WITH THE SURFACE SATURATION (SS) APPROACH: THE THEORETICAL BACKGROUND

The diffusion of water in the soil adherent to obsidian surface can reasonably be expected to be much faster than diffusion of water in the glass. This effect, together with the mechanism of water molecule diffusion kinetics, the particular stereochemical structure of the obsidian, as well as the environmental parameters (temperature, pH, Rh, pressure), lead to the formation of a constant composition boundary value, called surface saturation, at a certain depth which depends upon the former effects.

Glass surface dissolution is ignored, assuming this boundary fixed in space. If, however, such dissolution is present, it may occur throughout the diffusion time. As the system obsidian-water-soil-environment is in a dynamic state, the resultant depth-concentration profile inheres this dissolution effect, as well as any other environmental variables.

The water concentration (C) in three-dimensional diffusion in a non-steady-state and semi-infinite medium is a func-

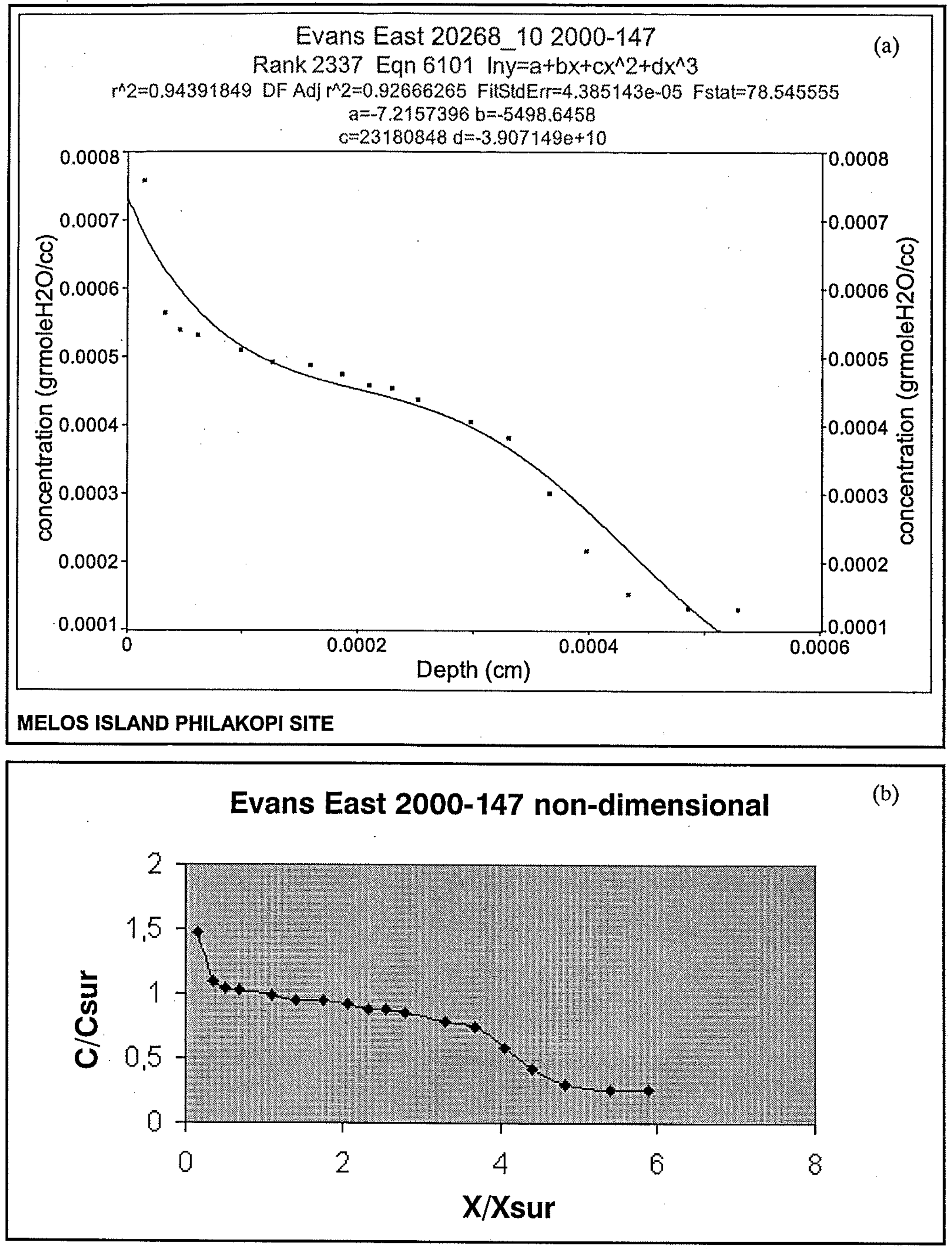

Figure 1. Philakopi (2000-147), Melos, Aegean Sea, Greece. (a) SIMS H+ concentration versus depth profile (dots) and the fitted curve, (b) non-dimensional plot of C/C_o, versus, X/X_o ($X_{sur} = X_s$, $C_{sur} = C_s$).

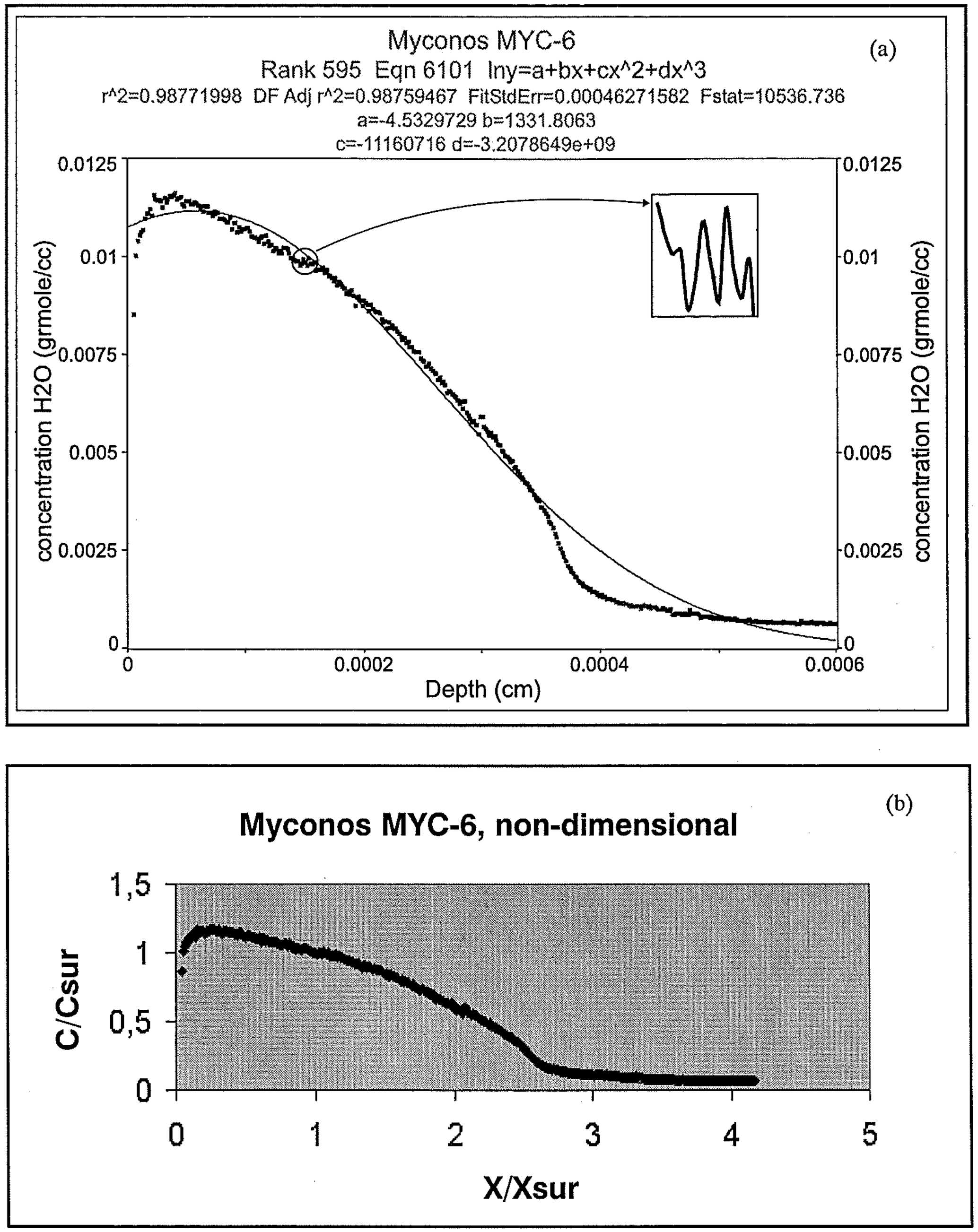

Figure 2. Mykonos (ORNL, USA), Aegean sea, Greece (a) SIMS concentration versus depth profile (dots) and the fitted curve, indicating the surface layer, which consists of twenty data points, (b) non-dimentional plot of C/C_o, versus X/X_o ($X_{sur} = X_s$, $C_{sur} = C_s$).

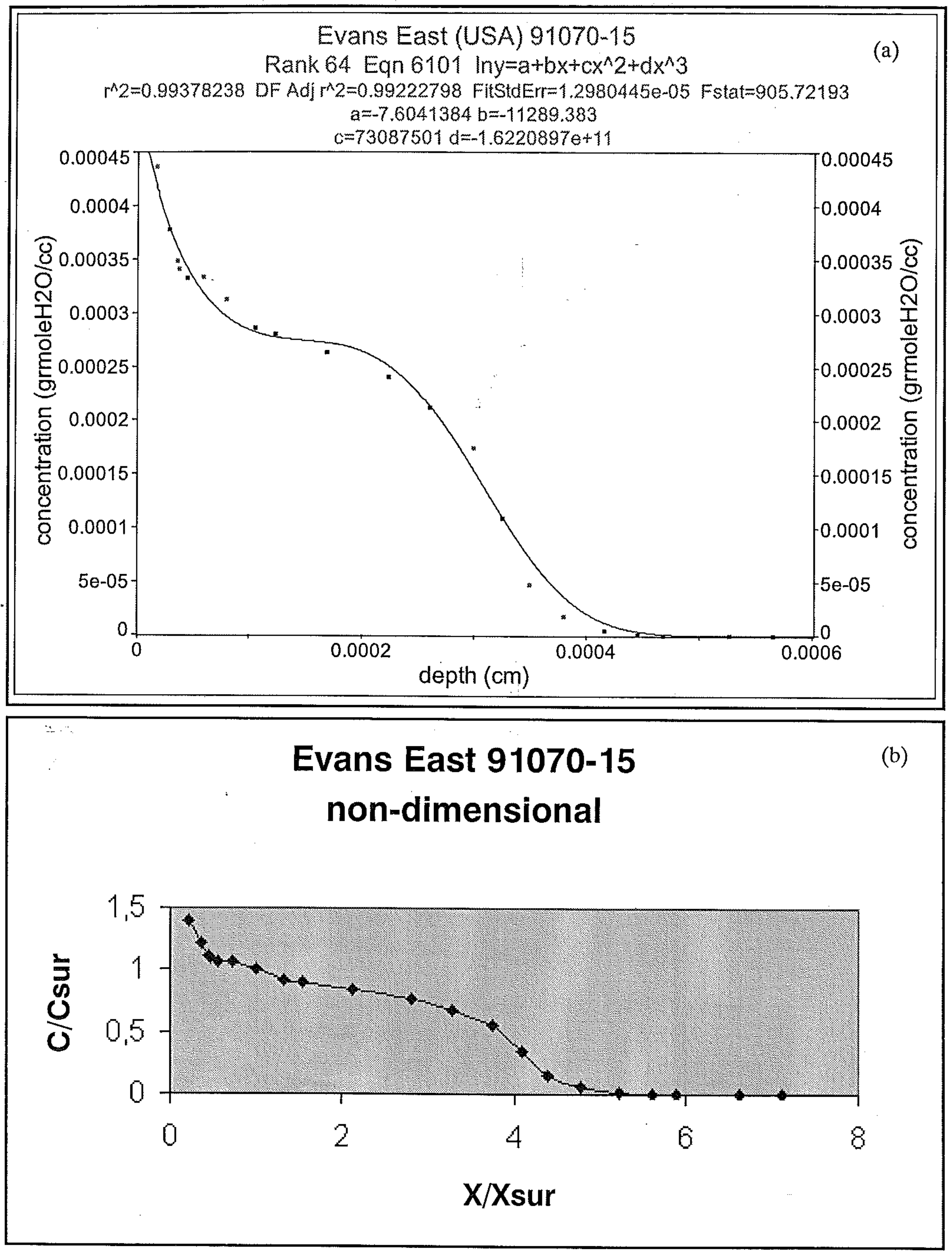

Figure 3. Evans East (91070-15), USA (a) SIMS H$^+$ concentration versus depth profile (dots) and the fitted curve, (b) non-dimentional plot of C/C_o, versus, X/X_o ($X_{sur} = X_s$, $C_{sur} = C_s$).

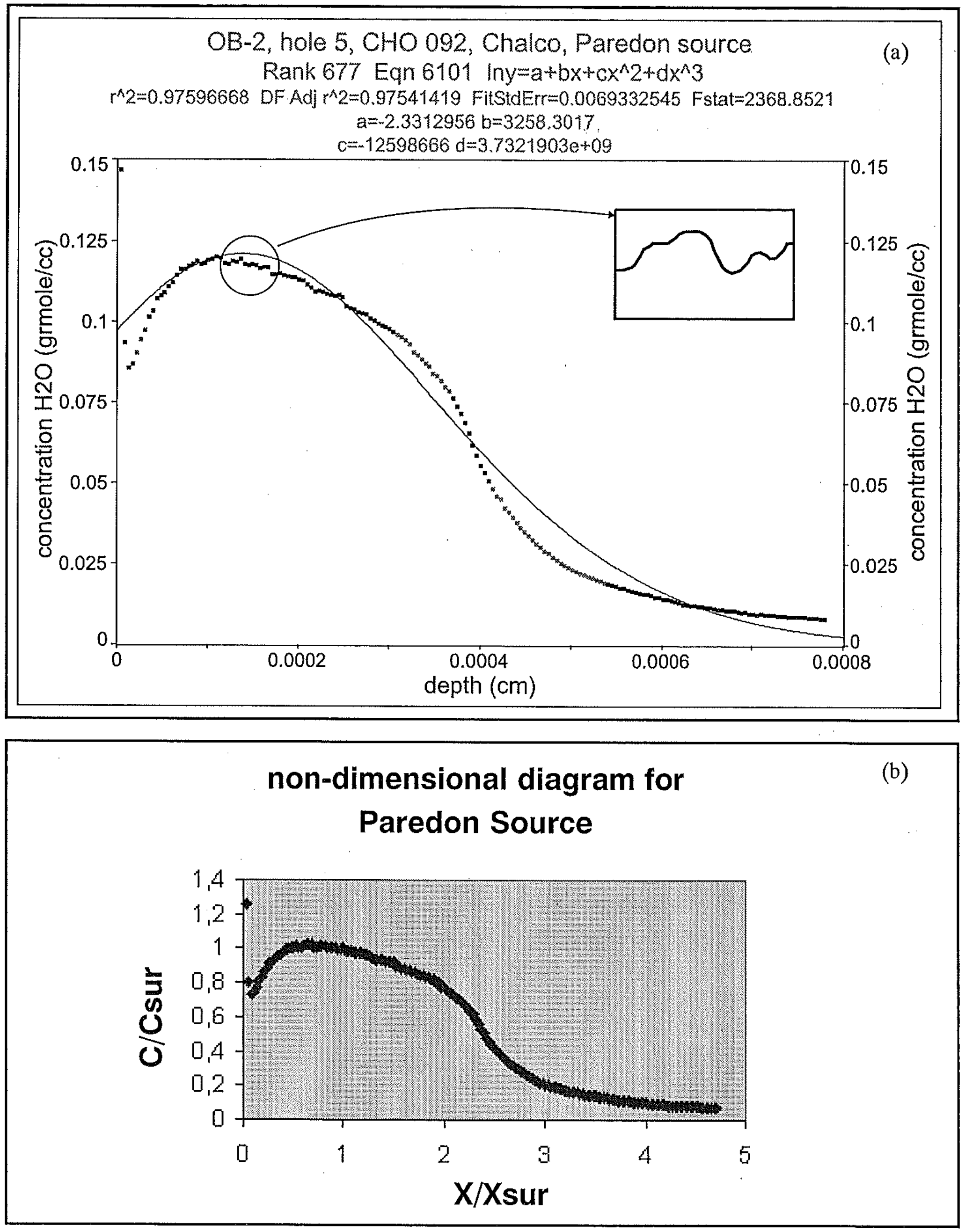

Figure 4. Mexico, Chalco, Paredon source (OB-2, hole-5, CHO 092), (a) SIMS H$^+$ concentration versus depth profile (dots) and the fitted curve, indicating the surface saturation layer, (b) non-dimensional plot of C/C_o, versus, X/X_o ($X_{sur} = X_s$, $C_{sur} = C_s$).

tion of diffusion coefficient (D), where D depends on the time t for which diffusion has been proceeding, given by eq.(1):

$$dC/dt=\partial(D\partial C/\partial x)/\partial x+\partial(D\partial C/\partial y)/\partial y+ +\partial(D\partial C/\partial z)/\partial z \qquad (1)$$

Considering the case of one-dimensional diffusion through obsidian surface, the D as a function of C derives from eq.(2):

$$\partial C/\partial t=\partial(D\partial C/\partial x)/\partial x \qquad (2)$$

If D=constant then from eq.2

$$\partial C/\partial t = D\partial^2C/\partial x^2 \qquad (3)$$

i.e. Fick's 2nd law.

However, D is not constant during water diffusion into the obsidian but depends on C.

Boltzmann showed that for certain boundary conditions, provided D is a function of C only, C may be expressed in terms of a single variable and therefore eq.(2) may be reduced to an ordinary differential equation (Crank 1975).

This differential equation can produce many numerical solutions, which depend on the system's initial and boundary conditions.

For our obsidian-water system we consider an exponential diffusion coefficient in a semi-infinite medium and for initial and boundary conditions of:

Initial condition:

$C=C_o$, C_o is the uniform initial concentration, i.e. the intrinsic or structural water concentration, $x > 0$ (x, water diffusion depth) for the diffusion time, $t = 0$.

x= water diffusion depth > 0

t=diffusion time= 0

Boundary condition:

$C=C_S$= obsidian surface saturated water concentration

$$x=0 \quad t>0 \qquad (4)$$

If the exponential diffusion coefficient is given by

$$D = D_s\exp(K\ C/C_s) \qquad (5)$$

where, D_s the diffusion coefficient for $C=C_s$, K=constant, and introduce auxiliary variables following Boltzmann's procedure, then it is possible from eq.(2) to produce eq.(6):

$$-D_s(\partial C/\partial x)_{x=o}=-1/2(Ds/t)^{1/2}(Co- -Cs)(dC/dys)_{ys=o} \qquad (6)$$

which relates, the flux across obsidian's surface at x=0 with the time, that this flux has occurred, the concentration C_S, the C_O and the diffusion coefficient D_S for the surface concentration C_S.

From SIMS profiling the H^+ concentration is obtained which is converted to water concentration profiles (Fig.1a-4a). Shortly after the onset of diffusion at t=0 (compared to total diffusion time), a little surface saturation layer is formed, which can be considered as this initial constant concentration from which further water diffusion to deeper layers follows. It is this surface saturation layer which provides obsidian surface water concentration a starting constant layer for the subsequent diffusion (Brodkey and Hershey 1988). A condition for the depth of this layer is that it should be away from very near surface, i.e. >0.5 um from surface, because in very near surface it is more prone to variations due to the environmental factors.

The SIMS profile of concentration-distance is re-plotted as a non-dimensional diagram of C/Cs versus X/Xs (Fig.1b-4b) For the non-steady state condition considered here, a collection of curves have been produced between non-dimensional distance and concentration. These family curves correspond to certain functional dependence of D from C, e.g. linear, exponential.

The shapes of the concentration-distance curves are characteristic of the diffusion coefficient and of the boundary conditions. They do not conform to quite such a simple classification, as do the corresponding curves in the steady state. Thus, whenever D increases as C increases, concentration-distance curves are convex away from the distance axis.

Thus, the family curves of Fig. 5 (reproduced Fig. 9.9 of Crank 1975) show that for these diffusion coefficients the statement holds also for sorption by a semi-infinite medium over the greater part of the concentration range, but that there is an important difference in behavior in the region of low concentration.

This difference is a direct consequence of the boundary condition. In the steady state, the condition is that the concentration shall have some fixed value, possibly zero, at the face of the membrane through which the diffusing substance emerges. When diffusion occurs into a semi-infinite medium, however, the condition that the concentration shall approach zero at infin-

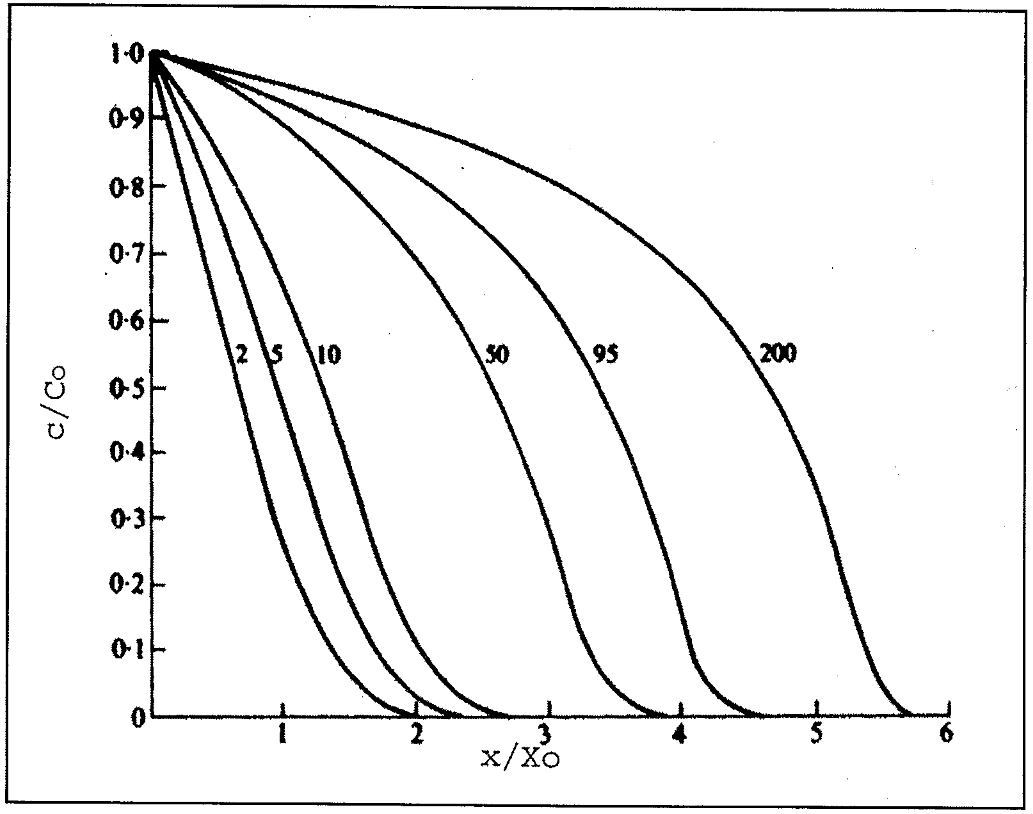

Figure 5. Concentration-to-distance curves for exponential diffusion coefficient during sorption for $D=Doexp(K.C/C_o)$, and $X_o = 2\sqrt{D_o t}$. Numbers on curves are values of $ek = D\ (C=C_o)\ /\ D\ (C=0)$ (adapted from Crank, 1975, fig. 9.9).

ity means that the gradient of concentration tends to zero at the limit of penetration into the medium. This produces a point of inflexion in any concentration-distance curve, which is convex away from the distance axis at high concentration.

Comparing Figs.1b-4b with family curves of Fig.5, the particular curve C′ is recognized which is similar with the shape of Fig.1b-4b. Therefore, we consider that the functional behavior of D=f(C) in our obsidian-water system is exponential and described from the same equation as curve C′.

The family curves are characterized (and thus distinguished) from a constant coefficient, K.

The numbers on the curves (2, 5, 10, 50, 95 and 200) are values of e^k being the ratio of D at $C=C_O$ to D at C=0 or

$$e^k=D^{(C=Co)} / D^{(C=0)} \qquad (7)$$

Therefore, the K-value can be calculated from the particular shape of the curve.

From eq.(5) the ratio of C_O/C_S is considered which justifies eq.(7).

In eq.(6) the constant dC/dy_S, for $y_S=0$, is given by,

$$dC/dy_S=1.128/(1-0.177r) \qquad (8)$$

However, for the solution of eq.(6) we have set

$$r=KC_O/C_S \qquad (9)$$

Thus, from eq.(8) the constant dC/dy_S is calculated.

From eq.6 the parameters of C_O, C_S, dC/dy are known and $(\partial C/\partial X)_{x=o}$ is the first derivative of fitted curve of SIMS profile. This curve fitting (excluding first very high values) is made with appropriate functions from TABLECURVE 2D statistical software, being of the form,

$$C = \exp(a+bx+cx^2+dx^3) \qquad (10)$$

where, a,b,c,d are constant terms. The variation of these coefficients in the present data is -6.65 to -7.35 for a, -4130 to -14200 for b, $1x10^6$ to $920x10^6$ for c, and -$2x10^9$ to -$236x10^9$ for d. In spite of this wide variation, it is observed that the coefficients of samples from similar sources/sites form tide clusters.

In all cases the fitting was of high significance (Rsq.=0.91-0.99).

We accept that the slope in every data point of SIMS profile curve, i.e. its tangent, dC/dX, is the diffusion coefficient (D).

$$dC/dX = (b+2cx+3dx^2) \exp(a+bx+cx^2+ +dx^3) \qquad (11)$$

Thus, for C=Cs and X=Xs the diffusion coefficient D=Ds = dC/dX, for X=Xs.

From the above, the time (t) that water diffusion has taken place in an obsidian tool, is determined from the following age equation (eq.12).

$$t= [(Co - Cs)^2 (dC/dys)^2_{ys=0}]/ /[4Ds(\partial C/\partial x)^2_{x=0}] \qquad (12)$$

Thus, the first derivative of the Sigmoid fitted function essentially provides the diffusion coefficient at each point (or at each time during the past that the diffusion took place) of the SIMS profile, i.e. it provides the apparent hydration rate, which inheres all environmental parameters that affect this rate. By this way, the calculated time of diffusion accounts for any uncertain variations affecting the rate of diffusion, thus providing the most accurate time of diffusion, that is the age for an obsidian tool.

DISCUSSION

For the application of the ODDSIMS-SS model the following points are considered:

1) Regarding dissolution, which occurs since the onset of diffusion, it certainly alters the hydration rim and shifts the surface saturation layer to inner layers (Doremus 1979). We do not have studied this phenomenon in detail, but from the so far obtained results of well known age samples, if dissolution occurs it may not affect the age calculated by our ODDSIMS surface saturation approach On the other hand, the apparent near-surface disturbances in the water profile and the other alkali cations, possibly reflect, either, a) exchange between obsidian and clays in the soil, b) a result of SIMS equilibration during sputtering, or, c) different amounts of available moisture contents present during the hydration history of the artifact. At present we exclude these first few high points from the fitting.

2) The selection of Cs and Xs should satisfy the particular functional shape of the non-dimensional curves of concentration-depth, which correspond to eq.5. The characteristics of the particular shape concern the sloping, the inflection point at the tail, and the way C asymptotically meets background (a tail effect).

3) The formed crater from sputtering should follow a smoothed well, checked by profilometry sections. Irregular sections provide problematic results for depth and shape estimations.

4) So far, it has been assumed that the diffusion coefficient is an exponential function of C. But, widths of diffusion profiles in short-term experiments show square-root of time dependence, which probably explains, in many induction experiments and relatively young artifacts, their compliance to the classic OHD model (x^2=K.t). No test of our model on such young artifacts was made.

5) For SIMS profiles on irregular surfaces, the functional shape of diffusion provides a steeper exponential curve without the inherent details pertinent to diffusion mechanism. The shape details refer to the preservation of the sigmoid curve with initial rise of H^+ with formation of the SS layer, which keeps a constant value in time with progressive sloping through deeper layers, where a more drastic drop occurs, when the diffusion front reaches asymptotically background. This steeper (sloped) exponential shape is not appropriate to use for dating purposes, and another SIMS profile should be chosen.

6) One of the main uncertainties derived from the data comes from the determination of the surface saturation plateau. Only by inspection on point-by-point basis of data points one can recognize the almost constant C with the largest length of plateau valley (not easily detected from relevant plots). Drawing this plateau through scattered data points around a mean value inheres the uncertainty of variation of hydrogen concentration (counting statistics), and the overall analytical precision estimated to be 1-5%. In practice the plateau concentration value with the associated uncertainty derives from standard summary statistics; our average plateau values vary less than ±1% but occasionally up to 5%.

Correspondingly, a similar uncertainty arises for the Xs location, the end point of the SS plateau. A concentration-plateau test will illustrate this procedure. For example, sample OB-2, Chalco, Paredon source, in Table 1 below, gives the Cs and Xs and corresponding ODDSIMS-SS age. It is noted the constant Cs around 0.117 grmoleH_2O/cc, for Xs=0.000139441 to 0.000165587, and the change occurs after

TABLE 1: ODDSIMS-SS age, respective pairs of Xs and Cs, following the maximum, and the surface saturation plateau (in bold), for OB-2, Chalco, Parendon source. (± 1-5% errors from overall precision of SIMS profile; see Table 2).

ODDSIMS-SS Age, Years	Xs, $x10^{-9}$ cm	CsgrmolH_2O/cc
-2303	130720	0.118642
-6168	135084	0.119392
9412	139441	**0.117802**
2635	143799	**0.117541**
1546	148156	**0.117875**
1088	152514	**0.117577**
831	156872	**0.116736**
683	161229	**0.117009**
579	**165587**	**0.117103**
484	169944	0.114824
427	174302	0.114695
347	183017	0.114323

Cs=0,117103 grmoleH_2O/cc dropping to 0.114824 grmoleH_2O/cc. In general, the location of SS layer should be close to the surface, but, at any rate, empirically speaking, no less than about 0.5 um neither beyond around 2 um, and its identification requires particular care and expertise, and a technique is needed for its safer location.

The age, in this example, is susceptible to significant changes in the third decimal point for Cs and in the sixth decimal point for Xs. In general, for the different concentration values, it is the percentage variation from average of the plateau layer that is of concern. Certainly, 5-10% errors in Cs and Xs from SIMS transmit a higher error in the age (see, eq.12).

7) Another uncertainty derives from the accuracy of the fitted polynomial. In the presented examples the statistical tests for goodness of fit (overall model significance with the F-ratio statistics, the standard error of the fit, the adjusted Rsq according to degrees of freedom in the model), are quite good; the Rsq varies between 91%-99%. However, the present fitting of our modeling, even excluding the rise or the drastic drop of initial points, does not seem to have any effect on age.

The H^+ concentration can be measured quite accurately, from appropriate calibration (via Si^+ or from a set of glass standards) and precise determination of the relative sensitivity factor.

In addition, the determination of K-value may induce some uncertainties if the non-dimensional plot does not coincide with the reported curves of Crank (1975). In the present cases the tautology was quite eminent. Otherwise, interpolated curves must be produced.

Overall, many more applications should be performed on well dated samples, further consideration of the surface saturation layer is needed, and further statistical elaboration is required.

FIRST APPLICATIONS

Nine SIMS profiles were processed on samples derived from controlled excavations of well-known archaeological age. Five samples come from the Aegean sea region, Greece; three from Philakopi, a Bronze age settlement in Melos (Renfrew and Wagstaff 1982), and two from Ftelia Neolithic settlement, Mykonos (Sampson 2002; Stevenson *et al.* 2002; Riciputi 2002, personal communication), two samples from Mexico (Anovitz *et al.* 1999;

TABLE 2: Calculated data of some samples, along with the deduced ODDSIMS-SS ages compared to archaeological and C-14 dates. The errors of Cs, Co and Xs are of the order of 1-5%. Laboratory reference and citation of the obtained data is mentioned.

SAMPLE REF.	Cs, grmoleH_2O/cc	Co, grmoleH_2O/cc	Xs, cm	e^k	Ds, cm^2/year
MEXICO					
Pachuca Mexico 7-26H2 (Anovitz *et al.* 1999) C-14: 610±80 BP ODDSIMS-SS: 597 BP	0.131715	1.26E-02	1.49E-04	95	3.30555E-10
Paredon Mexico 7-25H4 (Anovitz *et al.* 1999) C-14: 580±60 BP ODDSIMS-SS: 580 BP	0.117103	8.40E-03	1.65587E-04	95	7.28461E-11
HOPEWELL SITE OHIO STATE, USA					
Evans East 91070-15 83-99 (Stevenson, pers. comm.) ARCH.& C-14: 1900±? BP ODDSIMS-SS: 1915 BP	0.000321268	4.5575E-8	0.65354E-04	200	1.0594E-12

Evans East 91070-16 83-103 (Stevenson, pers. comm.)	0.000315457	3.98E-08	1.24913E-04	10	4.504E-13
ARCH & C-14.: 1900±? BP ODDSIMS-SS: 1640 BP					
AEGEAN SEA, GREECE					
Melos Philakopi-2 (2000-145, Evans East) (Stevenson *et al.* 2002) ARCH. & C-14: 2000-2500 BC ODDSIMS-SS: 2100 BC	0.000846754	6.83E-5	1.3838E-04	50	1.132E-12
Melos Philakopi-3, tomb (2000-146, Evans East) Stevenson *et al.* 2002) ARCH. & C-14: 2000-2500 BC ODDSIMS-SS: 2040 BC	0.000278101	1.72E-4	1.287E-04	2	0.833E-12
Melos, Philakopi-3, tomb, at Kapari (2000-147, Evans East) (Stevenson *et al.* 2002)	0,000518014	0,000136975	8.994E-05	200	1,196525E-12
ARCH. & C-14: 2000-2500 BC ODDSIMS-SS:2180 BC					
Mykonos-1, Ftelia (2000-148, Evans East) (Stevenson *et al.* 2002) ARCH. & C-14: 4500-5100 BC ODDSIMS-SS: 4720 B.C.	0.001568986	0.000118712	1.53E-04	95	2.6E-12
Mykonos, Ftelia MYC-6 (ORNL) ARCH. & C-14 : 4500-5100 BC ODDSIMS-SS : 4850 BC	0.009901	0.000642	1.44E-04	50	2.13E-11

Stevenson *et al.* 2001), and two from Ohio, USA (Stevenson, personal communication), were used.

Figs. 1-4 (a,b) show representative SIMS profiles along with their respective fitted exponential curves (a), and the non-dimensional plots (b). The surface saturation layer is indicated in two cases, because the raw data provided for these samples were in tabular form, and the location of the SS was easily recognized (point-by-point). In the other cases the data were provided as plots in electronic diagrams with many points from which several, but adjacent ones, were chosen with caution to keep the profile shape unaltered, but due to such smoothing it is not easy to indicate the SS in the plots, although it has been rigorously worked and the SS detected, prior to smoothing. We have checked that such a smoothing does not affect the age calculation.

Table 2 gives the calculated data along with the deduced ages compared to archaeological and/or C-14 dates. The satisfactory concordance of the ages for materials of such wide geographical distribution lead us to consider the new approach as a very promising method of dating obsidians.

SUMMARY OF ODDSIMS-SS APPROACH AND ERRORS

The ODDSIMS with the SS approach consists of the following steps:

1) obtain the SIMS profile of H^+ ions versus depth, converted to gram moles of H_2O / cubic centimeter versus depth in cm.

2) Fit an exponential to these data with a polynomial exponent (usually of 3rd order).

3) Define the surface saturation layer from (1) at (Cs, Xs), following the concentration-plateau test.

4) Construct the non-dimensional plot of C/Cs versus X/Xs.

5) Compare (4) with Fig.5 family curves, and identify which curve is similar to (4) and specify the K-value.

6) Define Ds from the first derivative of (2) at X=Xs (the negative sign indicates only flow direction). Metric units in Ds is conventionally expressed in um/kyr, but due to (1) they are in cm^2/unit of time, where unit of time is chosen 10^{12} years.

7) Calculate the following: $r=K(Co/Cs)$, $dC/dy_s=1.128/(1-0.177r)$, and $dC/dX(x=0)$ of eq.8 - eq.11.

8) Get Cs, Co=Cintrinsic from (1).

9) Substitute (7) and (8) to the age equation (12) and define time (t).

10) Error estimation (sources of error derive from SIMS counting statistics, sample flatness, primary beam standardization). Several more profiles are required for the same sample and an error analysis for C, and the change in susceptibility of the sigmoid shape, in order to attach a detailed error figure to the age. Nevertheless, the obtained results provide satisfactory precision independently of the required accuracy. Quoted overall errors for SIMS is 1-5% (Anovitz *et al.* 1999), and 3-5%, for repeated cycles (Stevenson *et al.* 2001a).

CONCLUSION

The water diffusion into the obsidians takes place as a concentration-dependent procedure, and H_2O concentration (C), against, hydrated rim thickness sigmoid profiles, made by SIMS, were used to develop a new dating methodology — the obsidian diffusion dating by SIMS of surface saturation layer, or ODDSIMS-SS approach.

Based upon the surface saturation layer of the diffusion profile, and commencing from the Fick's 2^{nd} law of diffusion, for semi-infinite medium and for certain initial and boundary conditions, a solution was made defining diffusion time. Application of this new method on well-dated archaeological obsidians from the Aegean, Mexico and USA, produced satisfactory results.

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