ISOTHERMAL TIME-SERIES DETERMINATION OF THE RATE OF DIFFUSION OF WATER IN PACHUCA OBSIDIAN*

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Friedman and Smith's (1960) article introducing an exciting, potentially precise and inexpensive method of dating obsidian artefacts has thus far failed to reach its potential. Numerous efforts to refine, improve and even redevelop the method since that time have similarly failed to achieve the original promise. Only within the last eight years have significant improvements been made, due to both improved analytical techniques and a better understanding of the hydration process. However, most of our mechanistic under-standing of the interaction of water with rhyolitic glass is based on experiments performed on melts and glasses at temperatures above their glass transitions, conditions inappropriate for investigation of near-surface environmental conditions. Unfortunately, studies detailing the temporal evolution of the diffusion profile at low temperatures are rare, and few useful data are available on the low-temperature diffusive hydration of silicate glasses.

This paper presents data on the experimental hydration of obsidian from the Pachuca source (a.k.a. Sierra de las Navajas, Basin of Mexico) at 75℃ for times ranging from 3 to 562 days, and compares these results with data for samples obtained from a stratigraphic excavation of the Chalco site in the Basin of Mexico. Samples have been analysed using secondary ion mass spectrometry (SIMS) to provide concentration/depth data. While 75℃ is still significantly above the temperatures at which archaeological obsidians hydrate, it is well below the glass transition temperature (approx. 400℃) and thus processes are likely to be similar to those that occur in nature, but fast enough to be observed over a laboratory timescale. The results demonstrate that a simple square-root-of-time model of the evolution of the diffusion profile is not adequate to describe the diffusion process, as measured diffusion profiles exhibit the effects of concentration- and time-dependent, non-Fickian diffusion. With progressive hydration, characteristic diffusion coefficients first decrease, then increase with time. Surface concentration increases with time, but an intermediate plateau is observed in its time evolution that is consistent with results obtained from the suite of Chalco samples. Both of these effects have been observed during diffusion in glassy polymer systems and are associated with the build-up and relaxation of self-stress caused by the influx of diffusing material.

KEYWORDS: OBSIDIAN, DIFFUSION, EXPERIMENTS, DATING, SIMS, CHALCO, BOLTZMANN–MATANO, RELAXATION, POLYMER, CONCENTRATION-DEPENDENCE, TIME-DEPENDENCE

INTRODUCTION

The concept of obsidian hydration dating (OHD), originally proposed by Friedman and co-workers (Friedman and Smith 1960; Friedman *et al.* 1966; Friedman and Long 1976), holds significant promise for dating of both archaeological and geological materials and as a natural analogue for analysis of the long-term stability of glasses proposed for use for storage of radioactive wastes. Unfortunately, numerous reports (Braswell 1992; Braswell *et al.* 1996; Nichols and Charlton 1996; Ridings 1996; Anovitz *et al.* 1999) indicate that the standard approach to OHD is generally unreliable, yielding both significant scatter and mean age values that disagree with results from other, well-established techniques.

In our first discussion of this problem (Anovitz *et al.* 1999), we suggested that the difficulties observed in attempts to apply standard OHD are caused by inadequate analytical and mathematical approaches used in standard applications. We showed that optical measurement of the position of the diffusion 'front' yields an unreliable and misleading estimate of the depth of hydration, both because the 'front' is not actually a sharp boundary and because of uncertainties in the optical technique itself. We then demonstrated that the actual shape of the diffusion profile was far more complex than implied by the 'square-root-of-time' law typically used to obtain chronometric information, which is based on the equation:

$$x = Dt^{1/2} \tag{1}$$

where x is the depth of the hydration 'front', t is time and D is the diffusion coefficient. We proposed an alternative approach called ODDSIMS, for Obsidian Diffusion Dating using Secondary Ion Mass Spectrometry. This approach addressed the analytical problems inherent in the standard optical OHD approach by using SIMS to obtain a concentration versus depth profile of the hydration rim, and employing a mathematical model based on a concentration-dependent diffusion coefficient to model the growth of that rim with time. This paper did not, however, provide the kind of time-series data needed to evaluate the temporal evolution of the diffusion profile.

Our second paper in this series (Riciputi *et al.* 2002) examined the temporal evolution of the diffusion profile, and evaluated the applicability of the ODDSIMS approach by applying it to a series of Pachuca obsidian samples from the Chalco site in the Basin of Mexico for which well-associated ^{14}C dates were available (range 600–1500 CE). Anovitz *et al.* (1999) showed that the 'square-root-of-time' model did not appear to be mathematically reasonable, but noted that some power law might be suitable for dating purposes. Several authors have continued to employ and defend the square-root-of-time approach (e.g., Torrence and Stevenson 2000; Hull 2001), but analysis by Riciputi *et al.* (2002) of the Chalco data showed that, when the diffusion profile is measured using SIMS, the apparent value of D calculated from equation (1) increased with time. Thus, equation (1) cannot be a suitable chronometric equation. This result is consistent with the results of Meighan and co-workers (Meighan *et al.* 1968; Meighan and Haynes 1970; Meighan 1983; Meighan and Scalise 1988), who suggested that rim growth shifted towards linear with increasing time.

The Chalco data also showed that the surface concentration of hydrogen was not constant, but increased with time. Because of the complexity of this situation, a finite difference model of the hydration process was presented. This model was based on a concentration-dependent diffusion coefficient and a time-dependent surface concentration, and yielded dates with a precision equal to that of the ^{14}C results used to calibrate the model. Unfortunately, the lack of archaeological samples younger than 1500 CE does not allow us to fully understand the evolution of the hydration profile, as shorter-term processes are unconstrained. In addition, no data on the effects of temperature could be derived from these data.

Despite the archaeological evidence that, at least in some cases, a square-root-of-time approach is inappropriate, this conclusion remains insufficiently substantiated because of the imprecision and uncertainties associated with the archaeological samples. Carefully controlled experiments are, therefore, needed. Although Friedman *et al*. (1997; see also Liritzis and Diakostamatiou 2002) noted that, to date, 'no published experimental data suggests other than a square root rate', the available experimental data are insufficient to test this hypothesis.

Riciputi *et al*. (2002) also made another important observation about obsidian hydration. We showed that, while the hydrogen content of the glass dramatically increased in the hydrated rim, the oxygen content did not. This implied that it is hydrogen rather than water that enters the glass, and that the diffusion mechanisms may be fundamentally different from those usually assumed to occur. While the mechanisms of such a 'hydrogenation' process are unclear, and this result requires verification, this provides an important constraint for future micro-structural diffusion models. References in this paper to diffusion of 'water' into the glass should be read with this in mind.

In this paper, we present the results of an isothermal, multi-temporal experimental study of the hydration of a sample of Pachuca obsidian, and compare them to those obtained from the naturally hydrated Chalco samples (Riciputi *et al*. 2002). The purpose of this paper is to evaluate, from both an experimental and an archaeological perspective, whether the square-root-of-time model is appropriate and to assess the importance of more complex parameters. These experiments were performed at 75°C for times up to 562 days, and longer experiments are still ongoing. This temperature was chosen so as to be as close as possible to temperatures of archaeochronometric interest (approximately 0–40°C, with typical averages near 20°C), while still permitting hydration mechanisms to be observed over a feasible laboratory time-scale. The temperature of these experiments is well below the obsidian glass transition temperature (see discussion below), and thus the hydration mechanisms are likely to be similar to those occurring under archaeological conditions. Thus the 75°C data should be a good proxy, mechanistically, for lower-temperature diffusion. Comparison between our experimental results and data from the Chalco samples (Riciputi *et al*. 2002) can provide a preliminary temperature-dependence and an opportunity to look at both long- and short-term hydration processes. Additional experiments are also ongoing at 30, 50, 100 and 150°C that will further clarify the effect of temperature.

EXPERIMENTAL TECHNIQUE

Experiments were performed using reaction vessels fabricated by minor modification of off-the-shelf parts. A schematic diagram of these vessels is shown in Figure 1, and photographs are shown in Figure 2. These were built from VCR-type vacuum fittings, and sealed using a Cu washer. They are relatively inexpensive, require only minor modification, and provide good long-term seals at pressures and temperatures up to 213 bars and 538°C (based on the rating of VCR-type fittings, the temperature depending on the gasket type). The design is cost-effective, and allows a reasonably large number of vessels to be obtained (we currently have 40). It also provides space for simultaneous hydration of a number of samples, and is completely sealed, avoiding problems with water loss associated with designs that require an external hole from which to hang a support (cf., Davis 1994). For long-term runs a given vessel can be quenched, opened and one block and/or powder sample removed for analysis. The seals can then be re-polished and the vessel cleaned and reassembled with the remaining samples and replacements to continue the experiment.
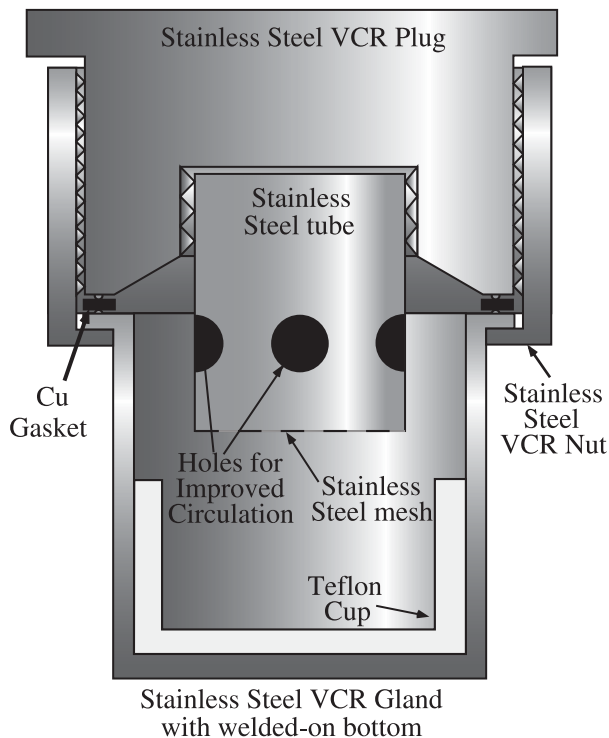
Figure 1 *A schematic diagram of the experimental vessels.*

To prepare the vessels for an experiment, the seals were polished using green rouge on a 6 inch cotton buffing wheel mounted in a high-speed buffer. The vessels were then washed with water, acetone and ethanol, and baked dry at 150°C. Prior to assembly, water is placed in a Teflon cup seated in the vessel bottom. This prevents direct contact between the steel and the liquid phase during the experiment and limits steel corrosion. Sufficient water is placed in the vessel to form a saturated two-phase liquid–vapour system at the temperature of interest, but the amount added is small enough that the samples on the mesh will be suspended in the vapour phase, above the liquid. As has been noted previously (cf., Stevenson *et al.* 1989; Mazur *et al.* 1991), under these conditions the chemical potential of water at the surface of the glass remains identical to its value in the liquid, but the solubility of the glass in the vapour is several orders of magnitude less than in the liquid (for a summary, see Cohen 1980, 78; also Lindsay 1989, fig. 7-30). Thus, this experimental design allows diffusion to be studied independently from dissolution. The samples are then placed on the mesh, and the vessel sealed.

All experiments were performed using obsidian from the Pachuca source, located in the Sierra Madre Oriental, north-east of the Basin of Mexico. The geology of the Pachuca source and the chemistry of the obsidian have been summarized by Cobean *et al.* (1991), who note that this 'was probably the most important obsidian quarry in northern Mesoamerica during Prehispanic times', probably because of the unique green colour of the obsidian. The outcrops cover a large area near the town of Huasca, Hidalgo, and most of the mining was on the southern slopes of a mountain called Cruz del Milagro. Optically the glass is green, and shows a slight
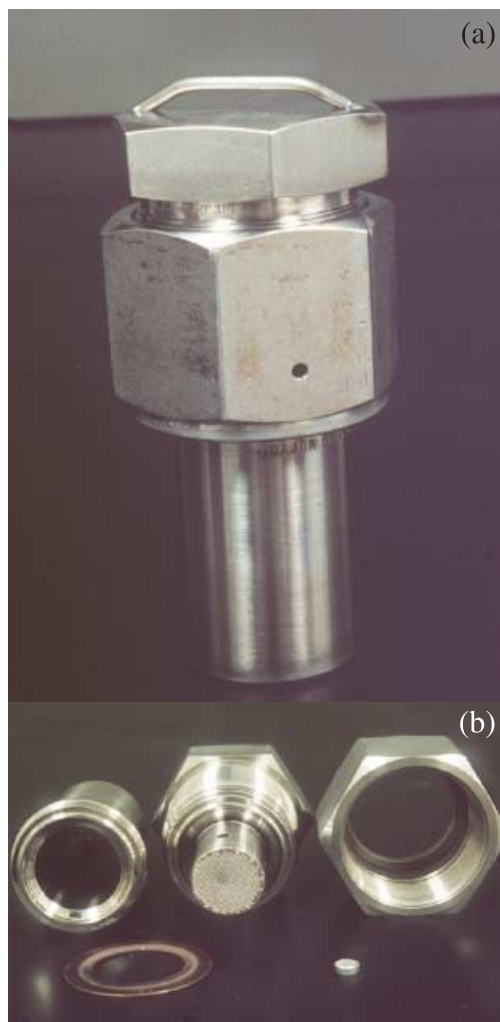
Figure 2   *Photographs of the experimental vessels: (a) the assembled vessel; (b) the individual parts. The scales are slightly different in the two photographs, but the plug that makes up the top of the vessel is 4.1 cm across, flat to flat.*

schiller in some directions due to microscopic vacuoles. The materials used for our experiments are largely free of macroscopic ash inclusions, although a few exist that were avoided during sample selection. Trace element data show that Pachuca obsidian is relatively rich in Mn, Zr, Hf and Cl, and relatively low in Ba relative to many other Mesoamerican obsidians.

In our experiments, two types of samples were placed in each vessel: blocks of Pachuca obsidian 2–3 mm on a side polished on two parallel faces, and small aluminium cups containing approximately 50 mg of finely powdered Pachuca obsidian. The latter was stored in a dessicator prior to use, and was intended for use in diffuse reflectance infrared analyses that will be discussed elsewhere. The water used was a distilled, deionized water obtained from a Barnstead NANOpure ion exchange ultrapure water system, with a conductivity of approximately 18.3 MΩ, prepared initially for isotopic exchange studies (water W1; Horita *et al*. 2002).

To provide the necessary heating for these experiments, all of the 75°C runs reported here were performed in a water bath. Inside each bath, vessels were placed in a 1.25 inch hole in a 0.25 inch thick polycarbonate plate supported on PVC legs to prevent tipping. Water baths provide rapid heating, good temperature control and a large thermal mass, all of which lead to good thermal stability (± < 1°C, usually ± 0.01°C). Water baths also provide a faster sample heating rate than air furnaces, and good thermal uniformity. To minimize evaporation, the ethylene glycol/water mixture typically used in such baths was replaced with mineral oil.

SECONDARY ION MASS SPECTROMETRY (SIMS) TECHNIQUES

For analysis of diffusion rates and processes in any material of interest, data on the concentration of a given element with depth are essential (Crank 1975; Doremus 1975, 1979, 1994; Lasaga 1983; Kirkaldy and Young 1987; Chakraborty and Ganguly 1991; Morioka and Nasagawa 1991; Anovitz *et al*. 1999; Riciputi *et al*. 2002). Diffusional processes are best quantified by measuring and modelling the evolution of these depth profiles as a function of time. In this project, as in our previous studies, we have used SIMS to examine the rims formed during obsidian hydration. The details of this technique and the specific procedures used in our laboratory have been presented elsewhere (Anovitz *et al*. 1999; Riciputi *et al*. 2002), and are only summarized below.

SIMS provides an excellent method of obtaining detailed, high-precision information on the concentration of water as a function of depth, and therefore is an ideal technique for investigating the process of obsidian hydration. When utilized in depth-profiling mode, and fully optimized, SIMS can resolve concentration variations occurring over a few nanometres for a wide variety of elements, over depths ranging from a few nanometres to several microns (see various papers cited in Lareau and Gillen 1998; Larocque and Cabri 1998; McKibben and Riciputi 1998; Valley *et al*. 1998).

Depth-profiles for this project were obtained using a modified Cameca 4f ion microprobe (a doubly focusing magnetic-sector mass spectrometer). To prepare samples for analysis, five to six holes were drilled in 1 inch diameter, 3/8 inch thick aluminium discs. Epoxy was used to mount the samples in these holes with the hydrated surface exposed. A sample of freshly polished glass was also mounted in each disc to provide an internal standard. The finished discs were coated with a thin layer of gold to provide surface conductivity. To minimize adsorbed water, samples were baked at 45°C for 12–18 h and then put under vacuum a minimum of 12 h before analysis. Tests of the effects of this heating process and the high-vacuum SIMS environment demonstrated that neither had a significant deleterious effect on the measured profile (Riciputi *et al*. 2002).

For these analyses, the primary beam consisted of mass-selected, negatively charged, ^{16}O primary ions, accelerated at 12.5 keV. The beam had a diameter of ~50 μm and a current of ~130 nA, and was rastered over an area of 150×150 μm to produce a well-shaped (roughly square) crater with a flat bottom. Only ions from the central 33 μm of this crater were transmitted through the secondary mass spectrometer for analysis. Analyses are reported here as ratios of raw counts of ^{1}H to ^{30}Si. Crater depths were measured using a Tencor Alpha-Step 200 profilometer. The craters were very regular in shape, with wide, flat bottoms, indicating that depth resolution was optimized. Repeated depth measurement on craters sputtered on flat samples indicates that the reproducibility of the depth measurement is better than 3%.
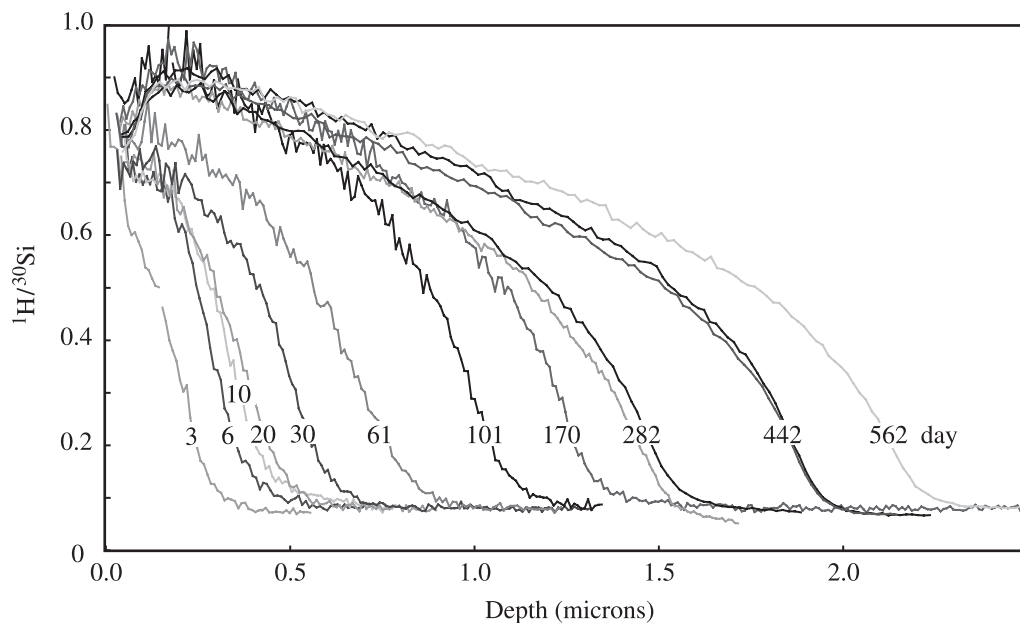
Figure 3   *Depth profiles of $^1H/^{30}Si$ for Pachuca obsidian samples experimentally hydrated at 75°C.*

RESULTS

The results of our experiments at 75°C are shown in Figure 3 and the times and other data are listed in Table 1. Several regularities are apparent in these data. First, longer runs yielded deeper profiles. Although this was to be expected, it implies that diffusion in these samples is indeed a regular process, and that no other processes occur that seriously affect different samples at different rates. The profiles also show a decided increase in the maximum water concentration with time. This is consistent with our earlier observations on samples from the Chalco site in the Valley of Mexico (Riciputi *et al*. 2002), which showed that the surface concentrations in archaeological specimens with ^{14}C dates ranging from 560 to 1525 CE increased with time. The naturally hydrated obsidians suggest that surface hydration is relatively slow, and this conclusion is supported by the new experimental results.

The profiles also show a distinct drop in $^1H/^{30}Si$ near the surface. This is evident in many of the longest profiles in Figure 3, and was also observed in many of our previous analyses (Anovitz *et al*. 1999; Riciputi *et al*. 2002). While this does not appear to be an artefact of water loss to the high-vacuum environment, the cause of this pattern remains unknown. Experiments to determine the origin of this effect are ongoing, and the results will be reported in a later communication.

Characteristic point analysis

There are a number of ways to analyse diffusion profiles. From a theoretical standpoint, the best approach is to model the entire profile as a function of time by solving Fick's second law:

Table 1 *Data for the 75°C experiments and Chalco samples*

(a) 75°C experiments

Run number	Time (min)	Approximate time (days)	Half-fall distance (μm)	Inflection point (μm)	Surface concentration, $^1H/^{30}Si$
1	4 417	3	0.184	0.243	0.73
2	8 675	6	0.269	0.269	0.73
3	14 231	10	0.327	0.342	0.73
4	28 725	20	0.387	0.387	0.77
5	44 685	31	0.450	0.484	0.77
6	89 218	62	0.577	0.634	0.82
7	145 314	101	0.857	0.987	0.96
8	242 068	170	1.068	1.260	0.98
9	403 020	282	1.161	1.410	0.92
10	403 020	282	1.188	1.463	0.90
11	632 321	442	1.527	1.869	0.96
12	632 321	442	1.513	1.869	0.94
13	805 003	562	1.731	2.117	0.94

(b) Chalco samples (Riciputi *et al.* 2002)

Sample	Time (min)	Date (CE)	Half-fall distance (μm)	Inflection point (μm)	Surface concentration, $^1H/^{30}Si$
CHO110	2.4930E+08	1525	1.97	2.18	0.90
CHO110	2.4930E+08	1525	2.11	2.30	0.91
CHO086	3.3345E+08	1365	2.08	2.21	0.89
CHO081	3.3871E+08	1355	2.19	2.38	0.90
CHO081	3.3871E+08	1355	2.28	2.44	0.90
CHO120	3.9657E+08	1245	2.23	2.41	0.88
CHO015	4.4390E+08	1155	2.41	2.63	0.94
CHO018	4.4390E+08	1155	2.48	2.85	0.91
CHO047	7.1214E+08	645	3.79	4.19	1.02
CHO055	7.5684E+08	560	3.81	4.25	1.00
CHO051	7.5684E+08	560	4.00	4.40	0.985

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left\{ D(C, x, t)\frac{\partial C}{\partial x}\right\} \tag{2}$$

or some modified version of it, where C is concentration, t is time, x is distance and $D(C, x, t)$ is a diffusion coefficient that may be a function of any of the other three variables. Solution of this equation may, however, require a significant amount of mathematical analysis, and it is, therefore, useful to perform preliminary analyses of the data using characteristic point analysis (cf., Riciputi *et al.* 2002). In this approach, a single point on the curve, definable in a repeatable way for all profiles, is used as a proxy for the curve itself. While this does not give an adequate representation of the shape of the curve, and therefore of the factors which influence that shape, it does provide a way of quantifying changes in hydration depth with time. As

a single depth is used at each time, a single, characteristic diffusion coefficient can also be defined. While there are an infinite number of ways to do so, it is convenient to modify equation (1) as follows:

$$x^2 = D_{ch}t \tag{3}$$

where x is the characteristic depth, D_{ch} is the characteristic diffusion coefficient at that depth and t is time. This puts the units of D_{ch} in the standard (distance)^2/time form. If, as we have previously argued (Anovitz *et al.* 1999; Riciputi *et al.* 2002), equation (3) is not suitable for chronometric determinations, D_{ch} will not be a constant. The opposite is not, however, the case. Even if D_{ch} were to prove constant for the experimental data, the timescale of the experiment may be insufficient to distinguish such variations. Changes in the value of D_{ch} as a function of time provide input into the assessment of diffusion mechanisms.

Riciputi *et al.* (2002) discussed the strengths and weaknesses of two types of characteristic points—the half-fall distance and the inflection point. The half-fall distance is the distance at which the concentration is the average of the surface and background values. This is very close to the depth defined by equation (1) (which actually gives the depth for 52% of the difference for an error-function type diffusion profile; cf., Anovitz *et al.* 1999). As the exact value of the surface concentration is unknown, it may be estimated, or the maximum concentration may be used as a proxy if a maximum exists. Calculation of the inflection point is based on the fact that all of the hydration profiles in this study, and most others reported in the literature (cf., Anovitz *et al.* 1999; Riciputi *et al.* 2002; and references therein), are S-shaped (or Z-shaped, depending on the plotting orientation). Thus, there is a single depth at which the curve changes from being concave down to concave up. This point is defined mathematically as a minimum in the first derivative of the curve, and a zero in its second derivative. Both characteristic point approaches have been used in this study for comparison.

The time-dependence of D_{ch}

Figure 4 shows depths obtained from the two characteristic point approaches plotted as a function of $\log_{10}$ of time for both our 75°C data and the Chalco samples. Figure 5 shows the values of D_{ch} calculated from these characteristic depths for the 75°C experiments, and Figure 6 shows the same coefficient for the Chalco data. Both characteristic point approaches yield a similar magnitude and variation in D_{ch} with time. The absolute differences between them are due to the different locations of the characteristic points. In the 75°C data, D_{ch} initially decreases rapidly with time, and then flattens out after approximately 2.7×10^6 s at an average value of 6.64E–8 µm^2 s^{-1} for the half-fall points and 9.20E–8 µm^2 s^{-1} for the inflection points. Previous studies (Haller 1963; Friedman *et al.* 1966; Zhang *et al.* 1991a,b; Behrens and Nowak 1997; Nowak and Behrens 1997; Anovitz *et al.* 1999; Zhang and Behrens 2000; Riciputi *et al.* 2002) have, however, shown that hydroxylation of silicon–oxygen bonds should cause the diffusion coefficient to increase with increasing water content. Thus, this initial decrease must be due to a different mechanism. Regardless, the failure of the square-root-of-time model to describe the data is obvious, as this would yield a D_{ch} value that is constant with time.

The Chalco data (Fig. 6) suggest the opposite of the effect observed in the 75°C experiments. While there is some scatter, probably due to uncertainties in the ^{14}C data used to date the samples, the diffusion data suggest that D_{ch} increases with time. Again, this is inconsistent with the square-root-of-time model. If, however, these data can be combined with the 75°C
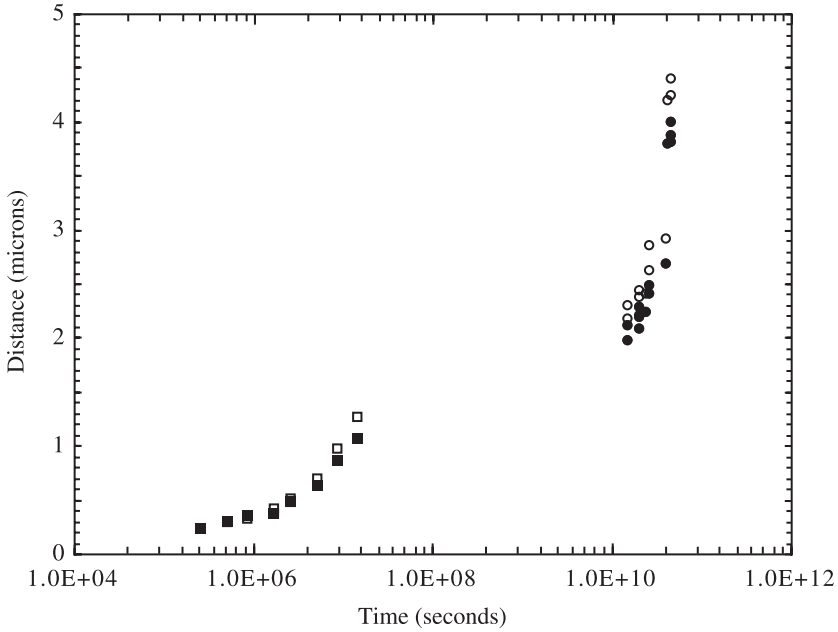
Figure 4   *Half-fall (solid symbols) and inflection-point (open symbols) depths as a function of log$_{10}$ time for our 75°C (squares) and Chalco (circles) data.*
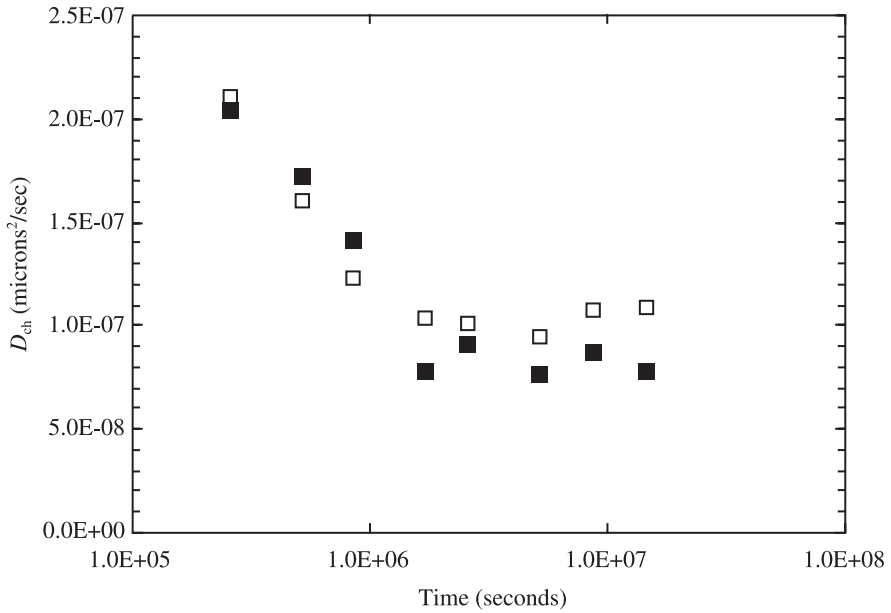

Figure 5   *Characteristic half-fall (solid symbols) and inflection-point (open symbols) diffusion coefficient D$_{ch}$ as a function of log$_{10}$ time for our 75°C data.*
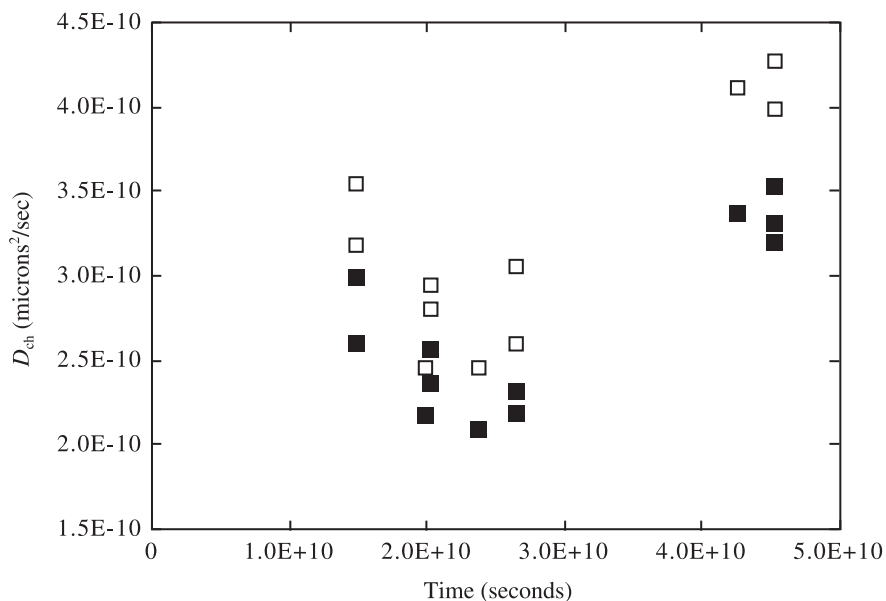
Figure 6 *Characteristic half-fall (solid symbols) and inflection-point (open symbols) diffusion coefficient D_{ch} as a function of $\log_{10}$ time for the data from the samples of Pachuca obsidian from the Chalco site (Riciputi* et al. *2002).*

data—that is, if there is no mechanistic change caused by temperature or environment between the two—this suggests that the characteristic diffusion coefficient first decreases, and then increases with time as hydration proceeds. Alternatively, the average temperature in the Basin of Mexico from 600 CE to the present may have been somewhat higher than the average temperature in that area from 1200–1400 CE to the present, which would cause the apparent increase in D_{ch} with time in the archaeological samples.

The time dependence of the 'surface' concentration

In our work on the Chalco samples (Riciputi *et al.* 2002), we noted that the concentration of hydrogen at the surface of the glass appeared to increase with the age of the sample, and we modelled this effect assuming an exponential approach to equilibrium that remained incomplete after 1500 years. Similar results have been observed experimentally in silica glass by Wakabayashi and Tomozawa (1989) at 200–750°C and by Helmich and Rauch (1993) at 160–200°C, and possibly by Rauch *et al.* (1992) in an indochinite tectite. The data from the first two of these studies have been modelled by Doremus (1995), who interpreted it as the result of slow formation of silanol groups at the glass surface. These results, and those described below, directly contradict the assumption of Liritzis and Diakostamatiou (2002) that the concentration in their 'surface saturation layer' is constant with time.

Not surprisingly, finite difference modelling of the Chalco samples shows that the time-dependence of the surface hydrogenation has a profound effect on the evolution of the hydration profile as a whole (Riciputi *et al.* 2002). Unfortunately, our ability to closely define the kinetics of surface hydration at ambient conditions was limited by the lack of samples hydrated for relatively short times (< 475 years). Nonetheless, the model suggested that the hydration
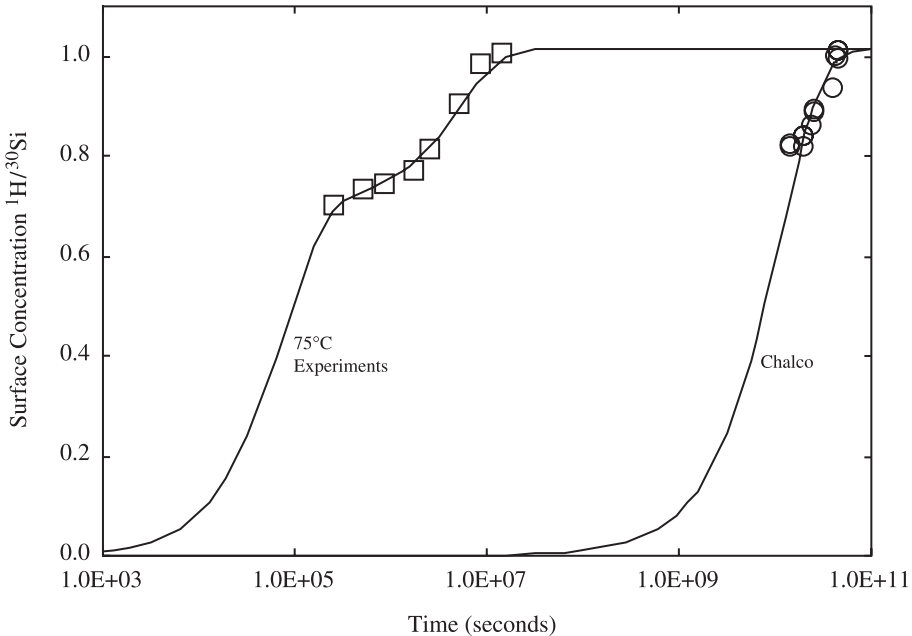
Figure 7   *Extrapolated surface values for our 75°C and Chalco samples as a function of log_{10} time. The curves shown were calculated using equation (5) and the coefficients given in the paper.*

rate was initially relatively rapid, that it had slowed significantly by the age of our youngest sample, and that equilibrium may not have been achieved after 1440 years.

The experimental data obtained here provide a basis for corroborating and expanding the results obtained from the Chalco samples, further quantifying the time- and temperature-dependence of surface hydration. Examination of the profiles from our experimentally hydrated samples confirms the importance of surface hydration kinetics to the development of the hydration profile. As noted above, the data in Figure 3 clearly show that the maximum hydrogen content increases with time. Unfortunately, due to the uncertainties in the SIMS data very near the sample surface, quantitative determination of the hydrogen content at the surface itself is difficult. Figure 7 shows extrapolated surface concentrations as a function of time for the 75°C and Chalco samples. For the Chalco data, these have been extrapolated to zero depth on the basis of finite-difference fits to the profiles (Riciputi *et al.* 2002). For the 75°C data, the values have been extrapolated on the basis of the shape of the hydration profile calculated for the Chalco samples. Nonetheless, it must be remembered that the actual shape of the concentration profile in the near-surface region may be unknown and may not follow the smooth curves used here. There are some data on hydration of float glass (Lovell *et al.* 1999; Richardson *et al.* 2001) that suggest that water concentration in the very near surface region may increase sharply. Thus, it is also possible that the actual surface concentration equilibrates very rapidly, but that significant changes occur in the shape of the profile in the first hundreds or thousands of angstroms, leading to the marked increase in the plateau values with time observed in both our experimental results and the Chalco samples.

Riciputi *et al.* (2002) modelled the surface concentration with time as a sum of two exponentials, using the equation

$$C_s(t) = C_o(2 - A * \exp(-\beta t) - (2 - A) * \exp(-\gamma t)) \qquad (4)$$

where C_s is the surface concentration at some time t, C_o is half the equilibrium surface concentration at saturation, and A, β and γ are fitting parameters. In this equation, the value of β is primarily controlled by the initial hydration rate, and the values of A and γ depend on the value of β. Because there were no short-term archaeological data available to constrain this part of the equation, a value was chosen that resulted in the best model ages for the Chalco samples. This yielded $C_o = 0.5085$, $A = 0.0803$, $\beta = 1.23584E–3$, and $\gamma = 2.84704E–3$ for time in years BP.

The 75°C data clearly demonstrate the double exponential effect. When plotted as a function of the logarithm of time (Fig. 7), the data show a plateau at less than approximately 45 000 s (~31 days). This is consistent with the double exponential equation, and suggests that at least two processes, operating at different rates, control changes in the surface concentration with time. Unfortunately, while the surface values of the shortest 75°C experiments are uncertain, these experiments also appear to have surface concentrations on the plateau. Thus, there are no data on the time at which the surface concentration goes from zero to the plateau value, although it must be less than three days. Preliminary modelling efforts (Anovitz *et al*. in prep.) suggest that it should be about 40 000 s, but this is model dependent. Nonetheless, using this approximation, fitting these data to equation (4) yields $C_o = 0.4700$, $A = 1.4927$, $\beta = 443.3$ and $\gamma = 7.827$, also for time in years (365.2442 days per year). This reproduces the observed surface concentration versus time data reasonably well (Fig. 7). The model used to constrain the initial hydration is somewhat different from that of Riciputi *et al*. (2002), however, and thus it is unclear whether the two sets of coefficients are directly comparable.

Boltzmann–Matano analysis

While characteristic point analysis is useful for qualitatively evaluating changes in diffusion as a function of time, and may have significant applicability for archaeochronological purposes, it is of limited utility in quantitative analysis of the relationship between the diffusion coefficient, composition, and time. This can be evaluated using Boltzmann–Matano analysis. While the derivation and details of this analysis are beyond the scope of this paper (see Crank 1975; Lasaga 1998), the method involves first finding the Matano depth (X_m) for the profile. To do so, we define the surface concentration as C_o, the concentration at the Matano depth as C_m and the concentration of the unhydrated sample as C_∞. The Matano depth is then defined as follows:

$$\int_{C_o}^{C_m} x \partial C = \int_{C_m}^{C_\infty} x \partial C \qquad (5)$$

The diffusion coefficient at a given depth in the profile is then calculated from the gradient, dx/dC, as

$$D_{c=c_1} = -\frac{1}{2t} \frac{dx}{dC} \int_{c_1}^{c_\infty} x dC \qquad (6)$$

where the integration is performed assuming that $x = 0$ is the Matano depth. For our profiles, this approach required extrapolating the surface concentration and smoothing the data using a boxcar average to remove analytical noise, but the analysis was otherwise straightforward.
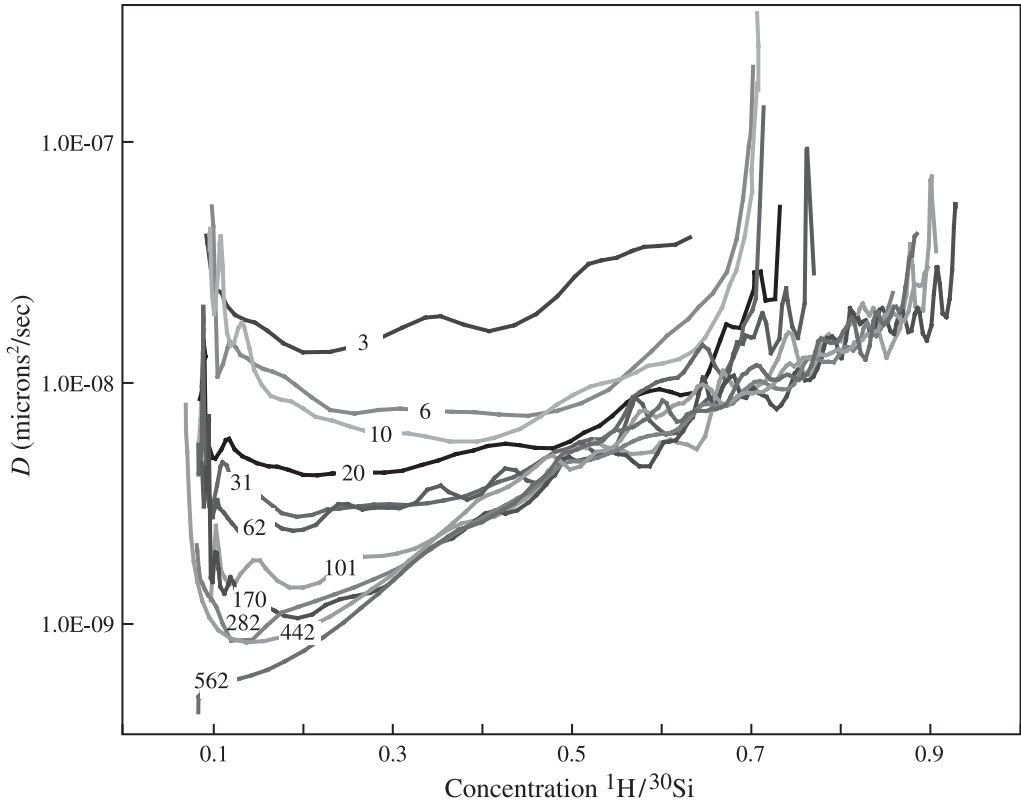
Figure 8   *The diffusion coefficient as a function of composition, calculated from the 75°C experiments using the Boltzmann–Matano approach. The labels on each curve give the number of days each experiment was run.*

Figures 8 and 9 show the diffusion coefficient (D) as a function of composition calculated for the 75°C experiments and the Chalco samples, respectively. Examining the data from the 75°C experiments, several patterns are evident. As a function of hydrogen content, the diffusion coefficient curves are essentially U-shaped, with an initial steep drop in D at low hydrogen concentrations, followed by a linear increase and then a steep increase in D at the highest concentrations. The minimum value of D decreases with time, and the initial section of rapidly decreasing D becomes restricted to progressively lower concentrations. The final increase is hard to distinguish in most curves because the near-surface data are not available from the SIMS analysis as discussed above. Diffusion coefficients for some samples appear to drop at the very lowest compositions, but this is probably an artefact of the SIMS analysis in the baseline region. Most of the curve is in the linear region by 562 days, although by 101 days most of the curve above $^1H/^{30}Si = 0.3$ remains essentially constant with time. The increase in the surface concentration with time is also evident.

The Chalco data (Fig. 9) show more similarities, and fewer changes with time, than the experimental data. Slightly more than half of the samples show the sharp decrease in D at low concentrations observed in the 75°C experiments. In addition, there is some evidence of the high concentration upturn as well although, as before, this is largely lost in the uncertainties in the SIMS data near the sample surface.
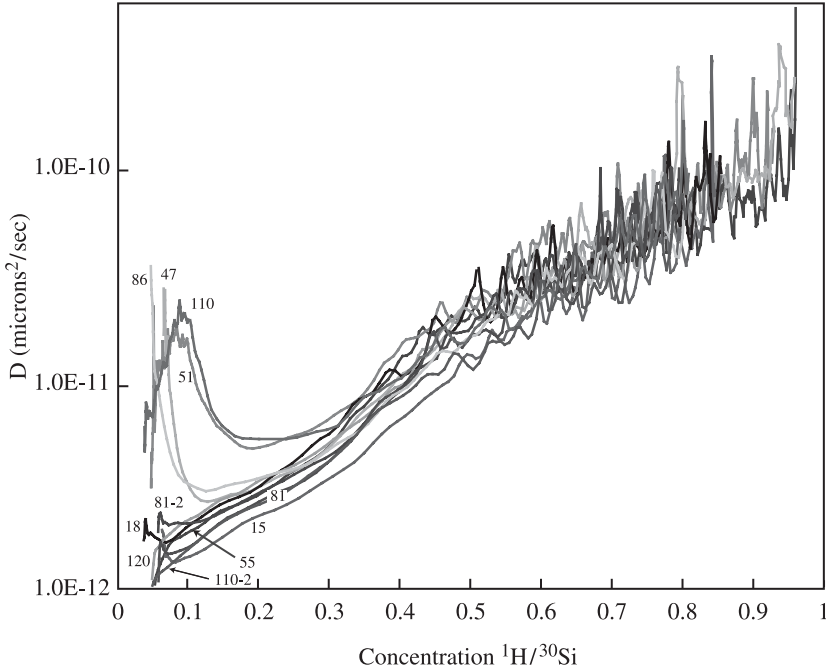
Figure 9 *The diffusion coefficient as a function of composition, calculated from the Chalco samples using the Boltzmann–Matano approach.*

While we cannot conclusively prove, at present, what caused the various features observed in Figures 8 and 9, several suggestions can be made. At low water concentrations, addition of water may slow diffusion due to interactions between the water or hydrogen molecules. The so-called 'intrinsic water' in the sample (e.g., Stevenson *et al*. 1993) is unlikely to have a similar effect, however, because it entered the glass while it was still in the liquid form, above its glass transition temperature, and has already equilibrated. This is consistent with a model known in metals in which transported protons (H$^+$) are trapped at sites within the glass as H$_2$ molecules (Glicksman 2000, 273–8). Defining the hydrogen site partitioning as

$$K(T) = [\text{H}^+]^2/[\text{H}_2] \qquad (7)$$

the following equation for the effective diffusion coefficient D_{eff} can be obtained:

$$D_{\text{eff}} = \frac{D_{\text{H}^+}}{1 + 2C_{\text{H}^+}/K(T)} \qquad (8)$$

which, for small values of $K(T)$—that is, large percentages of trapping—has the same shape as our data at low hydrogen concentrations. In this model, the change in the concentration-dependence of D observed with time is equivalent to a decrease in $K(T)$. This implies that, as the leading edge of the diffusion 'front' progresses farther from the surface of the glass, hydrogen trapping becomes easier. This is consistent with the decrease in D_{ch} with time. The reason for the time-dependence of this phenomenon is unknown, but it may be related to stresses generated during initial hydration and their subsequent relaxation, or to differences between the surface and interior of the glass.

The upturn in the diffusion coefficient at high concentrations is probably a saturation effect. Once water in this area is no longer reacting with the glass, but simply passing through, the diffusion rate is expected to increase, essentially undoing the trapping effect, although it is unclear whether 'new water' would pass through or displace water absorbed earlier. The central region of the concentration versus diffusion coefficient curves, where $\log_{10}$ of the diffusion coefficient is a linear function of composition, may be related to the chemical potential of the reaction between the water (or hydrogen) and the glass structure, or to the interaction between trapping and saturation, but this remains unclear.

Two caveats must be added in regards to the above discussion. The first is that the derivation of the Boltzmann–Matano solution depends on Boltzmann's variable, which contains a $t^{1/2}$ dependence, and our data suggests that, at least for the initial stages of the hydration process in our experimental data and for the archaeological data, this dependence does not hold. In fact, derivation of diffusion coefficients using this approach assumes that the diffusion coefficients are concentration-, but not time-, dependent. In addition, the derivation assumes that the surface concentration is constant with time. While, as noted above, a constant surface concentration is possible, the calculations performed here cannot include the effects of highly discordant near-surface profiles whose details are, as yet, unknown. Thus, while the results of the Boltzmann–Matano analysis performed here again indicate that the evolution of the diffusion profile of water (or hydrogen) in obsidian is not described by a simple $t^{1/2}$ dependence, the absolute values of the diffusion coefficients obtained in the Boltzmann–Matano analysis are unlikely to be exactly correct.

<center>DISCUSSION</center>

Combination of the 75°C experimental data with those from the Chalco site yields two important patterns. First, in neither case does the temporal evolution of the diffusion profile fit a square-root-of-time model. In fact, if the temperature differences between the two data sets can be ignored qualitatively (Ambrose cell measurements at Chalco yielded an average yearly temperature of 19.4°C and 97.5% relative humidity, and an upper value of 20.0°C and 100% relative humidity; Riciputi *et al.* 2002), although there is obviously a quantitative difference in the diffusion rate as a function of temperature, the characteristic diffusion coefficients calculated from equation (3) appear to initially decrease, and then increase at longer times. Thus, multiple mechanisms, operating at different timescales, may control the hydration rate.

Second, both data sets require a two-term exponential equation to describe changes in the surface concentration as a function of time, again suggesting that at least two processes control the temporal evolution of the surface hydrogen concentration. To our knowledge, the time-dependence of the surface concentration is previously undocumented in obsidians. While, as noted above, Doremus (1995) interpreted similar results in other types of glasses as reflecting the slow formation of surface silanol groups, other processes may be important as well. One such process is surface stress relaxation. The presence of unrelaxed stresses in hydrated obsidian is indicated by the optical anisotropy of the hydrated rim (see illustrations in Anovitz *et al.* 1999). While the magnitude of these stresses is unknown, they are probably due to the transport of water (or hydrogen) into the glass structure, which remains under stress because the hydration process occurs at temperatures below the glass transition of the obsidian. As noted by Scherer (1986), 'The glass transition is a region of temperature in which molecular rearrangements occur on a scale of minutes or hours so that the properties of the liquid change at a rate that is easily observed.' The glass transition is, therefore, a kinetic boundary, that

separates temperature regions with real differences in glass behaviour. At higher temperatures deformation is viscous, and resultant strains remain once the stress is removed. At lower temperatures, relatively large stresses result in elastic strains that only relax in the absence of the applied stress (i.e., if the water is removed). While no data are available on the magnitude of this effect or its impact on diffusion in obsidian, data on analogous glasses, where it has been shown that the effect on diffusion rates can be large, can provide important insights as discussed below.

Silicate glass analogues

Several authors have considered the effects of stress and strain on diffusion in silicate glasses. The earliest may be the work of Charles (1962), who showed that compressive strain caused a decrease in the mobility of alkali elements. Analysis of the oxidation of silicon (Deal and Grove 1965; Doremus 1976, 1984; Eernisse 1979; Rosencher *et al*. 1979; Mikkelsen and Galeener 1980a,b; Mikkelsen *et al*. 1981; Cristy and Condon 1981; Pfeffer and Ohring 1981; Razouk *et al*. 1981; Rigo *et al*. 1982; Fargeix and Ghibaudo 1983; Fargeix *et al*. 1983; Hsueh and Evans 1983) demonstrated that the process is dominated by linear kinetics, and several of these studies attributed this to strains imposed by oxidation.

Tomozawa and co-workers have performed the most extensive analyses of the effects of stress on diffusion in silicate glasses (e.g., Acocella *et al*. 1984; Nogami and Tomozawa 1984a,b; Tomozawa 1985, 1988; Wakabayashi and Tomozawa 1989; Davis 1994; Tomozawa *et al*. 1994, 1998; Agarwal *et al*. 1995; Davis and Tomozawa 1995, 1996; Davis *et al*. 1996; Li and Tomozawa 1996; Shin and Tomozawa 1996, 1997; Agarwal and Tomozawa 1997a,b; Lee *et al*. 1997; Peng *et al*. 1997a,b; Tomozawa and Peng 1998; Tomozawa and Shin 1998; Varughese *et al*. 1998; Tomozawa and Davis 1999; Tomozawa and Lee 1999). Most of these have involved the effects of water on silica glass, but other compositions have also been examined, including alkali silicate and soda–lime silicate glasses, and several provide important insight to understanding the hydration process in obsidian. Nogami and Tomozwa (1984b) showed that stress can have a profound influence on diffusion rates. They showed that compression increased surface concentration and decreased the diffusion coefficient, while tension did the opposite. Wakabayashi and Tomozawa (1989) demonstrated that surface water concentrations increase with time in silica glass and that, at low temperatures and short times, the dependence on the square root of time does not hold. They also showed that high-temperature data cannot be extrapolated to predict low-temperature diffusion rates. All of these conclusions were reached, however, on the basis of only a few data points.

The most extensive study on silica glass was performed by Davis (1994; see also Tomozawa and Davis 1999), who found that during the early stages of diffusion the diffusion coefficient decreases and the surface concentration increases with time. During later stages, they found that the diffusion coefficient increases, and the surface concentration decreases. Except for the long-term decrease in surface concentration, these results are analogous to ours. Davis (1994) showed that water increases the rate of structural relaxation, which, in turn, controls the diffusion rate. Tomozawa and Davis (1999) suggested that these results are due to the relative timing of stress and structural relaxation. They further hypothesized that the rate of structural relaxation is controlled by diffusion of molecular water into the glass, and slow reaction between molecular water and the glass network forming hydroxyl groups. If, however, as suggested by our work (Riciputi *et al*. 2002), it is hydrogen, rather than molecular water that actually diffuses into the glass, this model may require modification.

The polymer analogue

In addition to silicate glasses, other glassy systems can be used as analogues. Perhaps the most important such systems are glassy polymers (for summaries, see Crank 1975; Frisch and Stern 1983; Subramanian *et al.* 1989; Odani and Uyeda 1991; Faupel 1992; Thran *et al.* 1999). Quantitative experimentation, analysis and modelling of diffusion of a range of penetrants in these materials has been ongoing since at least the 1940s, and results show a number of similarities to those from Pachuca obsidian. The available models for these materials can thus point in useful directions for our work, although they may not be universally applicable.

Glassy polymers are those for which 'the motions of the polymer chains or of portions thereof are not sufficiently rapid to completely homogenize the penetrant's environment' (Frisch and Stern 1983). That is, glassy polymers are substances that, on exposure to some change in their physical condition, do not rapidly relax to the new equilibrium state. As temperature is increased these polymers pass through a glass transition, and at higher temperatures are 'rubbery', and relaxation is essentially instantaneous.

It has long been recognized that diffusion in such systems is far from simple (cf., Crank 1953). Relaxation at temperatures below the glass transition is very slow. Therefore, stresses imposed by swelling due to the addition of a penetrant remain and have a profound effect on the rate of diffusion. This effect even precedes the penetrant into the polymer, and by analogy may do so in silicate glasses. The unhydrated core of the glass restricts the expansion of the hydrated region, and the core is, therefore, under tension.

A large number of investigators have modelled diffusion in glassy polymers. Alfrey *et al.* (1966) categorized diffusion in these materials into three possible cases: Case I, where penetrant mobility is much slower than stress relaxation; Case II, where the opposite is true; or Case III, known as non-Fickian or anomalous diffusion, where the rates of mobility and relaxation are similar. Most current polymer diffusion models are based on either the 'free-volume' approach (cf., Fujita *et al.* 1960; Fujita 1961; Fang *et al.* 1975; Stern *et al.* 1983), developed for rubbery polymers, or the 'dual-mode' approach, developed for glassy polymers (cf., Stannett *et al.* 1972; Vieth *et al.* 1976; Stannett 1978; Paul 1979; Felder and Huvard 1980; Stern and Frisch 1981; Chern *et al.* 1983; Frisch and Stern 1983; Petropoulos 1985, 1990; Rogers 1985; Odani and Uyeda 1991). An alternative, less commonly employed approach, first developed by Frisch (1964, 1966), is based on the formalisms of irreversible thermodynamics (see also Thomas and Windle 1982; Durning and Tabor 1986; Nettleton 1988, 1993; Jou *et al.* 1991, 1999; Perez-Guerrero and Garcia-Colin 1991; Camacho 1993a–c; Goldstein and Garcia-Colin 1993, 1994; Beris and Edwards 1994).

One group of polymer diffusion models that directly addresses the effect of unrelieved stress began with the work of Crank (1953), who assumed that the diffusion coefficient is affected by unrelieved stresses, but that the surface concentration is constant. He obtained reasonable fits to experimental sorption curves, but did not reproduce all of the observed properties of the process, especially change in surface concentration with time. Bagley and Long (1955), Long and Richman (1960) and Park (1961) showed that changes in surface concentration with time (C_s) could be modelled as

$$C_s = C_i + (C_e - C_i)(1 - e^{-\beta t}) \tag{9}$$

where C_i and C_e are the initial and final surface concentrations, and β is a fitting constant. This equation is very similar to one we derived from our analysis of archaeological obsidian samples from the Chalco site in Mexico (cf., Riciputi *et al.* 2002, equation 5).

In polymers, the change in surface concentration with time is believed to be due to surface relaxation (Flory 1953; Newns 1956; Petropoulose and Roussis 1969; Crank 1975). Thus, the surface must be at or above its glass transition temperature. In rhyolitic glasses, this temperature varies with composition. Typical values for dry silicate glasses are as follows: SiO_2, 1433 K (Hetherington *et al*. 1964); albite ($NaAlSi_3O_8$), 1038 K (Cranmer and Uhlmann 1981); rhyolite, ~1085 K (Sowerby and Keppler 1999)—but these are decreased significantly with the addition of water (Dingwell 1998; Sowerby and Keppler 1999). Sowerby and Keppler found that addition of 11.21 wt% water to a rhyolitic glass, an amount similar to that found in obsidians hydrated at low temperatures (~12 wt%—Anovitz *et al*. 1999; Riciputi *et al*. 2002), dropped the glass transition temperature to approximately 500 K. Surface free energy can also dramatically decrease the temperature of the glass transition (B. Wunderlich, pers. comm.), and thus the ability of the glass to relax after hydration may be much greater at the surface than in the bulk of the material.

Additional insights can be obtained from the results of Kwei and co-workers (Frisch *et al*. 1969; Kwei and Zupko 1969; Wang *et al*. 1969; Kwei *et al*. 1972; Wang and Kwei 1973—modified by Harmon *et al*. 1987, 1988; Wang *et al*. 1999), who modelled the diffusion of a penetrant into glassy polymers by adding a term to Fick's first law to make the flux a function of the partial stress caused by the penetrant as well as the gradient in chemical potential. From this, they derived a modified version of Fick's second law that can be solved analytically assuming that the diffusion coefficient (D), the relaxation rate (v) and the surface concentration are constants. One important result of their equation is that, at all but short times, the depth (x) at which a concentration of interest occurs is given as

$$x = 2k\sqrt{(Dt)} + vt \qquad (10)$$

where k is another constant. Thus, the diffusion rate will vary as the square root of time at shorter times, but trends towards linear with time at longer times. This is identical to the result suggested by Meighan and Haynes (1970) on the basis of their work on samples of late Pleistocene age from Borax Lake, California, and is consistent with our data from Chalco (Riciputi *et al*. 2002). The model of Kwei and co-workers does not, however, account for temporally variable surface concentrations, concentration- and time-dependent D-values, and the initial decrease in D_{ch} with time; nor does it quantitatively reproduce the observed shapes of our diffusion profiles.

IMPLICATIONS FOR ARCHAEOCHRONOMETRY

While the data presented here have implications for such widely varied fields as geology, materials science and nuclear waste storage, the primary goal of this paper is to provide results applicable to archaeology. While the data are not, as yet, sufficient to provide a fully mechanistic model of use for archaeological chronology, several important conclusions can be reached. First, comparison of the 75°C and Chalco results clearly shows that the diffusion rate depends strongly on temperature, and is a complex function of time. While the fact that the diffusion coefficient is a function of temperature has been known for some time, the quantification provided here has several implications. From room temperature to 75°C, the diffusion coefficient changes by two to three orders of magnitude, confirming the well-known sensitivity of the intrinsic dating technique to assumed local temperature. If we ignore, for the moment, the time-dependence of D_{ch}, we can fit D_{ch} as a function of inverse temperature using the

longer time average half-fall D_{ch} value from our experiments, and a value of 3.35E–10 µm s^{-1} at 19.4°C obtained from averaging the results from the oldest of the Chalco samples, as

$$D_{ch}(\text{half-fall}) = -1.21079E{-}4/T(K) + 4.142E{-}7 \tag{11}$$

While we do not endorse the use of this equation for archaeochronometry, it can be used to give some idea of the temperature sensitivity of the intrinsic method. Using equation (11), a 4 µm half-fall depth required 1515 years to form at 19.4°C, 429 years to form at 20°C, 196 years to form at 21°C, and 7.6 years to form at 75°C. This extreme sensitivity, especially at the lower end of the temperature range, suggests that the effects of uncertainties in yearly temperature and changes in average temperature over time on calculated intrinsic ages are indeed large.

This does not mean, however that obsidian hydration is not of use chronometrically. As was shown by Riciputi *et al.* (2002), comparison of characteristic hydration depths with external calibration data such as ^{14}C can provide a very precise calibration curve that can be used to date parts of a site, and perhaps other sites in a localized region, for which other dating techniques are unavailable or unreliable. Such extrinsic, calibrated dating should be both possible and reasonably accurate, and this approach automatically factors in both local environmental factors such as temperature, and any changes that may have occurred in these factors over time.

As we have already shown (Anovitz *et al.* 1999; Riciputi *et al.* 2002), there are at least two approaches to this problem: (1) characteristic point analysis; and (2) modelling the evolution of the entire diffusion profile as a function of time, using either analytical or numerical approaches to the solution of Fick's second law. The data presented here clearly show that, from an experimental as well as an archaeological standpoint, the characteristic point approach is reliable and should provide a useful dating tool. The Fick's law approach should also provide a reliable method of obsidian dating, but several caveats must be considered. Any model attempting to actually calculate the temporal evolution of the diffusion profile must account for both the compositional and temporal changes in the diffusion coefficient and the change in the surface concentration with time. Other approaches may fit the data over a given time interval but, as they do not reliably describe the underlying mechanisms, such approaches are, at best, interpolation mechanisms, and cannot be reliably extrapolated.

Despite progress to date, several types of data are needed before a complete model of the diffusion of water in Pachuca obsidian can be obtained. Eight stand out: (1) data on samples hydrated experimentally for longer periods of time; (2) data on the natural hydration of archaeological samples at shorter times (e.g., 50–500 years); (3) more detailed data on the effects of temperature; (4) correlation of palaeoclimatic data on variations of temperature and relative humidity with time in the Basin of Mexico with hydration results on archaeological obsidian suites; (5) calibration of the thermodynamics and kinetics of hydroxyl group formation; (6) a direct calibration of the relationship between water content, stress and relaxation in the bulk of the glass and at the surface; (7) a quantitative mechanistic and thermodynamic understanding of the surface processes that convert environmental water to the hydrogen believed to be the actual penetrant; and (8) data need to be obtained on the effects of dissolution and dissolved species on obsidians hydrated in the liquid, rather than the vapour, phase (cf., Morgenstein *et al.* 1999; Wickert *et al.* 1999). Each of these factors is critical to a thorough understanding and calibration of the process of obsidian hydration, and to evaluating the extent to which experimental data can be applied to archaeological contexts. Work is currently in progress to obtain many of the needed results.

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