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THE DATING OF OBSIDIAN: A POSSIBLE APPLICATION FOR TRANSPORT PHENOMENA (A TUTORIAL)

Robert S. Brodkey
Department of Chemical and Biomolecular Engineering
The Ohio State University, Columbus, OH 43210, USA

Ioannis Liritzis*
Laboratory of Archaeometry
Department of Mediterranean Studies
University of the Aegean, Rhodes 85100, Greece

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

ABSTRACT

The obsidian hydration dating by diffusion has been advanced since the early work of Friedman and Smith (1960) with the application of secondary ion mass spectrometry (SIMS) profiling of H+ in archaeological obsidian tools. Here we present an analytical tutorial account of analogue transport phenomena of heat transfer, eddy transport and molecular transfer, and on the empirical, phenomenological and scientific approaches that may lead to obsidian diffusion dating. A preliminary elaboration on the total flux, through integration over the entire curve of SIMS H+ profile is suggested. The present alternative concepts follow the background of the novel SIMS-SS dating approach (Liritzis et al., 2002, 2004).

KEYWORDS: obsidian, hydration, diffusion, dating, transport, archaeological

INTRODUCTION

If there were a reliable means for the dating of obsidian samples that had been used by ancient people, we could provide a very useful tool for modern archaeologist. One suggestion is to utilize the fact that moisture can diffuse into solid materials. The concept is that a freshly exposed surface of obsidian would begin to take up the ambient moisture and that the depth of penetration could be a measure of the age of the sample from the time that its surface had been exposed. The concept is relatively simple, but to provide a reliable and rational approach for the date estimation is not as simple.

Diffusion of water into amorphous silicates (glass) has been investigated on a theoretical and experimental basis (Crank, 1975). Amorphous rhyolitic glass, or obsidian, has been studied for dating purposes based upon the rate of water diffusion into the surface. However, the traditional obsidian hydration dating (OHD) age equation ($X^2 = kt$, where X = hydration depth, k = diffusion rate in μm^2/1000 years, t = diffusion age, Friedman and Smith, 1960) is not highly reliable, since k depends on short-term temperature measurements. The hydration rims formed at elevated temperature were measured and used to calculate pre-exponential, A, and activation energy, E, and these constants were used to estimate archaeological hydration rates at ambient conditions with the Arrhenius equation ($K = Ae^{-E/RT}$).

The dependence of hydration rate on obsidian chemical composition has been addressed through theoretical considerations (Ericson, 1981) and by correlation of high temperature hydration rates with glass chemical constituents (Friedman & Long, 1976). Mazer et al., (1991) and Stevenson et al., (1993, 1998) has shown a strong dependence between the structural water content of the glass with the 100% relative humidity pre-exponential at elevated temperature A and E.

However, doubts are expressed on the validity of hydration proceeding as squared root of time (Anovitz et al., 2004), while accurate hydration rims have been advanced with infrared photoacoustic spectroscopy (IR-PAS) and secondary ion mass spectrometry measurements (SIMS) (Stevenson et al., 2002).

Our purpose here is to revisit this initial OHD concept, evaluate its potential, and make suggestions that could contribute to the eventual development of such a test method. To be considered are first, the types of data needed and second, how that data should be interpreted to provide the measure desired.

There are several approaches that can be taken for the analysis of moisture penetration results. The *empirical method* is in some sense the simplest, and requires the minimum of experimental data input and the simplest of correlation analysis. It does not consider any rational theory. For obsidian, one uses a measure of the depth of penetration of moisture and an estimate of the diffusivity in the Einstein diffusion equation, $x=2\sqrt{Dt}$, to calculate a time or one uses a correlation between the depth of penetration and age. In this method, any good fitting equation would be a good candidate to represent the age of the sample. Fore example, if you had *100 samples of known age*, you may take 25 to 50 of them at random (training sample) and use them to correlate the experimental measures with the known age of the samples. You accept whatever correlation you get between the depth of moisture penetration and the age. You then apply the equation to other known samples and see how good you do, since you know the age. More often than not, you will not do all that well because this method does not contain any understanding of the physics of moisture penetration. It works only because you might have a lot of data and can get a reasonable statistical correlation with the training sample. It is a simple approach, but may not work, if the number of cases available is small as a result of inadequate statistics. The method does not, of course, provide any understanding of the mechanism. As a parallel, consider C^{14} dating for age determination of wood and other organic samples. Many of the complaints of the inadequacy of the technique were resolved when it became possible to calibrate the technique using unambiguous measurements of tree ring samples of exactly known age. The problem with this approach for obsidian is that we don't have a well-established set of samples from archaeology with well-known ages and we don't have a parallel for calibration with results from tree ring dates.

At the other end of the spectrum of approaches is the *scientific method.* It is the ideal approach to the problem of the dating. We must understand the basic underlying diffusion process so that we can use it for the dating of obsidian samples: any samples from anywhere and of any age. Only if we understand the process in terms of the physics (or basic mechanism) can we do this. This is a tall order and we may not be able to establish the rational theoretical relations needed to solve the fundamental equations with their boundary conditions. Today, that might not be necessary as there is now the possibility of using fully numerical computations to replace the need for a solution of a fundamental and rational theory. It is also important to know that we are not just trying to develop an empirical technique that can give the correct results for a limited number of cases (see, Liritzis et al., 2004).

There is a middle of the road approach, called the *phenomenological method,* where we try to use theory even if we cannot determine all the constants fundamentally. For this, the mechanism for obsidian dating is assumed to be simply Fickian diffusion. The diffusion coefficient, D, can be nearly constant for equal molar counter diffusion in dilute solutions; however, for solids this would not be true. If the form of D can be specified, there may well be known solutions (both analytical and numerical) in the literature (Crank, 1975). To use this approach, a great deal more information than just the depth of penetration of moisture can be utilized for the analysis. The entire moisture (water concentration curve) as a function of the depth of the sample from the surface as measured by SIMS can be used. However, the method can be misleading as it is still based on empirical relations that are fundamental to the concepts of transport phenomena and are known not to be universally valid. There will still be unknown parameters involved (Liritzis and Diakostamatiou, 2002, Liritzis et al., 2004; 2005a).

As a classic example of the phenomenological method, Prandtl (Brodkey, 1988) suggested his mixing length theory in the early 1920's for the description of turbulent fluid flow. The theory itself was simple and based on molecular movement in gases. The final form of his equation for the velocity was

$$U^{+}=A\ln(y^{+})+B \qquad (1)$$

where U^{+} and y^{+} are nondimensional velocity and distance. The theory or Eq. (1) suggests that a semi-logarithmic plot of U^{+} versus y^{+} should be a straight line. Prandtl then plotted all the available data and found that indeed all the data fitted one single straight line as given by Eq. (1) and that the best fit was with $A = 2.5$ and $B = 5.5$. The concept uses a simple rational equation that is based in theory and uses experiments to determine in a known manner any parameters in the theory. It can then be used to predict other velocity distributions under other conditions. Liritzis and Diakostamatiou (2002) used the phenomenological approach as a possible improvement over the empirical method for the dating of obsidian.

To appreciate the problem that we have, we need to know more about transport phenomena. Thus, in Sections 2-5, we present a short tutorial on the subject. Much of this material is taken from Brodkey and Hershey (2003).

MOLECULAR TRANSPORT MECHANISMS

Heat transfer, mass transfer, and fluid flow are three old topics. What is new is the descriptive term "transport phenomena." The general approach is to formulate a mechanism, established the equations, and solved them.

The final results are tested in whatever ways that are possible to verify the validity of the approach. Applications to obsidian hydration dating are in reality, no different.

The basic premises of transport are by no means new: Sir Isaac Newton (1643-1727) introduced the law of viscosity, which is fundamental to fluid mechanics, Jean Baptiste Joseph Fourier (1768-1830) suggested the law of conduction, and Adolph Fick (1829-1901) added the law of diffusion. Based on *empirical observations*, a flux of the property (e.g., heat) was suggested to be a simple linear transfer as a result of a driving force. Such molecular transport may occur in solids, liquids, gases, or mixtures thereof.

The first simplest example of molecular transport is the conduction of heat from a high-temperature region to a low-temperature region through a rod, as shown in Fig. 1-(a). If one end of a rod at ambient temperature is held firmly while the other end is thrust into a roaring fire, heat is transferred to the hand-held end of the rod from the end in the fire by molecular transport. The hot molecules in the fire have more energy than the adjacent cooler molecules of the rod. As the molecules collide, energy is transferred from the hotter molecules to the cooler molecules. The process is repeated millions of times until the rod is too hot to hold. The difference in temperature (temperature of the hot fire minus hand temperature) is the driving force for the heat transfer.

In the second type, for mass transport, the situation is more complicated because there must be at least two species present. Consider two identical flasks joined through a valve as shown in Fig. 1-(b).Let one flask be filled with pure nitrogen, the other with pure oxygen, both at the same pressure and temperature. If the valve in the middle is opened, oxygen will diffuse into the nitrogen side and nitrogen into the oxygen side until each flask contains 50 percent nitrogen and 50 percent oxygen. Concentration is the driving force.

The third type of molecular transport, momentum transfer is the most difficult to explain briefly and concisely. The velocity of each molecule in the fluid changes from point to point in many flow problems. Mathematically the velocity gradient is ($\partial U_x / \partial y$). In describing heat and mass transfer, it is easy to visualize what is being transferred and the nature of the driving force. In the case of momentum transfer, momentum flux is being transferred, and the velocity gradient ($\partial U_x / \partial y$) is the driving force; both of these are difficult to visualize. Fluid flow is a simple example of momentum transfer. The driving force for fluid flow is a pressure difference. For example, when the valve in a drinking fountain is opened, the water flows out in a jet because the water pressure inside the fountain is much higher than the atmospheric pressure into which the jet discharges. Figure 1-(c) shows a simple example of the flow of a fluid (gas or liquid) in a pipe. If a very small pressure drop is used, the flow in the pipe will be relatively slow and will be laminar. If there is a large pressure drop, the flow in the pipe will be much larger and probably turbulent. Let Fig. 1-(c) represent smoke-filled air being blown through the pipe. In the laminar case (molecular transport), the fluid issues from the pipe in a smooth, ordered fashion. In the turbulent case, the fluid motion is chaotic with blocks of molecules (called eddies) moving in all directions.

In summary, the molecular mechanisms involve transport of heat by conduction, of mass by molecular diffusion, and of momentum as occur in laminar fluid flow. A limited analogy among these three transport phenomena can be used to help gain better insight into the processes of the transfer. However, care must be taken not to carry the analogy too far, and its limitations will be indicated as our development proceeds.

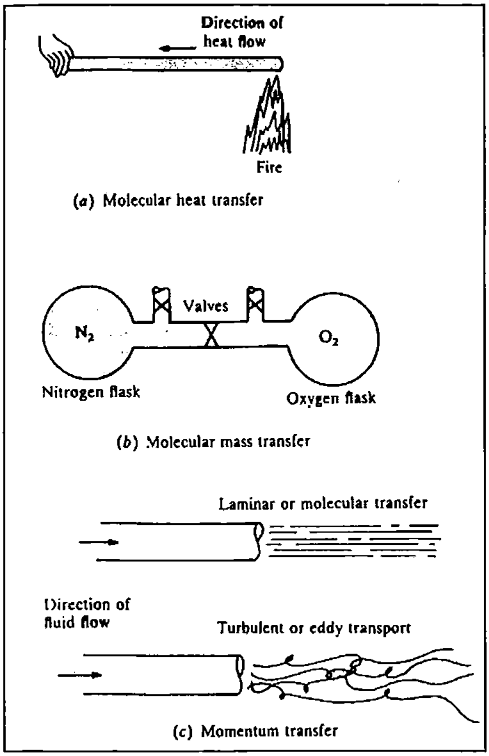

Fig. 1: Examples of transport as heat mass and momentum

THE ANALOGY

It is common to formulate a general rate equation as

(RATE) =(DRIVING FORCE)/(RESISTANCE) (2)

In Eq. 2, as the driving force increases, the rate increases. Also the larger the resistance, the smaller is the rate. Common sense verifies Eq. 2, and it is useful to begin discussion of the transport analogy with a simple example from our experience of heat transfer in the world around us.

The Case for Heat Transfer

In heat transfer, the driving force is the temperature difference. Our intuition and experience tells us that heat can be transferred from a hot region to a colder area. For example, consider a block of copper, in which the sides are insulated so that heat conduction occurs only in one direction, the x direction. Let the initial temperature of the block be 0°C. Initially, for all values of *x*, *T* is constant and equal to 0°C. Now a temperature difference is established by placing the copper block on top of a block of ice and by immersing the top of the block in steam so that the top temperature is instantaneously raised to 100°C. This has now become an unsteady state problem and the progression of the heating of the block to establish steady state is shown at the top in Fig. 2. The final steady state curve is when time equals infinity and the profile becomes a straight line. The linear temperature gradient is an experimental observation and, provided enough time is allowed, the linear temperature distribution is observed as long as the temperatures at the bottom and the top are maintained at the same preset values. The observation is attributed to Fourier. The heat being transferred per unit time and unit area, or what is called the heat flux, is directly proportional to the difference between the temperatures and inversely proportional to the distance:

$q/A = -k\Delta T$ Fourier's Law in vector form (3)

$(q/A)_x = k(\partial T/\partial x)$
One Dimensional Fourier's Law (4)

where q is the amount of heat transferred per unit time, A is the area, and the subscript x on the flux term denotes that in Eq. 4 the heat flux is considered in the x direction only. The proportionality constant k is called the thermal conductivity. It varies from material to material over a wide range and is an empirically determined parameter.

The minus sign in Eqs. 3 & 4 is required because the heat flows from hot to cold. In Fig. 2 the plot of T versus x shows that the gradient or derivative $(\partial T/\partial x)$ is positive. Common sense tells us that the heat will flow from the hot to the cold. Hence the heat flux *(q/A)* is in the negative direction, and Eq. 3 & 4 requires the minus sign. If Eq. 4 were to be rearranged into the form of the generalized rate equation:

$$\text{rate} = q \quad \text{resistance} = \partial x / kA$$
$$\text{driving force} = \partial T \tag{5}$$

The Case for Mass Transfer

For mass transfer in solids, which is the transfer of interest in this study, the analysis is almost identical to that of heat transfer. The curves in Fig. 2 for various times are nearly the same, and one might suspect that the equations are similar also. Fick in 1855 introduced this parallel empirical process and Eqs. 3-5 become

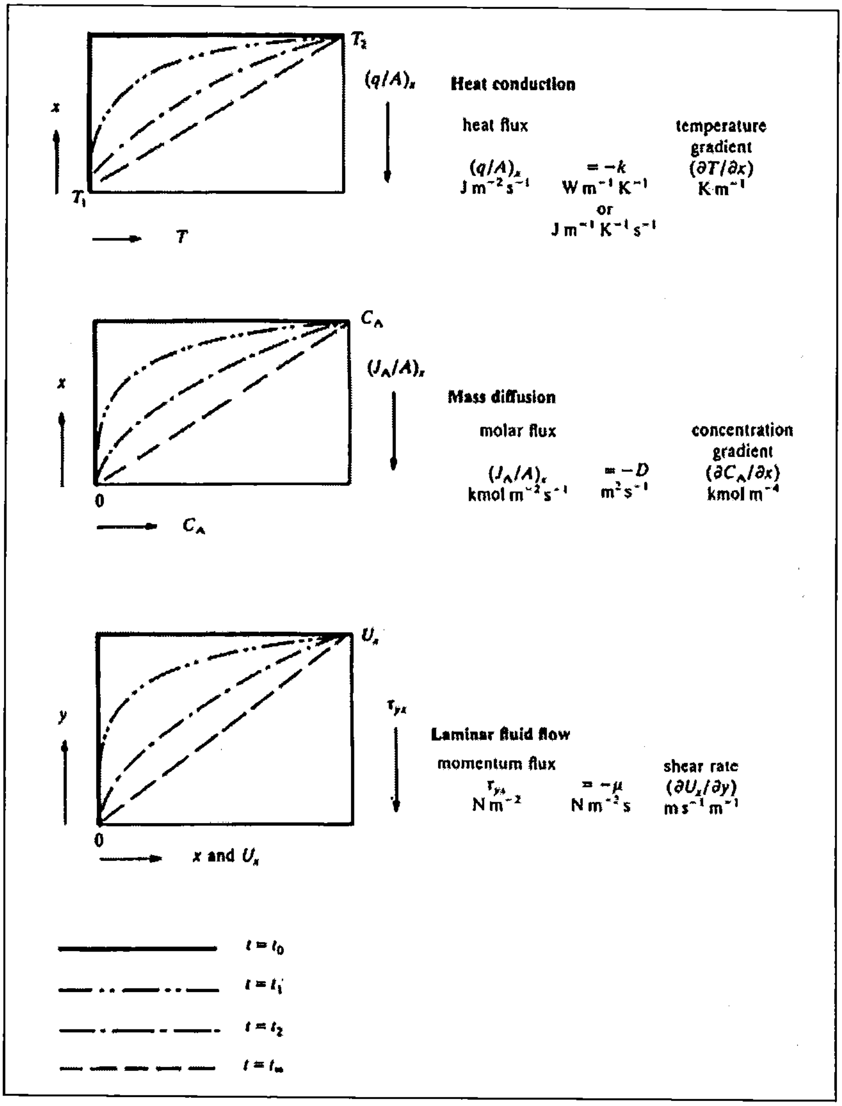

Fig. 2: The analogy of the transport phenomena

$$(N_A / A) = -D\nabla C_A \qquad (6)$$

Fick's Law in vector form

$$(N_A / A)_X = -D\,(\partial C_A\,\partial_X) \qquad (7)$$

One Dimensional Fick's Law

rate = N_A, resistance = ∂_X / DA
driving force = ∂C_A (8)

Here (N_A / A) is the moles of species A being transferred per unit time per unit area. The proportionality constant D is called the diffusion coefficient. Less commonly, D is referred to as the molecular mass diffusivity or just mass diffusivity. It is also empirically determined.

The Case for Momentum Transfer

For completeness, momentum transfer should be summarized. Because fluid flow is not of importance in the present work, we will leave the detailed discussion of momentum to textbooks. The parallel equations are

$$\tau = -(\nabla U + (\nabla U)^T) \qquad (9)$$

Newton's Law in Tensoral Form

$$F/A = \tau_{yx} = -(\partial U_x / \partial y) \qquad (10)$$

One Dimensional Newton's Law

However, we should note that these equations are 2nd order tensor relations and thus much more complex than the simpler vector forms of heat and mass transfer.

Three analogous equations (often called constitutive relations) have been introduced: Fourier's law for heat transfer, Eq. 4, Fick's law for mass transfer, Eq. 7, and Newton's law for momentum transfer, Eq. 10. In each of the foregoing equations, a minus sign has been used in the proportionality. As noted earlier, this was not arbitrary, for in each case the flux is transported down the corresponding gradient. Fluid mechanics developed as a subject earlier than heat or mass transfer. Momentum transfer is a modern way to look at fluid mechanics. For momentum transfer, momentum is transferred from the high-velocity region to the low and thus the negative sign is required in Eq. 10. However, in earlier days, before the momentum transport concept and the analogy, a positive sign was used. Since momentum transfer and its direction were not of concern, it did not matter what sign was used, as long as the use was consistent.

The three empirical laws established by observation many years ago are useful only when point properties are involved. Thus when the properties cannot be regarded as continuous these equations do not apply. Simply stated, the laws of Fourier, Fick, and Newton apply only to a continuum. The three proportionality constants in these equations are three fundamental properties. The first, k, is the thermal conductivity; the second, D, is the diffusion coefficient (the mass diffusivity); and the third, μ, is the viscosity (also called the molecular or dynamic viscosity).

The Analogous Forms

The analogy is of much more recent origin. The three equations are quite similar. Each involves a flux term, a proportionality constant, and a gradient of some measurable parameter. However, the equations are not exactly in their analogous forms. A general flux equation is

$$\Psi = -\delta\nabla\varphi \qquad (11)$$

Vector Form

$$\Psi_X = -\delta\,(\partial\varphi / \partial x) \qquad (12)$$

One Dimensional Form

The term on the left, Ψ, is the flux in units of the property being transferred per unit area and time (e.g., property/m^{2}s). The diffusivity, δ, is in units of area per unit time (e.g., m^2 s^{-1}) and the gradient of the concentration, $\nabla\psi$, is in units of property per unit volume and length (e.g., property/m^4).

The three transport equations become in this form:

$$(q/A)_X = -\alpha(\partial\rho c_p T / \partial x) \qquad (13)$$

$$(N_A / A)_X = -D(\partial C_A / \partial x) \qquad (6)$$

$$F / A = \tau_{yx} = -\nu(\partial \rho U_x / \partial y) \qquad (14)$$

Note that Fick's law is already in the analogous form. The three proportionality constants are *k*, *D*, and μ transport coefficients (15)

$\alpha = k / \rho c_p$, D and $\nu = \mu/\rho$ or δ (16)
Diffusivities

We must emphasize that the analogous forms are a *mathematical analogy* as applied to the three transport phenomena. The equations are the same from the mathematical standpoint. With a given set of boundary conditions, a solution for one is a solution for all; the only difference is in the symbols representing the various terms. This mathematical analogy in no way means that the physical mechanisms occurring in the three cases are in any way the same. The mechanisms are totally different. For the heat conduction example, the heat is conducted from the fire towards our hand through energy transfer mechanisms, which are dependent upon the material contained in the rod. In metals, the rapid migration of an energy containing "electron gas" is the primary energy transfer mechanism. Mass transfer often involves at least two materials, one material being transferred by relative motion through the other. In the latter case, the molecules move from one place to another, whereas in heat transfer through a solid rod the molecules are relatively stationary. Momentum transfer involves a combination of mechanisms, which, for the most part, are different from those of the other transports.

The concept of transport as a mathematical simplification of heat, mass, and momentum transfer has been introduced. In particular, the empirical nature of the subject and the fact that the transport coefficients are based on experimental measurements are emphasized. Of extreme importance is the limitation that must be recognized for each of the transfers. For example, not often are the transport coefficients constant as they should be, if the gradient concept is truly correct. The extreme example is that we call materials Newtonian, if they follow Newton's law of viscosity and non-Newtonian, if they do not. The entire subject area of 'rheology' is based on this difference. For the case of diffusion, which is of key interest here, there is an additional important transport consideration. In Eq. 6, the diffusion coefficient *D* has been assumed not to vary in any of the three coordinate directions. This is not expected to be valid for diffusion through solids.

THE BALANCE OR CONSERVATION CONCEPT

For the use of diffusion for dating analysis, we want to establish the time or how long the diffusion has occurred. For this, we require complex dynamic or time-dependent analysis rather than simple steady state. It is this time dependency that is used to establish the time. For this we must introduce the concept of a property balance. In its most simple form, it is a statement of what goes in (INPUT) plus what is made there (GENERATION) must come out (OUTPUT), or must stay (ACCUMULATION):

INPUT + GENERATION = OUTPUT + ACCUMULATION (17)

The Balance Equation in Differential Form

In our generalized mathematical notion (unsteady state and incompressible), the balance equation takes the form

$$\partial\psi / \partial t + (U.\nabla)\varphi = \varphi_g + (\nabla\delta\nabla\psi) = \varphi_g + \delta\nabla^2\psi \qquad (18)$$

$$\partial\psi / \partial t + (\nabla\delta\nabla\psi)$$
No Flow or Generation (19)

$$= \delta\nabla^2\psi$$
If δ is also constant (20)

For the case of one-dimensional diffusion through solids, δ or D will be variable. The property, ψ or C_A, is still the concentration of the material being monitored. For this specific case, the unsteady equation that must be solved becomes

$$\partial C_A / \partial t = (\partial D \partial C_A / \partial x^2) \qquad (21)$$

This is a full-blown partial differential equation but today can be solved easily by numerical methods. There are many solutions (both analytical and numerical) in the literature.

The basic concept of diffusion as described by Fick's law dates back to 1855. Newton's parallel law is still much older. The introduction of the transport concepts in the 1960's was more for a consolidation of topics to make teaching of the subject easier. It is nice to know that a mathematical solution for one of the transports might well be valid for all, as long as we do recognize that these apply to the limited analogous forms.

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 can be in common. These equations, based on the laws of Fourier, Fick, and Newton, apply only in a continuum, i.e., in applications where all properties are continuous. Again we must emphasize that this is a limited mathematical analogy and that the fundamental physical processes of the transfers are quite different. The word limited is used since the equations are by no means identical. In its more complicated form, heat transfer is described by a vector equation, as is mass transfer. However, mass transfer will usually involve at least two equations, since there must be equations for each of the species present. Finally, for momentum transfer one needs a second-order tensor equation and, in the most general case, there are nine component equations. Nevertheless, any given single component of these equations is of the same mathematical form as those in mass and heat transfer.

A COMPARISON OF THE TRANSPORTS

Let us return to the case of the diffusion between flasks [see Fig. 1-b] and try to picture our analogy in physical terms. Further, let us restrict our view to a very dilute gas. For mass transfer, in order to move a molecule from one flask to the other through the connecting tube, that molecule must be moved physically. For one such molecule, the movement is shown by the dotted line in Fig. 3. If the molecule should strike another molecule or the container wall during its transfer, it may not arrive at the other side; the dashed line indicates this situation. In this crude dilute gas experiment, a molecule has a difficult, tortuous path in order to be transferred from one side of the vessel to the other. This process of diffusion by random molecular collisions is called a "random walk" process, and it can be observed in the Brownian movement in suspensions. The mass diffusion process may be contrasted to the transfer of energy of the molecule as indicated in Fig. 4. As in the case of mass transfer, every time a molecule is moved, its temperature is transferred with it. However, there is another mechanism, which contributes even more to the transfer of heat. This mechanism is analogous to the transfer of energy encountered in playing pool, and the dashed line in Fig 4 shows it. There are both migration and collision mechanisms for the transfer of the energy or temperature. Thus, in relatively dense systems, the thermal diffusivity is greater than the mass diffusivity. The same is true for the momentum transfer case for which there are still other mechanisms as a result of its tensorial nature. To provide a simple comparison, the transport properties for liquid water at 0ΓC are compared:

$D = 1.36 \times 10^{-9}\ m^2\ s^{-1}$, $\alpha = 142 \times 10^{-9}\ m^2\ s^{-1}$ and $\nu = 1800 \times 10^{-9}\ m^2\ s^{-1}$

It is fortunate that, from an experimental standpoint, the various mechanisms are described by the same equation. Clearly, the various diffusivities, of mass, of momentum, and of heat, are not equal. If only one mechanism had been controlling all three phenomena, then these diffusivities would be identical. Final the diffusivity in solids is still much lower that in either gases or liquids.

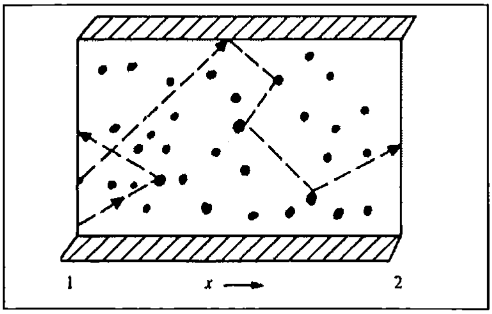

Fig. 3: Mass transfer mechanism

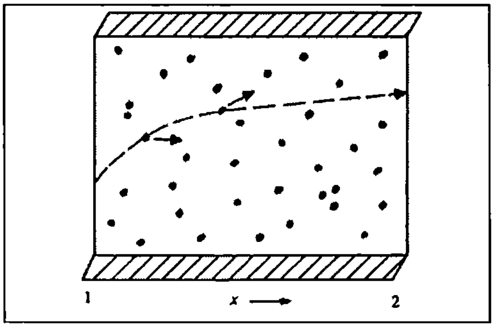

Fig. 4: Heat transfer mechanism

FICK'S LAW AND DATING: THE PHENOMENOLOGICAL METHOD

Applications of the transport phenomena approach are in reality no different from earlier classical approaches. A mechanism is formulated, the equations are established and then solved, and the final results are tested in whatever ways that are possible to verify the validity of the approach.

The mechanism is assumed to be simply Fickian diffusion. However, one does not expect that for solids, the diffusion coefficient will be a constant as it often is for equal molar counter diffusion in dilute solutions. Since the problem at hand is one-dimensional, Fick's law takes the form

$$(N_A/A) = -D(\partial C_A/\partial x) \qquad (7)$$

Here there are no restrictions on the diffusion coefficient, D; it could be constant or a variable function of either C_A or x. When Eq. (7) is combined with the balance equation for no flow or generation (Eq. 19) and put into mass transfer notation, one obtains Eq. 21:

$$\partial C_A \partial t = (\partial D \partial C_A/\partial x^2) \qquad (21)$$

For this case of one-dimensional diffusion through solids, D will be variable. The property, C_A, is still the concentration of the material being monitored. The solution to Eq. 21 is still a partial differential equation. Today these can be can be solved by numerical methods; however, such solutions are never really easy. If the form of D is specified, there are many known solutions (both analytical and numerical) in the literature (Crank 1975).

With the background of transport phenomena, we can now discuss the dating of obsidian in terms of the various possible approaches. We will not consider the empirical approach, as that was the starting point for the suggestion of using the diffusion of moisture as a measure of time. What we will briefly discuss is the phenomenological approach put forward by Liritzis and Diakostamatiou (2002). This will then be followed by a discussion of the *scientific method* and the possibilities that it holds for the solution to the problem.

Crank's Solution of Fick's Law Using an Exponential Dependence for D

Briefly, Liritzis and Diakostamatiou (2002) used the solution obtained by Crank (1975) for an exponential form for D in terms of C_A, which was presented by Crank in graphical form and reproduced here as Figure 5. The specific form for D is $D = D_o \exp (kC_A / C_s)$. By comparing various solutions with experimental data (in terms of non-dimensional concentration of the diffused water versus the non-dimensional distance), the best qualitative fit was for the exponential form. This dependency is a basic assumption of the technique and is supported by the research of others.

The geometry, initial and boundary conditions must also be selected. For the geometry, the system is assumed to be semi-infinite, since the diffusion, which starts from the surface of obsidian penetrates into the obsidian until the moisture content is homogeneous and not far from its initial value of moisture content. Since the time span is very large for this process and the distance very short, one assumes that the diffusion distance is infinite; i.e., the penetration depth is very small. For a glass like material like obsidian, before any diffusion has occurred, the initial moisture level should be the intrinsic water level that was a part of the obsidian when it was formed during the solidification process after being formed in a volcanic explosion. The initial condition is taken as

$C_A = C_o,\ x \exists 0,\ t = 0$, where C_o is the concentration of the intrinsic water in obsidian at the initial time of it forming.

The next step is to set the boundary conditions at the surface. The present solution uses a constant external surface concentration of water. Diffusion of water within the soil pore structure in the earth that is around the buried obsidian sample will be very much faster than that in the glass itself. Thus, the surrounding soil can be assumed to be at a constant moisture level. For a very small time period compared to the age of the sample, the surface layer of the obsidian becomes saturated with water. This layer is assumed to remain at a constant water concentration during diffusion. The boundary condition on the surface is taken as

$C_A = C_s,\ x = 0,\ t \geq 0$ where C_s is the surface concentration of water.

Conditions within the obsidian, very near the surface may not be ideal (micro porous structures, etc.) and the diffusion in this region may not follow the same Fickian diffusion as in the rest of the sample. For this region it will be desirable to eliminate the associated data points for now and redefine a new pseudo surface point as $x = 0$ where the Fickian diffusion analysis being used works. Thus, for time $t \geq 0$, the boundary condition of $C_A = C_s,\ x = 0,\ t \geq 0$ will remain the same, but with a newly defined origin. This has been used by Liritzis and Diakostamatiou (2002) and called the saturation layer.

So far, the key assumption that has been made is that there is an exponential dependence of the diffusion coefficient D on concentration given by:

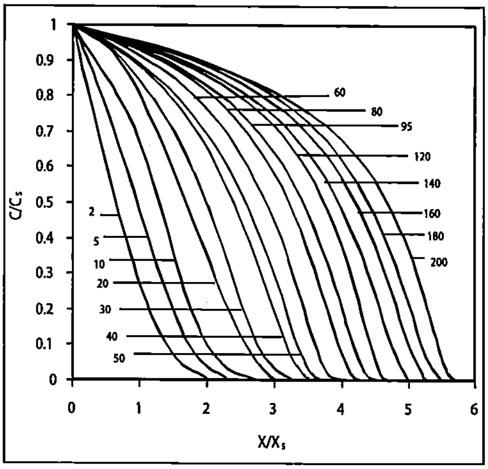

Fig. 5: Concentration versus distance curves for exponential diffusion coefficient during sorption of $D = D_o \exp (kC_A / C_s)$ and $x_o = 2(D_o t)^{½}$. C_s is the surface concentration. Numbers on the curves are the values of e^k, where $e^k = D_s / D_o$. D_o is the diffusivity at $C_A=0$.

$$D = D_o \exp(kC_A / C_s) \qquad (22)$$

When $C_o = 0$, $D = D_o$. The surface $(x = 0)$ is where $C_A = C_s$.

According to Crank (1975), one can now determine the total time for the diffusion to take place. This time should correspond to the age of the sample, since it is assumed that the diffusion of water in obsidian started when the surface was exposed. We will not go further into the details of this work, which can be found in Liritzis and Diakostamatiou (2002) and Liritzis et al., (2004). These references together with the recent PhD thesis (Diakostamatiou, 2004) offer a complete analysis of the problem and this approach. However, two major questions can be raised: 1) the selection of the surface saturation layer is critical, albeit scientifically sound. The technique applied of using successive regressions that define a plateau or saturated layer, the surface saturation (SS) layer, is occasionally unclear due to surface and sputtering effects. The exact causes is still unknown (Liritzis et al., 2005b), and, 2) an adjustable universal phenomenological constant is used to get the good fit. It might be possible to improve further this analysis by more refinement. However, an even more important advance might also be possible by returning to the more fundamental scientific approach.

The problem to get D_o in obsidian hydration dating

Figure 6 is the entire SIMS curve for the sample Evans East 91070-15. Figure 7 is a blow-up of region 2 with the y-axis being normalized. The Evans East sample comes from a Hopewell site in Ohio in the U.S.A (not far from Columbus).

The diffusion coefficient, D_o, is by definition the diffusion at the beginning of the surface region; i.e., at $X = 0.0001$ cm for the original data, which would be now $X = 0$ for the present analysis. This must be determined from experimental data in a fundamental manner that is based on the known physics. Since earlier sections show that we appear to have a case of Fickian diffusion with an exponential variation of the diffusion coefficient, we will use Fick's law to determine D_o. This law is defined as an empirical equation given by

$$N_A/A = -D\, dC/dx \qquad (23)$$

For our case, this equation becomes,

$$N_A/A = -D_o\, (dC/dx)_{x=0} \qquad (24)$$

where x = 0 is the start of the surface region, which is Region 2 of the original data plot (Figure 6). To get D_o we need both N_A/A and $(dC/dx)_{x=o}$. D_o will be the negative of the ratio of the two; i.e.,

$$D_o = -(N_A/A) / (dC/dx)_{x=o} \qquad (25)$$

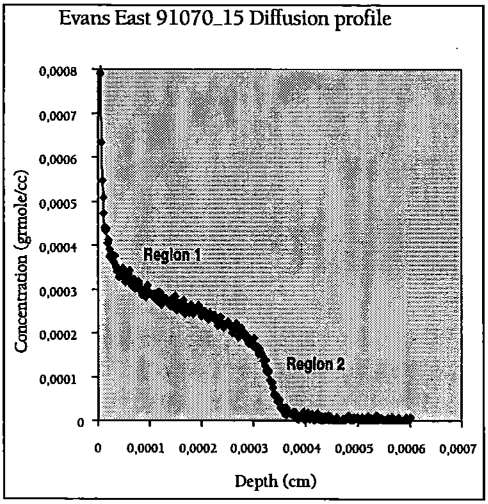

Fig. 6: Diffusion profile as determined by secondary ion mass spectrometry (SIMS)

$(dC/dx)_{x=o}$ can be obtained from the slope of the curve at x=0. A plot of this region is given in Figure 8, with the slope estimated by a simple fit (done in EXCEL). This value is -1280.5 cm^{-1}, since in Fig. 8, the concentration is a nondimensional ratio and the x-axis is in cm. If the initial concentration in this region is used, then the slope becomes

$$-0.36743\ (\text{gmol/cm}^3)/\text{cm} = -0.36743\ (\text{gmol/cm}^4)$$

Now comes the tough part, how do we get N_A/A, which we need if we are going to calculate D_0 from fundamentals given by Equation 25 above. For this we must go back and look at what Fick's law (Equation 23, 24, or 25) means and is describing. Also, for this, we must describe what we are currently trying to do to get N_A/A and thus D_0. This step is not as yet fully accomplished, but can be outlined. Therefore, let us continue with how we are going to get N_A/A, the flux of material.

Possible evaluation of the surface flux as a key required step

How do we get N_A/A, which we need, if we are going to calculate D_0 from fundamentals given by Eq. 7 and 22? For this we must go back and look at what Fick's law (Eqs. 6-8) means and describes in the earlier tutorial. It appears we have a case of Fickian diffusion with an exponential variation of the diffusion coefficient. The units on the flux are

N_A (grmole/sec), A (cm^2), and
N_A/A (grmole/cm^2 sec)

We want the flux at surface in Figs. 6 and 7 to go with the slope at this same point to define D_0. As our first step, we must first compare the actual data set with the theoretical curves to determine what, if not all, of the data is to be used in the analysis; i.e., there may be regions that simply do not follow the theory and cannot be fitted in any manner.

Visual inspection and the understanding of the nature of transport in such systems suggest that there are really two regions that must be considered. These are marked in Fig. 6. Region 1 would be from the surface at $x=0$ to $x = 0.0001$ cm (~1 micrometer). Region 2 would be the main part of the concentration curve from $x > 0.0001$ to the point where the concentration is very close to zero. Region 1 near the surface (~1 micrometer) is the region where it has been suggested that SIMS data might be questionable because of surface effects. It shows a very rapid drop off from the surface concentration at $x = 0$ to a lower value near $x = 0.0001$ cm. This observation does not mean that there is anything incorrect in the data, but rather, that the mechanism for transport of mass in this region cannot be the same as that in region 2. Thus, we need to consider region 1 later as it is clearly different from region 2. Perhaps this deviation is a result of micro porous structure that can form in the top layer of the sample, we do not know. Such pores would allow moisture to penetrate the layers close to the surface and give high moisture reading. Region 2 is similar to the curves in Fig. 5 and looks like Fickian diffusion with an exponential variation of D with concentration. Also of importance are the initial and the boundary conditions. Logically, we would treat regions 1 and 2 differently as the mechanism of transport may well be different.

With D_0 and the results of Crank's solution we can get D anywhere. In fact we need the flux at "A" (start at upper left of Fig. 7) to go with the slope at this point to define D_0. The flux is the amount diffused per unit of area per unit of time. The area through which the diffusion occurs is not a problem as we use a volume that is 1 cm x 1 cm x depth from the SIMS experiment (cm). The amount of material diffused is fairly easy as it is the integration of the curve in Fig. 7. The figure is normalized on the y-axis, so we must multiply by the zero concentration. This is the same as was done for the slope, earlier. However, the time for the diffusion is still a problem.

What is easy to get is the total flux, which would be the integration over the entire curve of Fig. 7 from point "A" to "B". This would be

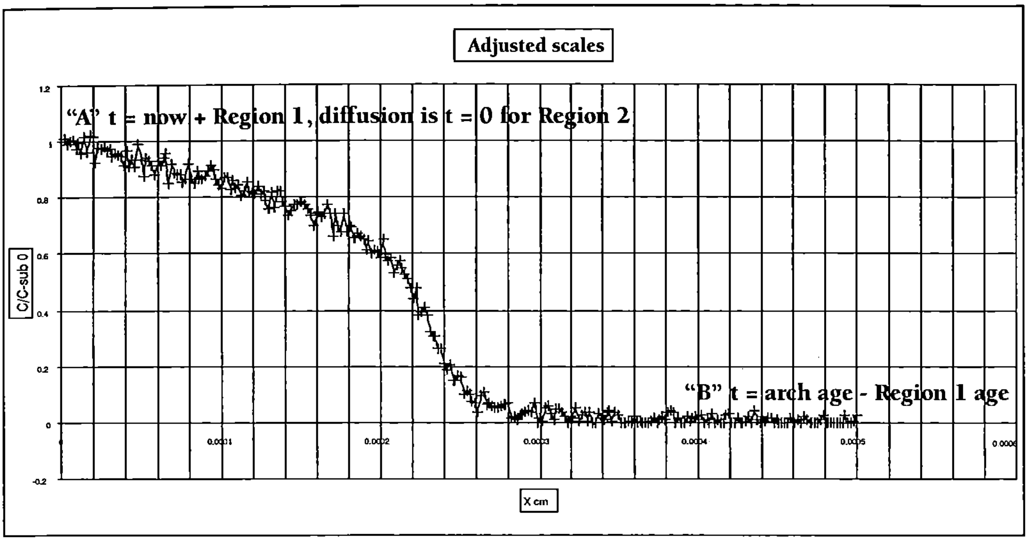

Fig. 7: The modified data set with the origin relocated to the inflection point of the original data set.

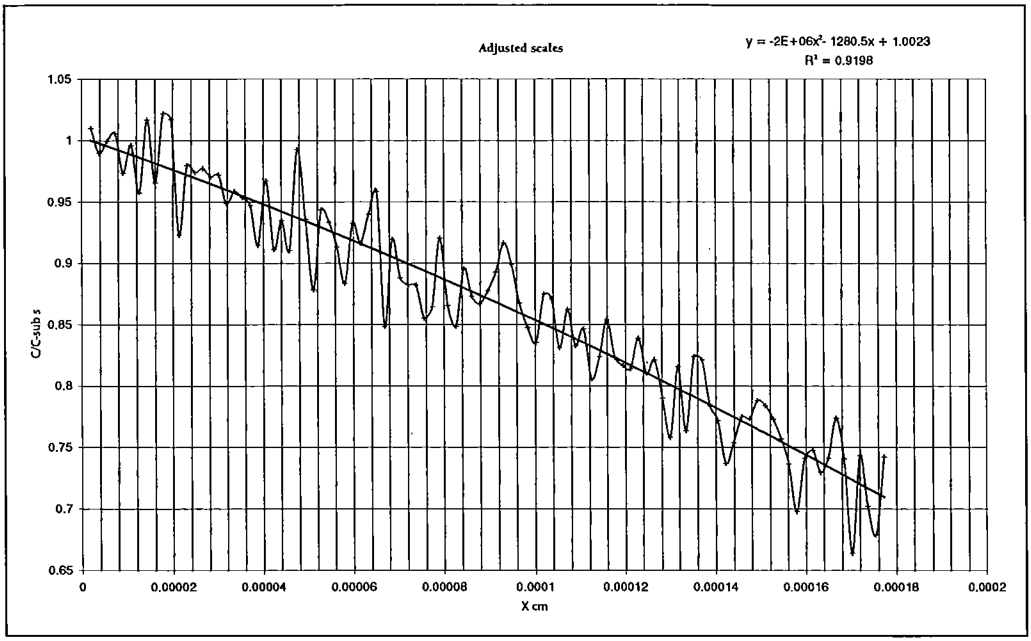

Fig. 8 : The initial data to determine the initial slope

satisfactory, if we were sure the flux was constant over the entire archeological age of the sample. But, we don't know if this is true. The intriguing part will be to get the flux at different depths between "A" and "B". Thus, the total flux and the flux at various depths might be the solution to the problem.

For this, the integration will probably have to be done in steps; i.e., for small increments of depth that could represent small periods of time where the assumption of a constant flux for that small region might be satisfactory. The first step would be to assume the flux constant over the entire age of the sample. We will need to guess an age and the archaeological age (±1000 years) can be a guide for this. In any event, the calculation will be by trial and error, since we have only an initial guess of the age.

This can be seen since the flux is in units of (grmole/cm^2•sec) and we will have (grmole/cm^3) from the integration. We would hope that almost any reasonable initial guess will do. With the guess for the age, we can obtain the flux, then the diffusion coefficient, D_o from eq. (25) above, which in turn can be used to get a new estimate of the time. This new age estimate is reused in the same manner until the age converges to the final value and does not vary further. It is important to emphasize that we are only using the age as guess to get started. Any value should be appropriate, because the trial and error procedure should converge on the final value, if we are lucky. This then would be the age of the sample from the Crank analysis. There still could be a bit more added for the Region 1 problem. However, a preliminary analysis indicated that this would be quite small. The full account that reflects the present ideas is in progress.

CONCLUSION

The obsidian hydration dating (OHD) procedure has advanced with the analysis of SIMS(+) hydrogen profiling. Here the water diffusion mechanism into this natural glass is paralleled through basic mass transport phenomena and an attempt is made to use scientific approaches to explain this diffusion. The adopted basic concept of surface saturation layer in diffused media to solids has led to a new OHD method based on SIMS – the SIMS-SS (Liritzis & Diakostamatiou, 2002; Liritzis et al., 2004, 2005a, b). This phenomenological approach is reinforced with further refinement of Crank's analysis and an alternative solution to obtain the diffusion time or age of an obsidian tool. Thus a scientific approach emerges based on a trial and error calculation of age via D_o, flux derived from the SIMS hydrogen profile and a guessed age.

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REFERENCES

Anovitz, L. M, Elam, J. M, Riciputi, L. R and Cole, D. R. (2004) Isothermal time-series determination of the rate of diffusion of water in Pachuca obsidian. *Archaeometry*, 46, 2, 301-326.

Brodkey, R. S. (1995) *The Phenomena of Fluid Motions*, Dover Pubs. Inc., N.Y. corrected republication of the work by Addison-Wesley Pub. Co., Reading, Mass. (1967). (Available from Amazon.com or Barnes & Noble Pub. Cos). Brodkey Publishing is currently reprinting this book again.

Brodkey, R. S. and Hershey, H. C. (2003) *Transport Phenomena, A Unified Approach*, Brodkey Pubs. Inc., Columbus, OH, corrected republication of the work by McGraw-Hill Pub. Co., NY (1988) in two volumes. Available from Amazon.com or Barnes & Noble Pub. Cos. (Both International and Greek editions are also available).

Crank, J. (1975) *The Mathematics of Diffusion, 2nd. Ed.*, Oxford University Press, London.

Ericson, J. (1981) Exchange and production systems in California prehistory: The results of hydration and chemical characterization of obsidian sources. *BAR International Series* 110, Oxford.

Friedman, I. And Long, W. (1976) Hydration rate of obsidian. *Science*, vol.159, 347-352.

Friedman, I. and Smith. (1960) A new dating method using obsidian: Part I, the development of the method. *American Antiquity*, vol.25, 476-522.

Liritzis, I., and Diakostamatiou, M. (2002) Towards a new method of obsidian hydration dating with secondary ion mass spectrometry via a surface saturation layer approach, *Mediterranean Archaeology & Archaeometry*, vol.2, No.1, 3-20.

Liritzis, I., Diakostamatiou, M. Stevenson, C. Novak, S. Abdelrehim, I. (2004) Dating of hydrated obsidian surfaces by SIMS-SS. *J. Radioanal. Nucl. Chem.*, vol. 261, No.1, 51-60.

Liritzis, I., Ganetsos, Th. Stevenson, C.M. and Novak, S.W. (2005a) Diffusion in Solids and the Dating of Ancient Obsidian Tools. *Materials Science* (in press).

Liritzis, I., Suzuki, M. Yanashina, A. Otake, N. and Watanabe, K. (2005b) SIMS(+) profiling of Japanese obsidians. *Obsidian Monograph*, Eds. M.Suzuki, W.Ambrose and G.Summerhayes, based on the *Obsidian Summit International Workshop*, 1-7 Sept, 21004, University of Rikkyo, Japan (in press).

Mazer, J.J., Stevenson, C.M., Ebert, W. L. and Bates, J. K. (1991) The experimental hydration of obsidian as a function of relative humidity and temperature. *American Antiquity*, vol.56, 504-513.

Nogami, M. and Tomozawa, M. (1984) Diffusion of water in high silica glasses at low temperature. *Physics & Chemistry of Glasses*, 25, 82-85

Newman, S., Stolper, E. and Epstein, S. (1986) Measurement of water in rhyolitic glasses: calibration of an infrared spectroscopic technique. *American Mineralogist*, 71, 1527-1541.

Stevenson, C., Knaus, E., Mazer, J. and Bates, J. K. (1993) Homogeneity of water content in obsidian from the Coso volcanic field: implications for obsidian hydration dating. *Geoarchaeology*, vol.8, 371-384,

Stevenson, C., Mazer, J. and Scheetz, B. (1998) Laboratory obsidian hydration rates: theory, method and application. In M.Steven Shackley (ed.), *Archaeological Obsidian Studies: Method and Theory*, Plenun Press, New York, 181-204.

Stevenson, C., Liritzis, I., Diakostamatiou, M. and Novak, S.W. (2002) Investigations towards the hydration dating of Aegean obsidian. *Mediterranean Archaeology & Archaeometry*, Vol.2, No.1, 93-100.