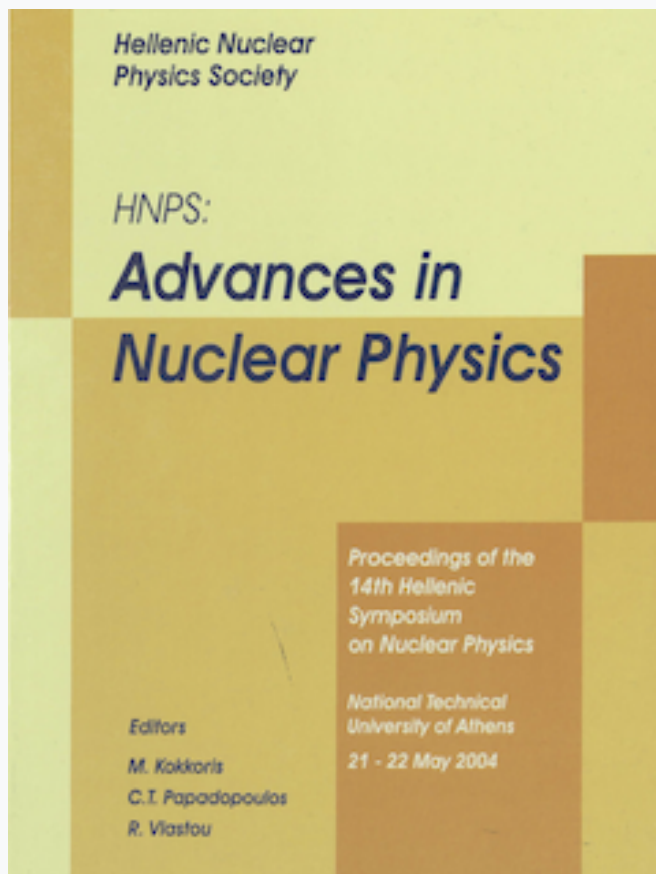


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*I. Liritzis, T. Ganetsos, N. Laskaris*

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# Dating of Obsidian Tools by Water Diffusion (SIMS-SS) with a Novel Software

Ioannis Liritzis<sup>a</sup>, Theodore Ganetsos<sup>b\*</sup> and Nikos Laskaris<sup>b</sup>

<sup>a</sup>Laboratory of Archaeometry, University of the Aegean, Dept. of Mediterranean Studies, 1 Demokratias Ave., Rhodes 85100, Greece

<sup>b</sup>TEI of Lamia, Department of Electronics, 3<sup>rd</sup> Km O.N.R. Lamia-Athens, Lamia 35100, Greece

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## Abstract

Diffusion of environmental water into the surface of obsidian tools of archaeological origin is monitored by secondary ion mass spectrometry (SIMS), which provides a H<sup>+</sup> concentration (C) versus hydration depth profile. The modeling of this diffusion process, as one-dimensional phenomena, is based on the idea that a saturated surface (SS) layer is encountered near the surface. A novel software program has been developed, using MATLAB, incorporating all numerical parameters for the dating of hydrated obsidians using the SIMS profile. This approach has been applied to several archaeological obsidians from the Aegean, Hungary, and Asia Minor and compared with samples from radiocarbon dated cultural phases where the agreement is excellent. © 2001 Elsevier Science. All rights reserved

*Keywords* : SIMS; obsidian; diffusion, dating, hydration.

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## 1. Introduction

Diffusion of water into amorphous silicates (glass) has been investigated on a theoretical and experimental basis (Doremus, 1969, 1979, 1995; Crank, 1975; Drury et al., 1962; Behrens and Nowak, 1997; Nogami and Tomozawa, 1984; Stevenson and Scheetz, 1989; Stevenson et al., 1998). Amorphous rhyolitic glass, or obsidian, has been studied for dating purposes based upon the rate of water diffusion into the surface. The traditional age equation ( $X^2 = kt$ , where X=hydration depth, k=diffusion rate, t = diffusion age) is not highly reliable, since k depends on short-term temperature measurements (Friedman and Smith, 1960). Other problematic areas include hydration depth measurement by optical microscopy that has an unacceptable error of +/-0.25  $\mu\text{m}$ .

Surface analytical techniques have been used to study ancient materials since the 1970s and secondary ion mass spectrometry (SIMS) is now well established as a surface technique, which provides elemental data and allows depth profiling, mapping or imaging [1-2]. The depth and shape of the hydrogen diffusion profile on ancient obsidian tools has been determined by SIMS (Anovitz

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\* Corresponding author. Tel.: +0-000-000-0000 ; fax: +0-000-000-0000 ; e-mail: author@institute.xxx .

et al. 1999; Riciputi et al. 2002; Liritzis and Diakostamatiou 2002; Liritzis et al. 2004; Stevenson et al. 2004). The obsidian hydration dating (OHD) method is based upon modeling the rate of water diffusion into the natural glass surface. A variety of strategies have been developed over the years to calibrate the movement of ambient water into glass. Many of these approaches have developed procedures for controlling the chemical composition of the glass and modeling the environmental history of the artifact context (e.g. temperature, humidity)[Friedman and Long 1976; Ambrose 1984; Mazer et al. 1991; Friedman et al. 1994; Stevenson et al. 1998, 2002]. However, the development of calibrations to compensate the variation in external variables has proven to be difficult. This has been the major impediment to making OHD a fully chronometric dating method comparable to radiocarbon dating.

In the past few years we have developed alternative solutions to the OHD age equation based upon the concentration-dependent diffusion water profile by modeling the concentration-to-depth sigmoid shape of the diffused water as determined by SIMS. In this procedure, the hydrogen profile incorporates all unknown environmental parameters, especially temperature. Thus, by modeling the H+ versus hydration depth (X) profile, an age equation can be obtained. This is based on the observation that in the course of water diffusion into obsidian a surface saturation layer forms where water concentration remains constant. The location of this plateau layer is achieved conducting successive regressions starting from the beginning of the shape to the point where the slope significantly changes. Statistically, this region is determined in the change of slopes from near zero to negative values. The exclusion of some initial points to achieve the best fit with the first half of S-curve is justified because of the near surface disturbances due to sputtering conditions and/or variable environmental effects (Stevenson et al. 2002; Brodkey et al. 2003).

## 2. SIMS-SS Dating approach

In diffusion dating applications, it is essential to establish the time over which diffusion has occurred. To do this, a time-dependent analysis is required. The mathematical theory of diffusion in isotropic substances is based on the observation that the rate of transfer of the diffusing substance, through a unit area, is proportional to the concentration gradient measured normal to the sectioned sample. It is expressed by the equation:

$$F_x = (N_A / A) = -D(\partial C_A / \partial x) \quad (1)$$

Here  $(N_A / A)$  is the moles of species A being transferred per unit time per unit area. Thus  $N_A/A=F_x$  is the rate of transfer of water moles per unit area ( $\text{kmol.m}^{-2}\text{s}^{-1}$ ) along x-direction, C is the concentration gradient of diffusing substance (mass per unit volume) acting as the driving force, x is the distance coordinate measured normal to the section or surface, and the proportionality constant D is called the diffusion coefficient ( $\text{m}^2.\text{s}^{-1}$ ) which up to the present is

empirically determined. The negative sign arises because the diffusion occurs in the direction opposite to that of increasing concentration.

One dimensional diffusion through an obsidian surface, where the diffusion coefficient  $D = \text{constant}$ , is commonly referred to as Fick's 2<sup>nd</sup> law of diffusion.

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

However, in concentration dependent diffusion,  $D$  is not constant during the hydration process but depends on changes in  $C$  over time. A family of curves that relates  $C$ -to- $X$  for an exponential diffusion coefficient during sorption is shown in Figure 2 and represents the calculated results for variable  $D$  for non-steady-state conditions (non-dimensional plot where  $k$ -values presented as  $e^k$  are derived from a family curves (based on Crank, 1975).

These family curves are similar in shape with the SIMS profiles obtained from obsidian surfaces. From numerical calculations and experiments, it follows the exponential dependence of the  $C$  from  $D$ . In our case we obtain:

$$D = D_s \exp(kC/C_s) = D_s \exp[\beta(C-C_s)] \quad (3)$$

where  $k$  is a constant,  $D_s$  the diffusion coefficient for  $C=C_s$  the concentration at Surface Saturation layer (see below), and  $\beta$  a constant. Based upon Crank's (1975) numerical solutions of diffusion, and Boltzmann's (1894) transformation, as well as *initial* ( $C=C_0=C_i$ , initial or intrinsic water concentration, for  $x>0$  and diffusion time  $t=0$ ) and *boundary* ( $C=C_s$ , for  $x=0$  and  $t>0$ ) conditions, auxiliary variables are introduced and mathematical processing transforms eq.(1) to

$$-D_s(\partial C / \partial x)_{x=0} = -1/2(D_s/t)^{1/2}(C_i-C_s)(dc/dy_s)_{y_s=0} \quad (4)$$

which relates the flux across obsidian's surface at  $x=0$  with the time the flux has occurred, the  $C_s$ ,  $C_i$  and  $D_s$  for  $C_s$ . With further elaboration of auxiliary variables and fitting polynomial, eq. (4) leads to the age equation:

$$T = [(C_i-C_s)^2 (1.128/(1-0.177kC_i/C_s)^2)] / [4D_s(b \exp(a))^2] \quad (5)$$

Where,  $C_i$  and  $C_s$  (both in gram moles of water per  $\text{cm}^2$ ), as well as  $X_s$  (in m) are measured parameters, while  $D_s$  (=flux/gradient,) and  $k$  are calculated, and (a) and (b) are constant coefficients.

According to Fick's 1<sup>st</sup> law of diffusion  $D_s$  is the inverse of gradient  $\times 10E-11$  years, assuming the flux is constant and taken as unity. The gradient  $dC/dx$  or the tangent at a certain point of the fitted curve or from another view, the rate of change, is attributed to the diffusion coefficient, where,

$$C = \exp(a + bx + cx^2 + dx^3) \quad (6)$$

In fact, the total flux would be the integration over the entire curve. This would be 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 and indeed this varies with temperature. Thus, the integration will need to be done in small increments of depth that represent periods of time where the assumption of a constant flux for that small region might be satisfactory. The diffusion

coefficient at any particular moment is expressed by the first derivative of the hydrogen profile. This is the apparent hydration rate.

This diffusion dating approach has been named SIMS-SS. In summary, the steps taken towards SIMS-SS dating include: 1) define non-dimensional plot of the C versus X profile, 2) define k-value from plots, 3) define polynomial fitting of the C vs. X profile, usually 3<sup>rd</sup> or 4<sup>th</sup> order, 4) define SS layer from linear regressions and thus determine Cs and Xs, and, 5) apply age equation. The procedure is processed via a software using MATLAB (Liritzis et al. 2004).

### 3. The structure of the program in MATLAB

In this part we will examine the structure of the software which appears in the following plan:

1. determining age
  - 1.1 transformation
  - 1.2 chronology
    - 1.2.1 Cint
    - 1.2.2 Csur
    - 1.2.3 Kdata
    - 1.2.4 STDEV

At the beginning, in order to change the data in the right size we use function transformation that is drawn up as follows:

$$[n,x]=\text{Transformation}(x,c)$$

which has as an entry the depth X multiplied with  $10^{-4}$  in order to change it from  $\mu\text{m}$  to cm, and the second entry is concentration C that is divided by  $2 \cdot 6.023 \cdot (10^{23})$  in order to change from atoms/cc to  $\text{g mol/cc}$ .

After the transformation we are ready to process the data presented in two tables, n and x, corresponding to depth and concentration.

These two tables become entries in function chronology that make all the essential calculations for defining the age and standard deviation. Chronology that is drawn up as follows

$$[C_{\text{sur}}, C_{\text{int}}, X_{\text{sur}}, \text{slope}, \text{dc dy}_s, \text{dc dx}, \text{dsurf in}, T, \text{SD}] = \text{chronology}(n, x)$$

and have as entry the depth and the concentration it calls in the beginning two other function the Cint and Csur. The Cint is drawn up as

$$[C_{\text{int}}] = C_{\text{int}}(x)$$

and calculate the initial concentration from the last values of data of SIMS profile. The function Csur that is drawn up

$$[S, SS, C_{\text{sur}}, X_{\text{sur}}, \text{slope}, \text{STDVc}, \text{STDVx}] = C_{\text{sur}}(n, x)$$

it is the most important function as it is the one that calculates the Csur and the Xsur. At the start, it fixes the format of numbers in long e thus the numbers have more decimal digits hence also bigger precision. Then the computer asks which

value of concentration will be the first in the calculation of the slope and in a second question for how many more (figure 1).

Which value of concentration will be the first in the calculation of the slope. (ex. the 35th value):  
And for how many more:  
Do you agree with the values? y or n :

Figure 1

Here is given the possibility in the user after it imports the two numbers to see with the help of a plot were the points of beginning and end are precisely and judge if he made the right choice (figure 2)<sup>1</sup>.

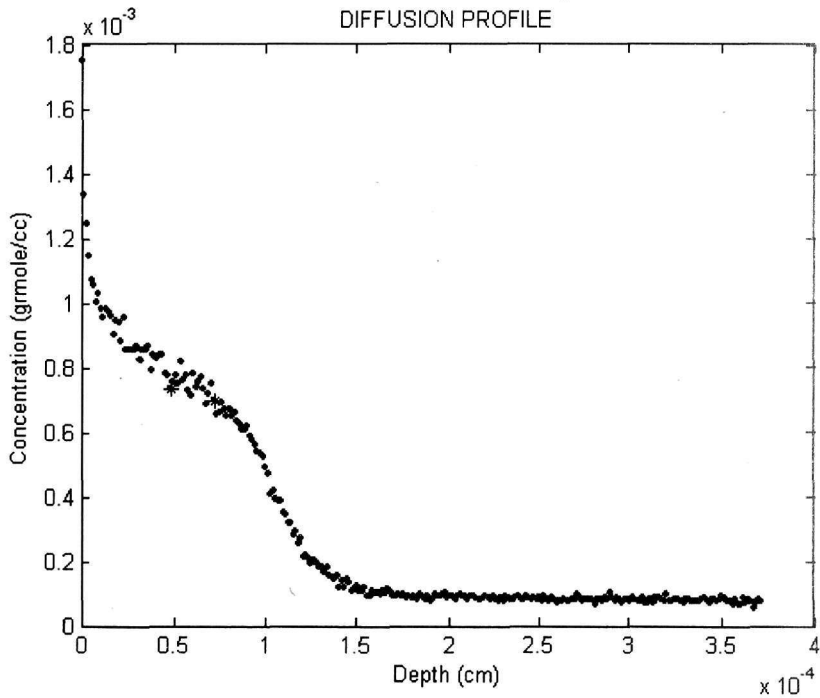


Figure 2

In the case where it judges that he has not made right choice computer gives the possibility, via a question for whether he agrees with the numbers that imported, to changes them.

When the user decides the interval for which the calculation of  $C_{sur}$  and  $X_{sur}$  are made the computer undertakes the task to calculate the slope between the each point and to keep in his memory the last positive numbers, before the slope change finally, and also the corresponding values of concentration and their depth.

<sup>1</sup> Figures 1 up to figure 6 are taken from the following demonstration.

Finding the values of depth and concentration of each number it calculates the concentration  $C_{sur}$ , the  $X_{sur}$ , the table of slopes, and standard deviation STDV of concentration (x) and depth (c) while it returns to S and SS that is the two final numbers that are imported from the user in the before mentioned questions. A user that wants to find only the slope, the  $C_{ur}$  and the  $X_{sur}$  can run just the function  $C_{sur}$  and for this the two exits S and SS are useless, that however has vital importance for the operation of dating. In the end of calculations, the  $C_{sur}$  apart from the desirable results provides also a graph (Figure 3) that is analytically the region for which the calculation of  $C_{sur}$  and  $X_{sur}$  is made. Thus the user can have better view of the region, judge with care and possibly select different points (first and final) for the calculations..

The implementations of subprograms Cint and Csur follow in the dating calculation. In the beginning after it draws diffusion profile with the start and stop marks (Figure 4) it asks the user for the values of coefficients a, b, c, and d, of a third degree polynomial ( $C = \exp(a + bx + cx^2 + dx^3)$ ) that fit with the data of SIMS profile. (Figure 5).

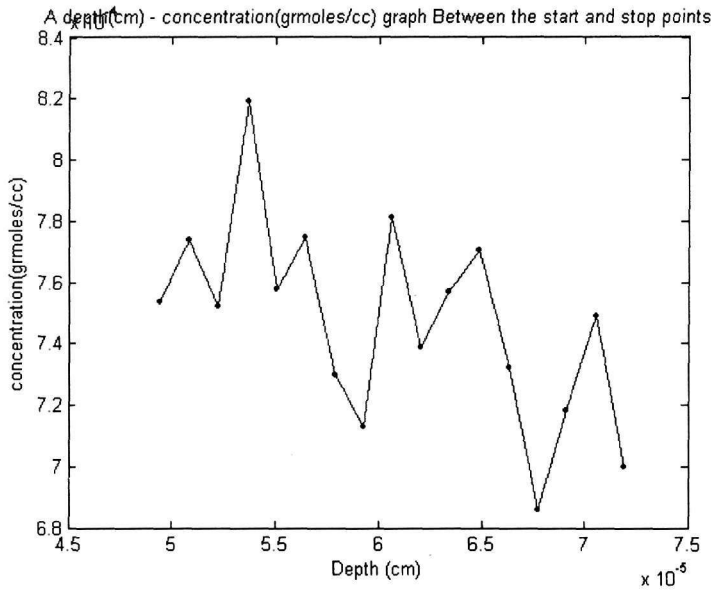


Figure 3

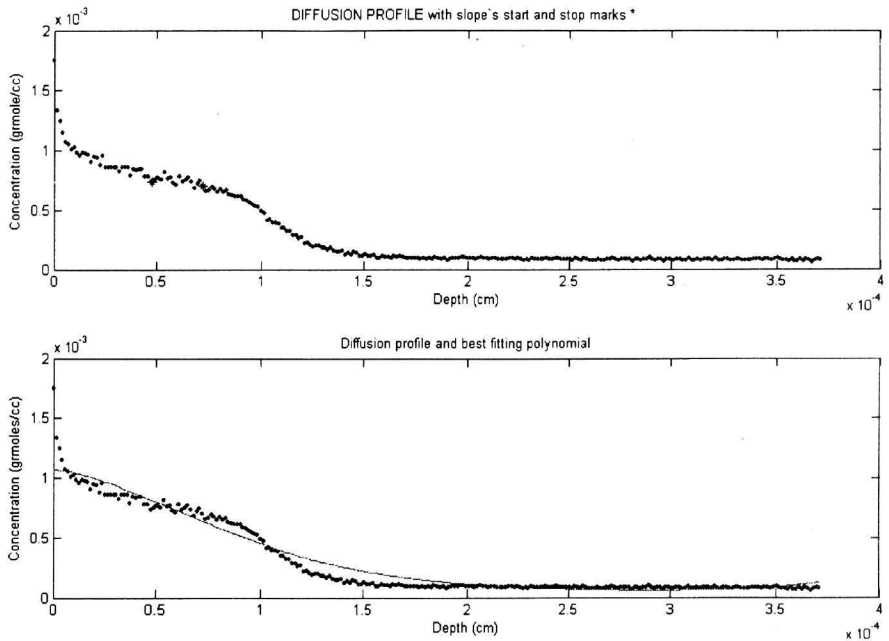


Figure 4

Enter the value of coefficient a:  
 Enter the value of coefficient b:  
 Enter the value of coefficient c:  
 Enter the value of coefficient d:

Figure 5

When the user finishes with that one more graph is made that is the data and the best fitting polynomial so that a comparison between them is made. Then the software calls the file of K-data that contains grouped the data of Crank's curves and prints out in the screen the last graph (picture 6) that gives the possibility in the user to see which Crank curve fits better with the data and thus answers in the last question that the program makes for  $e^{-k}$ . After user's answer to this, the program calculates  $dc/dx$ ,  $D_{sur}$ ,  $dc/dy_s$  and age. Before printing the data it calls the file STDEV in which with the use of STDV of  $x$  and  $c$  calculate the standard deviation of the age. Having done all the calculations, the program exports the data with the following form and order:

Csur  $\sigma$  gmoleH<sub>2</sub>O/cc  
 Cint  $\sigma$  gmoleH<sub>2</sub>O/cc  
 Xsur  $\sigma$  cm



$D_s \approx 6 \text{ cm}^2/\text{year}$

K

The age of the sample is (in years before today):

The Standard Deviation in years is    and    OR    % and    %

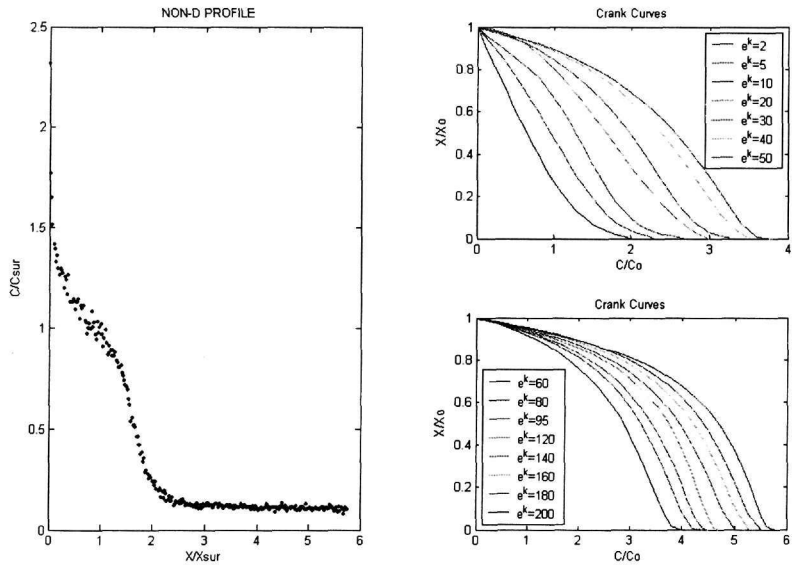


Figure 6

#### 4. Demonstration

Now we will see a demonstration of the program in Matlab using the SIMS data of Stofilas. For the beginning we have to clear the workspace using the command “clear” and then the command window with the command “clc”.

After that we open the Matlab m-editor and create an m-file with the data of depth and concentration. This file should have the structure as it shown in Figure 7.

```

x=[...
...
...];

c=[...
...
...];

```

Figure 7

Now we call the file strofilas\_data in the command prompt as below

```
>>strofilas_data;
```

in order to "charge" the two tables in the memory.

After that in the command prompt of Matlab we write the function Transformation in its right form as follows.

```
>> [n,x]=Transformation(x,c);
```

Now the matrix (n) of depth in cm and the matrix (x) of concentration in grmol/cc are available for the calculation of the age.

Finally we enter the function chronology in the right form (as drawn below) and the program starts calculation and requires a few more data.

```
>>[Csur,Cint,Xsur,slope,dcdys,dcdx,dsurfin,T,SD]=chronology (n,x);
```

The first question (figure 8) is about the value of concentration which will be the first in the calculation of the slope. Here we answer 35 which means the 35<sup>th</sup> value.

Which value of concentration will be the first in the calculation of the slope. (ex. the 35th value):	35
And for how many still: 17	
Do you agree with the values? y or n :	

Figure 8

The second question ask how many values and we answer 17 which means from the 35th up to 52th (35+17).

After we enter the two values, Matlab plots a graph with the data and the start and stop points marked (Figure 9) and ask us if we agree with the values we have just entered.

If we agree we answer "y" the program begins the calculations but if we don't agree we answer "n" and the program re-ask the questions in figure 8.

After we answer "y" and the calculations of the slope finish, Matlab plot in a half of a figure (figure 10) the data and the start and stop marks. The first figure now

has an analytical view of the region between the start and stop marks so the user has the opportunity to see and judge his answer (figure 11).

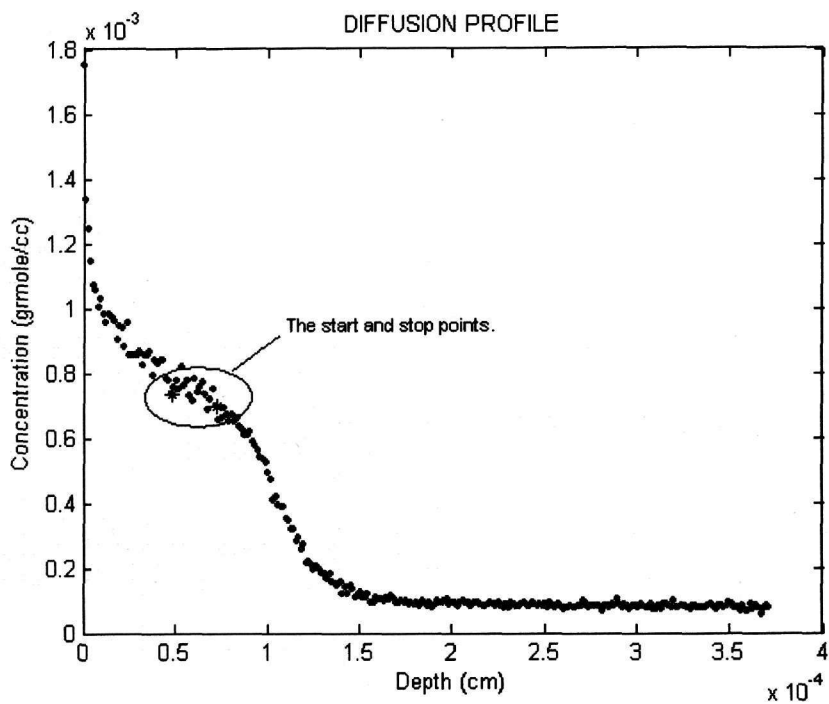


Figure 9

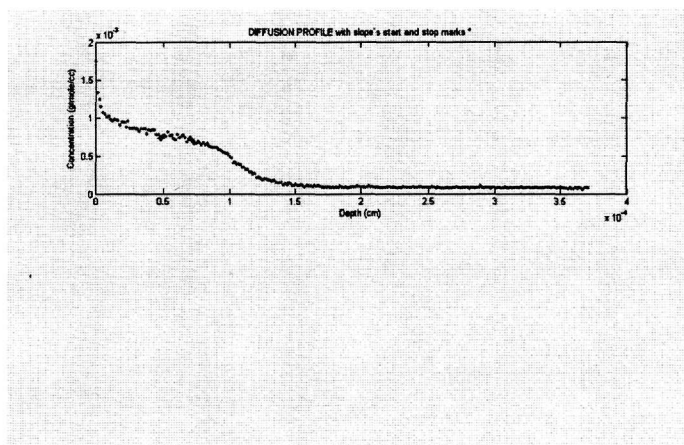
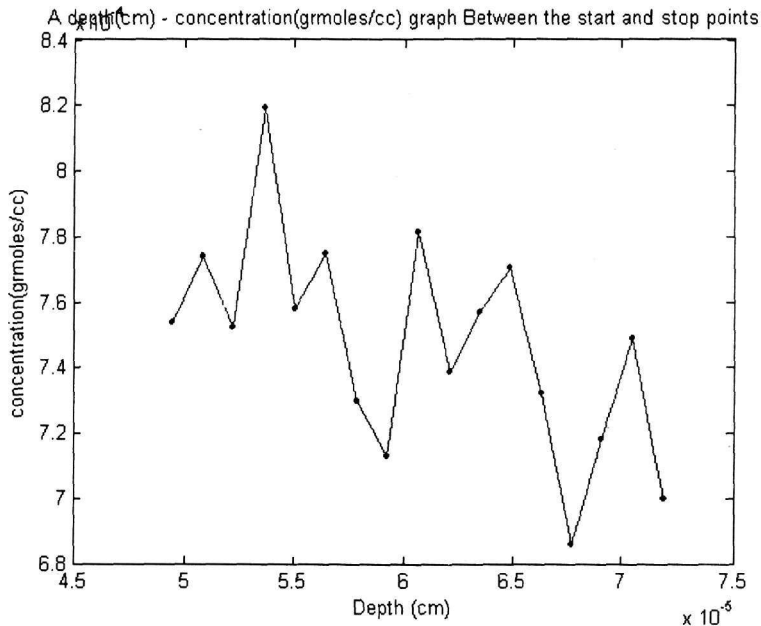


Figure 10



In the command window, Matlab ask for the values of coefficients a, b, c, d here we give the follow answers:

Enter the value of coefficient a: -6.8378919  
 Enter the value of coefficient b: -1821.9224  
 Enter the value of coefficient c: -90018537  
 Enter the value of coefficient d: 2.14092E+11

After the declaration of coefficients we can see the other half graph of picture 10 which is the data and the best fitting polynomial with the above coefficients (picture12).

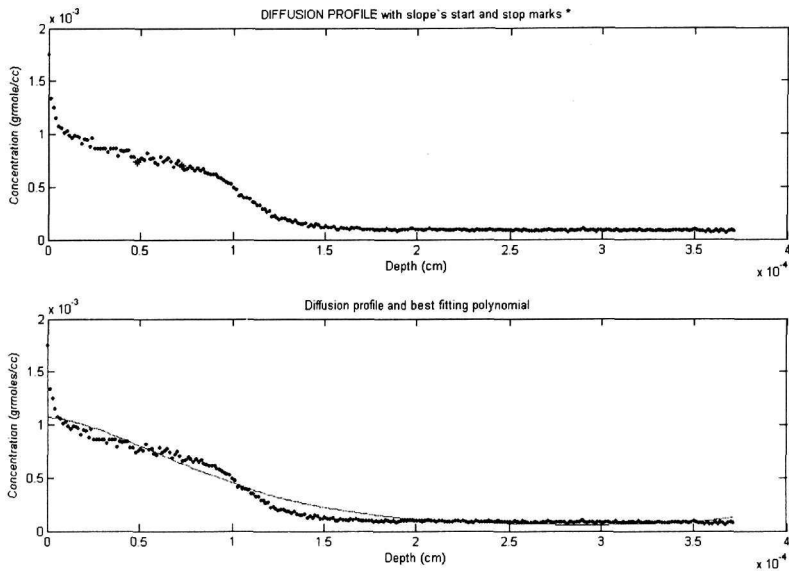


Figure 12

Matlab also plot another figure with the data and the curves of crank (figure 13) and ask the user to declare the value of  $e^k$ . After a careful examination of the figure we decide that the curve of  $e^k=10$  fit to the data so in the below question we answer 10. Enter a value for  $e^k = 10$

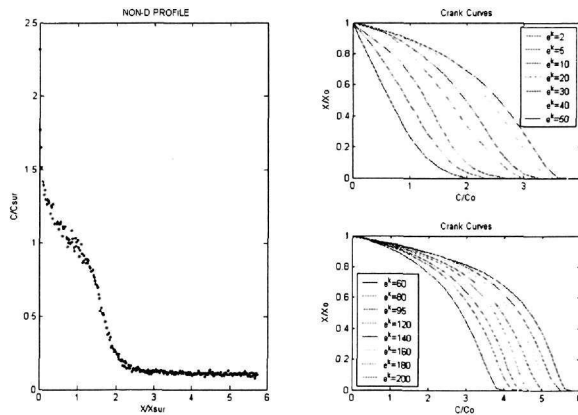


Figure 13

After that the program finishes and prints in the screen the results as they appear at the figure 14 so we can see that the result for the age is 5594.2395 years (any

decimal digit is without any meaning) before today and also it opens the matrix of slope (figure 15).

Results  
 -----  
 Csur= 7.555758e-004 grmoleH2O/cc  
 Cint= 7.653532e-005 grmoleH2O/cc  
 Xsur= 6.454117e-005 cm  
 Ds= 7.472837e-012 cm^2/year  
 K= 2.302585  
 The age of the sample is (in years before today): 5594.239551  
 The Standard Deviation in years is 65.072669 and -35.062063 OR 1.163208% and -0.626753%

Figure 14

0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
14.181	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
-0.5924	-15.361	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
12.462	16.238	47.069	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
38.397	14.177	2.088	-43.723	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
25.146	0.53151	0.41327	-15.944	11.809	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
-16.455	-43.542	-6.38	-17.955	-10.038	-31.906	0	0	0	0	0	0	0	0	0	0	0	0	0	0
-42.263	-68.986	-90.975	-17.13	-12.758	-21.862	-11.817	0	0	0	0	0	0	0	0	0	0	0	0	0
-19.199	-33.476	-39.036	-75.282	-10.636	0.23634	18.317	48.45	0	0	0	0	0	0	0	0	0	0	0	0
-22.842	-34.755	-39.244	-65.193	-18.736	-14.181	67.917	91.503	-30.112	0	0	0	0	0	0	0	0	0	0	0
-17.883	-26.422	-26.061	-44.728	0.58974	0.1687	57.252	63.777	-85.869	12.989	0	0	0	0	0	0	0	0	0	0
-1.07	-1.638	-15.883	-25.895	0.80364	1.73	59.576	64.381	-1.006	11.226	94.537	0	0	0	0	0	0	0	0	0
-14.964	-20.408	-20.969	-29.717	-0.41367	-0.028336	24.889	16.531	-47.266	-0.47425	-88.618	-27.16	0	0	0	0	0	0	0	0
-26.688	-33.075	-36.321	-45.487	-28.177	-30.523	-19.202	-37.757	-98.399	-93.343	-17.957	-30.123	-33.088	0	0	0	0	0	0	0
-27.849	-3.361	-36.477	-43.975	-29.538	-31.687	-23.139	-38.048	-81.439	-72.414	-11.579	-14.474	-50.223	23.043	0	0	0	0	0	0
-23.204	-2.749	-29.316	-34.405	-20.779	-20.944	-11.959	-2.107	-49.367	-33.756	-49.787	-40.757	56.498	22.444	21.846	0	0	0	0	0
-26.395	-30.544	31.688	-37.365	-26.291	-27.347	-21.159	-30.298	-54.346	-43.882	-58.226	-55.019	-0.11737	51.986	-64.937	-34.86	0	0	0	0

Figure 15

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