The Failure of Obsidian Hydration Dating: Sources, Implications, and New Directions

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Obsidian hydration dating (OHD) originally promised to be a rapid, inexpensive, simple and reliable method for dating obsidian artefacts. The perceived elegance of OHD resulted in rapid acceptance and widespread application despite questions concerning its theoretical rigor. With increased usage it has become evident that, while economical, simple and fast, OHD is unreliable. Here results of a secondary ion mass spectrometry (SIMS) study of obsidian and synthetic glass artefacts are presented that explain why OHD has not lived up to expectations. The results suggest that the standard OHD equations are inappropriate and that traditional optical measurements are inherently flawed. Although significant refinement will be needed, the results suggest that both chronological and palaeoclimatic data might be obtained from glass hydration rims through an improved analytical methodology and more rigorous treatment of the data.   © 1999 Academic Press

Keywords: OBSIDIAN, SECONDARY ION MASS SPECTROMETRY, SIMS, DIFFUSION, HYDRATION DATING, GLASS, BECKE LINE, ANISOTROPY, FINITE DIFFERENCE MODELLING, CHALCO, COPAN, XALTOCAN, MESOAMERICA, MATANO INTERFACE.

> "*Nor can they follow the atoms one by one*
> *To see the law that governs all events*"
> Lucretius
> De Rerum Natura, Book II

Introduction

Ridings (1996), in a review of obsidian hydration dating (OHD), raised the pointed question, "Where in the world does obsidian hydration dating work?" This statement reflects the frustration of many archaeologists and geologists over a dating technique that has been long on promise but short on results. This report demonstrates that the problems with OHD are due, in part, to use of both inappropriate analytical techniques and an improper model of the hydration process. The implications affect not only archaeological and geological applications of OHD, but also modelling of the decomposition of nuclear waste storage glasses. Our results suggest, however, that refinement of the OHD technique is possible in a manner which will both improve its accuracy and precision, and potentially expand its

utility by generating palaeoenvironmental as well as chronological data.

The potential of obsidian as a chronometer was first recognized by Friedman & Smith (1960). They noted that the exposed surfaces of ancient obsidian artefacts had absorbed water, that this hydration rim was visible under high-power magnification, and that its width was dependent on time, chemical composition (obsidian source), and temperature. Later work showed that dates could be obtained by two methods. In "empirical rate dating" (Meighan, Foote & Aiello, 1968; Kimberlin, 1976; Meighan, 1976; Findlow & Bennett, 1978), rim widths are correlated to independent chronometric data (e.g., radiocarbon). In "intrinsic rate dating", dates are produced by ratioing rim widths to laboratory-determined hydration rates, eliminating the need for independent chronometry (Friedman, Smith & Long, 1966; Ambrose, 1976; Friedman & Long, 1976; Michels, Tsong & Smith, 1983; Michels, Tsong & Nelson, 1983).

Intrinsic rate dating was received with great enthusiasm because it not only offered a means of directly dating obsidian artefacts, but was simple, rapid, inexpensive, and allowed a large number of chronometric determinations to be obtained from a single site. This meant that problems of chronology could be addressed from a statistical perspective, something rarely possible with other approaches. Despite this great promise, consistently reliable results have not been achieved.

Here, we present an overview of the theoretical basis of OHD, discuss reasons for its failure as currently applied, and provide possible solutions using new analytical and modelling approaches. We use concentration versus depth-profiles of hydrogen and other elements in obsidian rims, obtained using secondary ion mass spectrometry (SIMS), to show that the shape of the water profile is inconsistent with that predicted using current OHD equations, indicating that the theoretical basis for OHD is flawed. Furthermore, we present evidence that, from sample to sample, the position of the optically-measured depth used in traditional OHD varies relative to the actual water profile determined by SIMS, indicating that optical determination of hydration depth is, at best, uncertain. We demonstrate that the optically observed sharp front is partially an artefact of the optical properties of visible light, and that these uncertainties place severe limitation on the precision obtainable using optical methods. Thus, it is unlikely that optical measurements will ever provide a useful means of obtaining quantitative dates from hydrated obsidian. Finally, we present preliminary results of finite-difference modelling of water depth-profiles obtained by SIMS. These models take into account the concentration-dependent rate of water diffusion in obsidian, and demonstrate that the measured water profile can be precisely modelled. The results suggest, not only that it may be possible to obtain quantitative dates from hydrated obsidians, but also that it may be possible to derive valuable palaeoclimatic information from the hydration profiles.

Archaeological Background

Because of its perceived advantages, intrinsic-rate OHD has been employed to address chronological problems in a number of regions throughout the world where obsidian was readily available for use as tools (see Ridings, 1996, for a review). Its principal application, however, has been in Mesoamerica and the western portion of the United States. Although OHD has produced reasonable results in some instances (e.g., Stevenson, Carpenter & Scheetz, 1989; Stevenson, Sheppard & Sutton, 1996), it has more often proven unreliable even when the archaeological contexts have been well-controlled. In some cases, dates obtained by OHD are so different from previous data that significant controversies have arisen.

Nowhere has OHD been more controversial than in Mesoamerica, particularly in the Mayan area. At Copan, Honduras, a comprehensive programme of OHD was undertaken in order to test the widely held interpretation that Copan was abandoned suddenly (Webster & Freter, 1990). This project dated nearly 2000 obsidian artefacts by the intrinsic-rate method. The distribution of the resulting dates suggested that the Coner phase, or the terminal period of the city, extended into the 13th century CE; a result which suggests that the collapse of Copan occurred slowly over some 300–400 years. In contrast, monuments inscribed with long count dates, as well as the appearance of a new ceramic tradition, indicate that Copan collapsed catastrophically (cf. Manahan, 1996). The controversy that has ensued from these conflicting lines of evidence has led to considerable debate over the nature of the collapse of Classic Mayan civilization and the validity of OHD (Braswell, 1992; Freter, 1992; Webster, Freter & Rue, 1993; Manahan, 1996; Cowgill & Kintigh, 1997).

Recently, Braswell, Glascock & Neff, (1996) attempted to use an alternative method of intrinsic-rate OHD, based on measurement of hydrated fissures along the surfaces of obsidian artefacts recovered from Copan, in an attempt to eliminate possible error due to surface dissolution (Ambrose, 1994). Using this method, in combination with new *in situ* measurements of site temperature and humidity, which produced a rate constant nearly twice that employed in the original study, they calculated dates for six artefacts. Paradoxically, the distribution of the dates was similar to that obtained originally. This result strongly suggests that there must be a fundamental problem with the OHD method which, we show, lies in the use of an inappropriate model of the hydration process, and the inherent inaccuracy of the optical measurements.

In other areas of Mesoamerica, OHD has also failed to produce meaningful results. In the Valley of Oaxaca,
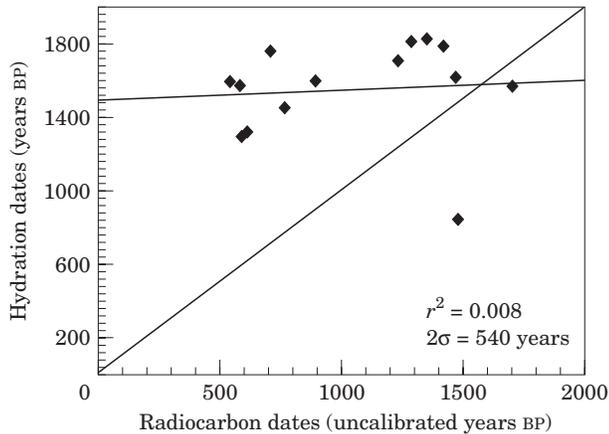
Figure 1. Comparison of hydration ages with associated radiocarbon ages from Mound 65 at the Chalco site, Basin of Mexico. Each hydration date is a weighted mean of a series of dates on six to nine samples from each dated stratum.

Mexico, the centre of ancient Zapotec civilization, more than 500 obsidian artefacts were dated to clarify demographic patterns and refine ambiguities in the Oaxacan ceramic seriation (Elam, 1993; Elam, Glascock & Neff, 1994). Despite use of a comprehensive dating protocol, which included both intrinsic and empirical approaches, the results so contradicted other chronological data that they failed to provide definitive conclusions. Another study at Chalco, Mexico, an important Aztec city-state, dated 120 obsidian artefacts to refine the site's settlement history (Elam, unpubl.). The results, however, agree poorly with radiocarbon dates directly associated with the dated artefacts (Figure 1). The discrepancy is so large that it cannot be attributed to faulty environmental monitoring or stratigraphic complexity, but again suggests the existence of a fundamental problem with the OHD method itself. Elam (1993) concluded that, while uncertainties in temperature and relative humidity undoubtedly contributed to the uncertainty of the results, the chief obstacle probably lay in the difficulty of modelling the hydration process in the natural environment.

Analysis of obsidian artefacts at the site of Otumba, Mexico, an important craft centre during Aztec times, also failed to produce easily interpretable results (Nichols & Charlton, 1996). This work was aimed at clarifying the Aztec period chronology of the site, but little insight was gained from the OHD data, which showed a great deal of scatter, and did not correspond well with associated radiocarbon dates. Careful excavation eliminated the possibility of error due to stratigraphic mixing, and the authors suggested that, again, the OHD method itself was at fault.

Two other studies in the Basin of Mexico, at Cihuatecpan and Teotihuacan, produced results that were only slightly better than those obtained at Chalco and Otumba (Evans & Freter, 1996; Manzanilla, Lopez & Freter, 1996). In addition, Cowgill (1996)

noted that the conclusions of the study of Evans & Freter (1996) were flawed by insufficient statistical analysis. Cowgill found that many of the conclusions could be explained as the result of simple statistical uncertainty. While both Evans & Freter (1996) and Manzanilla, Lopez & Freter (1996) claim that the limitations of their results merely reflects the nascent nature of the technique, it is clear from their results, as well as from those previously mentioned, that despite nearly 40 years of effort, OHD still cannot be relied upon to yield reasonable results in most cases. Even in those cases where it is successful, the availability of corroborating evidence from a second, more reliable technique is essential before the results can be accepted.

Similarly, OHD has not proven reliable, or particularly helpful, in other regions of the world where it has been employed. At the Borax Lake site in California, standard OHD techniques yielded dates as old as 48,000 years, although other data point to an age closer to 12,000 years. Interestingly, assumption of a linear hydration rate generated much more reasonable results (Meighan & Haynes, 1970). At other sites in the American west, results have also been mixed and the greatest success of OHD has been in relative dating of surface assemblages (Jones & Beck, 1990). Although OHD has been more sparsely applied in other areas of the world, the results have been equally unreliable. Attempts to date obsidian recovered from Pleistocene and Lower Holocene contexts at the Prospect Farms site in Kenya produced mixed results, often in poor agreement with other independent evidence (Michels, Tsong & Smith, 1983). In the south-eastern Pacific, several studies have attempted to date obsidian at a number of archaeological sites. Ambrose (1994) used an internal fissure technique to date obsidian from the Pamwak site in Papua New Guinea. In some instances, the dates accorded well with associated radiocarbon dates; in others the agreement was poor. While attempts to date obsidian from late prehistoric and early historic sites in New Zealand were more successful, none of the sites were more than 700 years old (Stevenson, Sheppard & Sutton, 1996).

All of these examples illustrate that OHD commonly produces poor results and, as in the case of Copan, these can directly contradict well-established epigraphic and ceramic data. OHD data also commonly contradict radiocarbon ages as well as results from other more reliable chronometric techniques. This suggests that, at best, OHD as it currently exists is an inconsistent and unpredictable dating method; at worst, it is entirely unreliable.

Theoretical Basis of Obsidian Hydration Dating

If OHD is to become a reliable chronometric tool, the hydration process needs to be properly understood and

rigorously modelled. Accurate modelling requires a knowledge of how water concentration changes as a function of depth in obsidian artefacts, data that has typically not been incorporated into previous modelling efforts. Such concentration versus depth profiles can also be used to clarify the relationship between the optically observed hydration rim and the chemistry of the glass.

In the original studies, Friedman and co-workers (Friedman & Smith, 1960; Friedman, Smith & Long, 1966; Friedman & Long, 1976) concluded that the position of the hydration front with time could be fit to a quadratic equation, and modelled on Fick's Laws as:

$$x^2 = Dt \qquad (1)$$

where x is the thickness of the hydration rim, D is the hydration rate and t is time. Because the hydration rate is temperature dependent (Friedman, Smith & Long, 1966; Friedman & Long, 1976; Michels, Tsong & Smith, 1983;, Michels, Tsong & Nelson, 1983), equation 1 was combined with the Arrhenius equation to give:

$$x^2 = Ate^{-E/RT} \qquad (2)$$

where A is a constant, E is the activation energy, R is the gas constant and T is absolute temperature.

While equation (1) is a "rule of thumb" for diffusion modelling, it is not a solution to Fick's Laws, as it does not describe changes in water concentration with distance and time. In addition, it applies quantitatively in few cases. One example of its derivation is as follows. In one dimension, and making no assumption about the concentration dependence of the diffusion coefficient (*D*), Fick's first and second laws are:

$$F = -D \frac{\partial C}{\partial x} \qquad (3)$$

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) \qquad (4)$$

where C is concentration, x is distance, and F is the flux. In the special case satisfying the assumptions: (1) of one-dimensional diffusion in a homogeneous medium, (2) that *D* is not a function of concentration, (3) that the initial concentration in a semi-infinite medium is constant (C_0), and (4) that the surface concentration is held constant (C_1), the following solution can be obtained (Crank, 1975):

$$\frac{C - C_1}{C_0 - C_1} = erf \frac{x}{2\sqrt{Dt}} \qquad (5)$$

Equation (1) is ultimately derived from the right-hand-side of equation (5). If we substitute equation (1) into
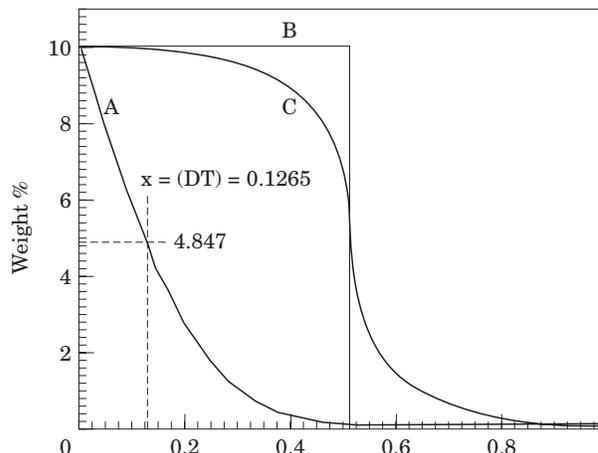

Figure 2. Theoretical depth/concentration profiles. Curve A was calculated using equation (5) assuming $C_1 = 10$, $C_0 = 0.1$, $D = 1E-9$, $t = 1.6E+7$ (arbitrary units). The depth/concentration point from equations (1) and (4) is also shown. Curve B is a theoretical oxidation profile, and curve C is a theoretical diffusion profile in which the diffusion coefficient is a function of the concentration of water.

the argument of the error function in equation (5) this yields

$$\frac{C - C_1}{C_0 - C_1} = erf \frac{1}{2} \qquad (6)$$

Rearranging to solve for the concentration we see that, at constant temperature, equation (1) gives the distance, under these assumptions and boundary conditions, at which:

$$C = C_1 + 0.5205 (C_0 - C_1) \qquad (7)$$

or where the concentration is approximately halfway between the initial and surface concentrations. This equation underlies optical OHD, as the optically observed sharp boundary is implicitly assumed to be at this depth. Therefore, the OHD approach is based on two critical assumptions: (1) that the special conditions allowing this solution of Fick's Laws, particularly that diffusion is not a function of water concentration, hold for obsidian hydration, and (2) that the optical measurement can be used as a proxy for the shape of the hydration profile.

The typical depth-profile predicted by equation (5) is quite distinctive (Figure 2, curve A). It is apparent, however, that the depth (x) does not represent any special discontinuity in the profile, and that the curve does not appear to represent the optically observed hydration rim in which a sharp boundary apparently separates the hydrated and unhydrated zones. This difficulty was recognized soon after the original presentation of OHD (Haller, 1963; Friedman, Smith & Long, 1966; Friedman & Long, 1976), but has never been adequately addressed.

A number of factors can complicate the simple profiles predicted by equation (5). The sharp front commonly observed optically is better approximated by curve B in Figure 2. Such a profile is typical of the parabolic growth of an oxide layer on a metal substrate. While the advance of this front can be modelled by an equation similar to equation (1), such behaviour is seldom observed in real materials (Kirkaldy & Young, 1987). Such oxidation layers commonly contain fast diffusion paths, whose concentration may change with time. Other complicating factors, which can generate more complex profiles, include situations in which the diffusion coefficient D is a function of the concentration of the diffusing substance (Figure 2, curve C), surface dissolution or reaction during corrosion, the effects of diffusion-induced stress and volume changes, reaction of the diffusing species with the matrix, and cross terms in the diffusion matrix for multi-component diffusion. In almost all of these cases equations (1) and (2) are not appropriate. Nonetheless, it remains possible that, with appropriate callibrations and analytical techniques, a power of t equation may be usable for dating purposes.

Previously Available Data

Evidence suggesting that equations (1) and (2) are poor models of obsidian hydration has been available for some time. Haller (1963) noted that, in general, deviation from error-function solutions to Fick's Law is a function of the degree of structural change produced by the migrating species. As water is a network modifier in glass, and lowers its viscosity, the diffusion coefficient of water in glass should increase with increasing water concentration. This was also noted by Friedman, Smith & Long (1966), who suggested that water concentration profiles in hydrated obsidian should approximate curve B or C (Figure 2), but failed to recognize the implications of such profiles for dating. In fact, it is well known that diffusion in silicate melts and many silicate glasses is concentration dependent. While this work has mostly been done at temperatures significantly higher than conditions associated with the hydration of obsidian artefacts (cf. Zhang, Stolper & Wasserburg, 1991a, b; Behrens & Nowak, 1997; Nowak & Behrens, 1997), the general principles are applicable to obsidian hydration.

Previous analyses of water concentration as a function of depth in hydrated obsidians (Lee et al., 1974; Lanford, 1977, 1978; Laursen & Lanford, 1978; Tsong et al., 1978, 1981) also fail to support the standard model. For obsidians, such profiles have been measured using secondary ion mass spectrometry (SIMS), Rutherford backscattering spectroscopy (RBS), and ^{19}F nuclear resonance. In most cases, S-shaped profiles are the norm. Once very near surface depths are exceeded, water concentrations are initially flat or decrease slowly. This is followed by a region in which water concentration decreases rapidly, then a long "tail" over which water concentration decreases slowly to background. Such profiles are diagnostic of concentration-dependent diffusion (Crank, 1975). Although the implications were not fully appreciated, the limited depth-profiles available for hydrated synthetic glasses, carried out in conjunction with corrosion studies of proposed nuclear waste forms, produced S-shaped concentration versus depth profiles for water (Lee et al., 1974; Lanford, 1978; Laursen & Lanford, 1978; Tsong et al., 1981; Michels, Tsong & Smith, 1983; Lodding, 1992; Oversby & Phinney, 1992; Wicks, 1992; Clark et al., 1993; Van Iseghem, 1993; Lodding & Van Iseghem, 1995; Salem et al., 1996). Only a few reports, analysing man-made glasses (Moulson & Roberts, 1961; Drury & Roberts, 1963; Roberts & Roberts, 1966; Cockram, Haider & Roberts, 1969; Burns & Roberts, 1970; Lanford, 1977; Nogami & Tomozawa, 1984; Wakabayashi & Tomazawa, 1989; Oversby & Phinney, 1992; Clark et al., 1993), clearly show error function-like profiles (similar to Figure 2, curve A), and several of these studies noted that diffusion was indeed dependent on water concentration, despite the profile shapes. These studies include two (Oversby & Phinney, 1992; Clark et al., 1993) in which the nuclear waste glass SRL-165 was hydrated under ambient conditions. Significantly, when this glass was hydrated at higher temperatures the resultant profiles were again S-shaped.

The implications of the available depth versus concentration data were noted by Doremus (1975, 1979, 1994) and Garcia-Barcena (1989). Doremus (1975, 1979, 1994) developed an approximate mathematical model for glass hydration assuming strict interdiffusion of hydrogen and alkalis. He noted that the break up of the silicate network of the glass by water increases the rate of water diffusion through the hydrated portions of the glass. This significantly increases the hydration rate. He also showed that the flux of water into or out of the glass may show $t^{1/2}$ behaviour initially, but will trend towards linear behaviour with increasing time. Thus, experimental studies which do not cover a sufficient time scale may yield deceptive results. Garcia-Barcena (1989) reviewed the available obsidian depth-profiles and suggested that the standard OHD model was oversimplified and that more complex concentration-dependent or reaction–oxidation models were needed. He concluded that at least some obsidians hydrate linearly with time, rather than at the $t^{1/2}$ rate of the standard OHD model. Similar conclusions have also been drawn from some experimental studies, where analyses of high-temperature run products showed that a variety of functions fit the data as well or better than the standard OHD model (Findlow et al., 1975; McGrail et al., 1988). Unfortunately, these studies have largely been ignored.

Additional evidence is also available from empirical OHD studies, which have often shown that the best fit to externally calibrated hydration data is

non-quadratic (Meighan, Foote & Aiello, 1968; Findlow *et al.*, 1975; Kimberlin, 1976; Meighan, 1976; Findlow & Bennett, 1978). In some instances a linear function produced a better fit, while in others a power function with an exponent other than 2 was preferred. In one case several different power functions each fit the data as well as a quadratic function (Findlow *et al.*, 1975).

The possibility of surface dissolution has also been recognized as a potential problem for OHD. This was first noted by Friedman & Smith (1960) who felt that it would be a problem only in rare instances. Stevenson, Carpenter & Scheetz (1989) identified surface dissolution as a source of error in experimentally-derived hydration rates, but failed to recognize that it could occur naturally at ambient temperatures (Ambrose, 1994). Efforts to correct for surface dissolution in archaeological samples have been limited to measuring hydration rinds in fissures located along the surfaces of artefacts (Ambrose, 1994; Braswell, Glascock & Neff, 1996), and even this approach has not resulted in significantly better dates.

All of these data lead to one basic conclusion—that equations (1) and (2) are not appropriate models for OHD. Both analytical results and theoretical considerations suggest that diffusion of water in obsidian is concentration-dependent, and that other basic assumptions may also be erroneous. Therefore, use of the standard equations is undoubtedly a principal source of inaccuracy in hydration dating.

SIMS Analysis of Obsidian Hydration

In a review of weathering phenomena in archaeological materials, Purdy & Clark (1987) noted that the obsidian hydration process needed to be properly understood before OHD could be reliably employed, and described the importance of data obtained from surface-analytical techniques for gaining such an understanding. 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 & Young, 1987; Chakraborty & Ganguly, 1991; Morioka & Nasagawa, 1991). The best constraints on diffusional processes are obtained by fitting such profiles. Thus, in order to test our assertion that equation 2 is inappropriate, we have used SIMS to examine the hydration rims on a variety of natural and man-made glasses. This enables us to better characterize chemical changes as a function of depth in the hydration rim on a range of glasses, and to determine something of the real complexity involved in glass hydration and OHD.

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 to use to investigate 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 tens of nanometres to several microns (see various papers in Gillen *et al.*, 1998). SIMS is the preferred method of obtaining depth-profile information in the semi-conductor industry, and is also widely applied in geochemistry for trace element and isotopic analysis (e.g., papers in Gillen *et al.*, 1998; McKibben & Riciputi, 1998; Valley *et al.*, 1998; Larocque & Cabri, 1998). The method is based on analysis of ions ejected from a sample during bombardment by a focused beam of primary ions accelerated at 2–20 keV. The composition of these secondary ions is representative of the composition of the sputtered surface, so that a mass spectrometric analysis of the secondary ions can provide a quantitative elemental or isotopic analysis of the sputtered volume. SIMS analysis can be compared to peeling an onion one layer at a time; as secondary ions are only removed from the upper few atom layers of the material, it is possible to obtain highly resolved depth-profiles by taking repeated measurements of the element(s) of interest while steadily sputtering into the sample. The depth resolution for each analysis can be varied considerably by controlling primary beam characteristics. In our preliminary work, the typical depth resolution for obsidian analyses is in the 0·02–0·04 μm range, although the instrument can be adjusted to obtain much finer resolution for shallow profiles.

Depth-profiles were obtained using a modified Cameca 4 f ion microprobe (doubly-focusing magnetic sector mass spectrometer) at Oak Ridge National Laboratory. Samples were sputtered using a mass-filtered, focused $^{16}O^{-}$ primary beam, with beam currents of 5–80 nA. The primary beam was rastered over a 150 × 150 μm square on the samples. Positive secondary ions with 80 ± 20 eV excess energy were extracted into the secondary mass spectrometer; a 33μm diameter field aperture was used to limit analysed ions to the central part of the flat-bottomed sputter crater, ensuring that depth resolution was maximized. Depth resolution varied from 0·01 to 0·04 μm, depending on the expected depth of the profile; deeper profiles were run at a higher sputter rate to reduce analysis time. Selected elements were analysed by sequentially peak jumping the secondary ion magnet among the masses of interest. Secondary ion signals were monitored using an electron multiplier, with count times of 1–3 s per element of interest. Typically, eight to 12 elements were analysed. A total of 100–1200 individual magnetic cycles (low to high mass) comprise each depth-profile, requiring from 30 min to 6 h of analysis time. The presence of sample charging during the analysis was monitored by scanning the sample accelerating voltage while monitoring the ^{30}Si peak, and accelerating voltage was automatically adjusted to maintain 80 eV excess energy.

Samples were mounted in epoxy in 2·5-cm diameter aluminium blocks with a relatively flat hydrated surface exposed. A thin gold-coat was applied to provide a conductive surface and minimize the potential for sample charging. To minimize hydrogen background (due to adsorbed water), samples were baked for 24 h at 50°C, and then inserted into the ion microprobe sample chamber ($0·5–1 \times 10^{-9}$ torr) overnight before analysis. Previous work in this laboratory suggests that this reduces the background to <0·05 weight % H_2O. The depth of the profile was determined by measuring the crater depth with a profilometer; the precision of this depth measurement is estimated to be better than 5%.

Absolute ion yields in SIMS are sensitive to the chemical composition of the matrix. Therefore, to perform quantitative analyses, the ion yields of the elements of interest must be calibrated using standards of known composition to generate a series of sensitivity factors. In addition, to normalize the ion yields, one element with an independently determined concentration, the reference species, must be measured during the SIMS analysis. In our analyses we used a set of synthetic glasses from NIST and glasses fused from USGS standards to calibrate ion yields to determine the sensitivity factors. Ion yields on the unknowns were converted into known concentrations using the equation

$$[M] = K_M(M^+/Si^+)[Si] \qquad (8)$$

where [M] and [Si] are the concentrations of the element of interest M and Si, M^+ and Si^+ the secondary ion intensities of the element of interest M and Si, and K_M is the relative sensitivity factor for element M determined by calibration to the set of glass standards. As the exact SiO_2 content of the individual specimens was not known, the SiO_2 content of the unknown samples was assumed to be 75 weight %, a reasonable approximation for natural rhyolitic obsidians. Natural variations in the composition of obsidian could introduce a relative error of up to 10% in the actual concentrations, but for more precise modelling purposes this uncertainty can be removed by analysing the SiO_2 content of the glass by electron microprobe or other appropriate techniques. The relative variations in concentration shown in the profiles, however, are independent of silica concentration. The overall analytical precision is estimated to be 1–5% of the amount present for the various elements. Apart from the first few data cycles during sputter equilibration, the Si count rate remained relatively constant in all profiles (varying by <5% from start to end), indicating that the Si concentration was essentially uniform through the entire profile.

The results for 11 of our samples are shown in Figures 3 & 4. Nine of these (Figure 3) are from obsidians and two (Figure 4) are from man-made glasses, all recovered from archaeological sites. The analysed obsidians were chosen to provide samples hydrated under a variety of environmental conditions and from a variety of obsidian sources (hydrated under the same conditions) to allow us to determine if environmental or compositional parameters exert a controlling influence on the nature of the hydration profile. The natural samples all show constant or slightly decreasing water (hydrogen) concentrations as a function of depth near the surface. This is followed by a region in which water concentration drops rapidly, then an asymptotic approach to baseline. In general, this is the same S-shaped profile observed in many of the previous depth-profiling studies. As the curves do not have the shape predicted by standard OHD equations (Figure 2, curve A), these data clearly show that equations (1) and (2) are not appropriate descriptions of the hydration process for any of our obsidians, and they should not be assumed correct for any glass without direct evidence of their applicability.

Discussion of SIMS Results

The physical explanation for the consistent signature observed in all of the measured obsidians, despite the fact that they were recovered from a wide range of environments, remains uncertain. The water concentration in obsidian apparently peaks near 10 weight%. This seems reasonable, as the solubility of water in silica glass due solely to silanol formation reaches 2–3 weight% (Roberts & Roberts, 1964), and solubility in more complex glasses due to molecular water and alkali exchange is known to exceed 20 weight% (Bartholomew, 1982). The consistency suggests that obsidian may saturate at this composition, or that more water-rich compositions exfoliate as perlite. However, the maximum does not appear to be limited by crystallization. Despite examination by transmission and scanning electron microscopy and reflection infra-red spectroscopy, we have been unable to find evidence of crystallization in the hydrated layer of obsidians.

In general, the effect of increased water content will be to increase the diffusion rate. If the water in this "saturated zone" is mobile, then the growth rate of the hydration rim will be significantly enhanced, as unhydrated glass is directly exposed to a fast diffusing water source. If not, the effects of lowered glass viscosity, hydrolytic weakening, and the possible formation of fast diffusion paths will also increase the diffusion coefficient as a function of concentration, and thus the rate of rim growth. This is consistent with the observation that the hydration rate is a function of the initial (intrinsic) water content of the glass (Stevenson, Carpenter & Scheetz, 1989).

The shape of the profile beyond the saturation zone may explain the apparent fit of simple diffusion models to short-term experimental data. In this region the change of water concentration with depth appears to
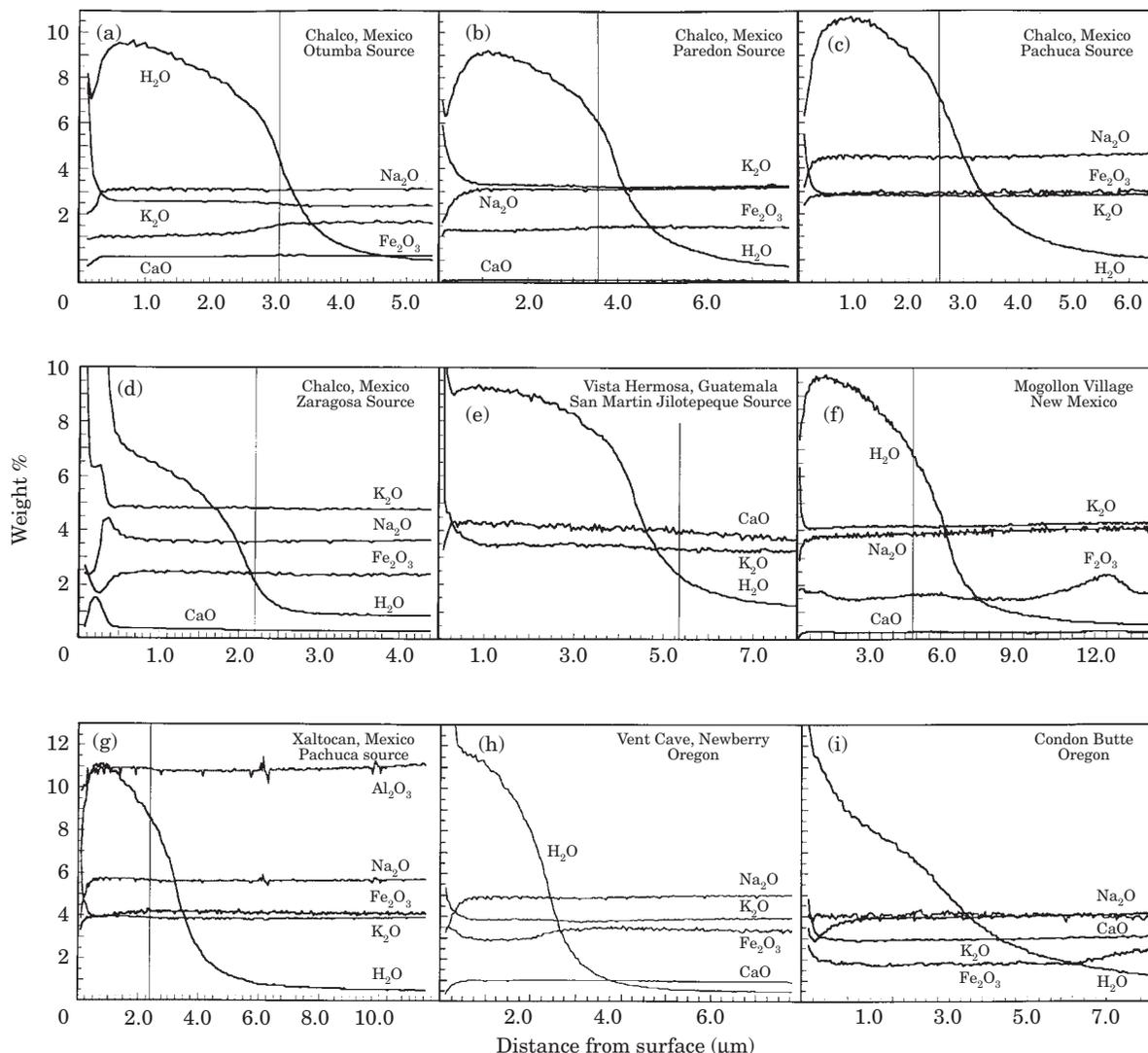
Figure 3. Depth/concentration profiles for archaeologically recovered obsidian samples. Vertical lines in (a)–(i) show the location of the optically measured hydration front. (a) Sample CHO 024, Profile 7-26H1. Measured hydration depth=3·09 μm. (b) Sample CHO 092, Profile 7-25H4. Measured hydration depth=3·57 μm. (c) Sample CHO 081, Profile 7-26H2. The Ca concentration is too low to be shown. Measured hydration depth=2·53 μm. (d) Sample CHO 102, Profile 7-25H5. Measured hydration depth=2·20 μm. (e) Sample FJB 1282, Profile 3-27H2. Na₂O and Fe₂O₃ not analysed. Measured hydration depth=5·37 ± 0·07 μm. (f) Sample FEA44, DL-92-156, Profile 12-4P1. Measured hydration depth=4·89 μm. (g) Sample 93–129, Profile 12-5P2. Measured hydration depth=2·38 ± 0·07 μm. (h) Sample LTV-A6, source at Newberry Caldera, Oregon, Profile 7-25H2. (i) Sample CON-A1, source at Obsidian Cliffs, Oregon, Profile 7-25H1.

exhibit an error function-like decrease. Similarly, in a relatively young (*c.* CE 1785–1800; Faulkner, 1984) man-made glass from the James White house in Knoxville, Tennessee (Figure 4) the hydration rim is quite shallow, shows no apparent saturation, and is error function-like in shape. This supports the assertion by Doremus (1975, 1979, 1994) that the widths of diffusion profiles in short-term experiments will show square-root of time dependence, and probably explains why many induction experiments appear to fit the classic OHD model, and also why the standard model works for some relatively young artefacts. However, as noted by Friedman, Smith & Long (1966), the diffusion

coefficient derived from such experiments is probably only valid for low water concentrations.

Unlike water, the concentrations of some elements do change exponentially with depth. The concentration profiles of Na, K and Ca are nearly exponential in the very near-surface regions (< approx. 0·5–1 μm) of many samples. However, in most cases water uptake is not balanced by alkali loss. With the exception of the man-made glass, the depths at which alkali concentrations become constant are significantly less than that of water, suggesting that their diffusion rates are slower, and that the interdiffusion model of Doremus (1975, 1979, 1994) is oversimplified. The Na/K profiles
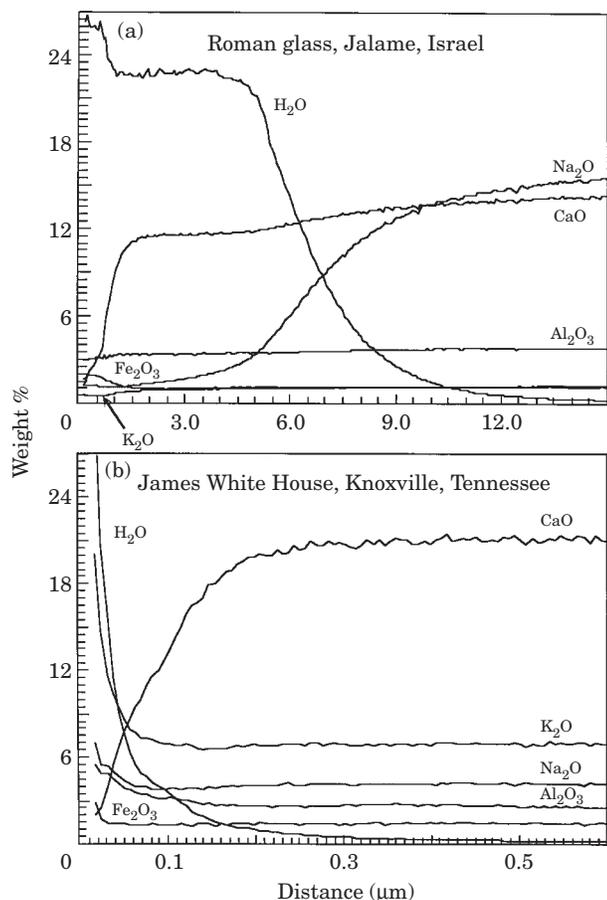
Figure 4. Depth/concentration profiles for archaeologically recovered man-made glass samples. Note that the concentrations of water in the rim appear to be significantly higher than in the obsidian samples, although this may partly reflect a different total SiO_2 content. There is also evidence that water uptake is partially balanced in these samples by loss of Ca, Na, and/or K. (a) Sample TRM-1, B114, Profile 12-5P3. (b) Profile 12-3P2.

do, however, appear to correlate well with one another and with near-surface disturbances in the water profile, possibly reflecting alkali exchange between the obsidian and clays in the soil. The simplicity of these profiles suggests that, if alkali diffusion rates were known, it might be possible to use them to obtain additional chronological constraints on the samples.

While qualitatively similar, the behaviour of different obsidians, and obsidians in different environments, is not identical. In the near-surface region, some samples exhibit strong water enrichments, and others show depletions. There is also significant variation in the change in water concentration with depth in the nearly saturated zone. In some samples concentration is nearly constant while in others it decreases steadily. Several authors (Friedman & Smith, 1960; Ericson, Mackenzie & Berger, 1976; Friedman & Long, 1976; Michels, Tsong & Smith, 1983a; Michels, Tsong & Nelson, 1983) have noted that hydration rates are dependent on both sample composition and en-

vironment. Thus quantitative OHD requires bulk composition-dependent, as well as temperature-dependent, diffusion coefficients.

The differences between samples are even more pronounced when man-made glasses are compared to obsidians. For instance, in the James White glass, Na, K and Al appear to be diffusing into the sample, while Ca is being lost, and the depths at which all four cation profiles stabilize are similar to that for water. These results contrast with those observed for obsidians. Other studies of the hydration of man-made glasses, both archaeological and for radioactive waste storage (Ericson, Mackenzie & Berger, 1976; Clark & Zoitos, 1992; Grambow, 1992; Vandiver, 1992) commonly show various leaching effects, formation of multiple layers, crystallization, and even the formation of sub-micron, rounded gel particles which may be opal-like. None of these has yet been observed in our obsidians. This implies that obsidians may be poor models of the long-term stability of vitrified radioactive wastes, although they potentially provide the only long-term data available for modelling the fate of such materials.

Comparison of water concentration profiles with optically measured hydration depths for eight samples from Chalco and one from Xaltocan in the Basin of Mexico, three from Vista Hermosa, Guatemala, and two from Mogollon Village, New Mexico (not all shown in Figure 3) partially explains the inconsistent results obtained from OHD. While in all cases the optically measured hydration boundary falls within the region of rapidly decreasing water content, this region is typically up to 1 μm wide, and the location of the optically-determined hydration boundary varies within it. This variation is sufficient to account for significant imprecision in OHD results. In relatively young specimens (≤ 2000 years old), this represents an imprecision of at least several hundred years. In older specimens, this uncertainty may be substantially larger. While there have been several attempts (Sheetz & Stevenson, 1988; Ambrose, 1994) to improve the optical measurement of hydration depths, it is apparent that no such improvement is possible, because the position of the optical boundary varies relative to the true diffusion profile.

In summary, at least three factors complicate OHD. First, the effects of water concentration-dependent diffusion have not been considered. In general, if the diffusion coefficient increases with water content, the rim will grow faster than predicted, and the calculated age will be too old. However, in some cases micro-channels formed during hydration of glasses have been shown to heal, and the rate of growth can slow with time (Nasedkin, 1964; Doremus, 1975, 1979, 1994; Morgenstein & Shettel, 1994). Second, the effect of surface loss due to dissolution needs to be accounted for (Bates et al., 1988; Tremaine & Fredrickson, 1988; Ambrose, 1994). Dissolution will tend to reduce the measured age. Finally, the erroneous assumption that the actual diffusion front is sharp, combined with the

variable position of the optical front within the real profile, adds scatter to the derived date. This is true irrespective of the hydration model employed. These results clearly show that intrinsic-rate OHD is almost certainly unusable in its current form.

While this conclusion may seem pessimistic, we are not proposing that OHD be abandoned. The regularity in the SIMS data suggest that improved analytical and mathematical approaches may permit more accurate and precise hydration dates, and possibly palaeo-climatic data (see below), to be obtained. To achieve these goals, high precision diffusion modelling is needed. Such calculations first require that the concentration of the elements of interest be well known as a function of depth. At present, the best way to obtain these data is using SIMS, the data from which are far more detailed than those obtainable by RBS or ^{19}F nuclear resonance (Lee *et al.*, 1974; Lanford, 1977, 1978; Laursen & Lanford, 1978; Tsong *et al.*, 1978, 1981). The variable relationship between optical and SIMS data shows that it is unlikely that optical measurements will prove useful.

Origin of the Optical Front

While our SIMS data have clearly shown that the sharp front observed optically is not a precise representation of the hydration front, the origin of the optical front remains to be understood. Two factors probably explain both its origin and the uncertainties associated with it: the inherent imprecision in any measurement done using visible light, and the formation of Becke lines.

Any physical observation is subject to an inherent limitation. The minimum size of the observable detail is limited by the wavelength of the radiation used to make the observation. For optical microscopic observations, this is known as the Rayleigh criterion (Robertson, 1941; Rochow & Tucker, 1994), which states that the resolution—i.e. the minimum separation distance between two points at which the two can be discerned as separate—is given by:

$$R = \lambda/(2NA_{eff}) \qquad (9)$$

where R is the resolution, λ is the wavelength of the light being used for the observation, and NA_{eff} is the effective numerical aperture, the average of the numerical apertures of the objective lens and substage condenser. The effect of this limit on OHD was considered by Sheetz & Stevenson (1988). They concluded that, even with a very good optical system, the best possible resolution is about $\pm 0.25\,\mu m$. This will affect not only the measurement of an individual artefact, but the experiments used to determine the hydration rate as well. Considering these effects, Sheetz & Stevenson (1988) calculated possible errors, from this factor alone, of -70 to $+33\%$, far too large to be used for

accurate chronology (see Braswell, 1992; and Elam, 1993, for discussions of the effects of this error range).

Regardless of the uncertainties in the optical measurement, however, the origin of the apparent sharp boundary remains to be explained. Our observations suggest that it is, in fact, a Becke line. This is a bright line which occurs in thin sections at the boundary between two materials with different refractive indices (cf. Bloss, 1961; Stoiber & Morse, 1981). Snell's Law relates the refractive indices of two materials to the path of a light ray passing between them as:

$$\eta_1 \sin\theta_1 = \eta_2 \sin\theta_2 \qquad (10)$$

where η_1 and η_2 are the refractive indices, and θ_1 and θ_2 are the angles between the light ray and a line normal to the interface between the two materials. Thus, a light ray passing between any two materials of different refractive index will be bent towards the normal in the material with the higher refractive index. Since, even in the best microscopes, not all light rays are perfectly parallel to the microscope axis, for two materials in which the boundary is essentially vertical (parallel to the light path, Figure 5) light rays passing from the lower to the higher refractive index material will also be bent towards the higher refractive index material, while those intersecting the boundary at a low angle from the higher refractive index side may be totally reflected. A similar result is also observed in thin edged grains. The result is a bright line, often with a dark edge on the low refractive index side, which moves into the material with the higher refractive index when the distance between the objective lens and the sample is increased.

Careful examination of the optically observed front suggests that it may indeed have this origin. Unhydrated, the glass is isotropic, with a constant refractive index in all directions. The distinctive birefringence of the hydrated rim, however, typically first-order grey in samples of appropriate thickness, is proof that the rim itself is anisotropic. Thus, the refractive index of the rim can be equal to that of the glass for light travelling in no more than two directions.

Figure 6 shows such a front for an approximately 17·4 μm wide hydration rim on a 149,000-year-old sample (dated by K/Ar) from Ethiopia (Wendorf *et al.*, 1975). Because of its unusual width, a number of observations can be made on this material to clarify the optical properties of the rim. For instance, Figure 6(b) clearly shows the interference fringes associated with the glass/mounting medium (probably Canada Balsam) interface. With the sample in focus (Figure 6(a)), the boundary between the hydrated and unhydrated portions of the glass is a bright line. No other boundary is visible at this location. When the stage is lowered (Figure 6(c)) both this line and a second line at the glass/mounting medium boundary move outward. This is true whether the rim is perpendicular or parallel to the vibration direction of the polarizer, and indicates

(a) High angle grain edge

Higher Refractive Index Material

(b) Thin edged grain

Outgoing Light Ray
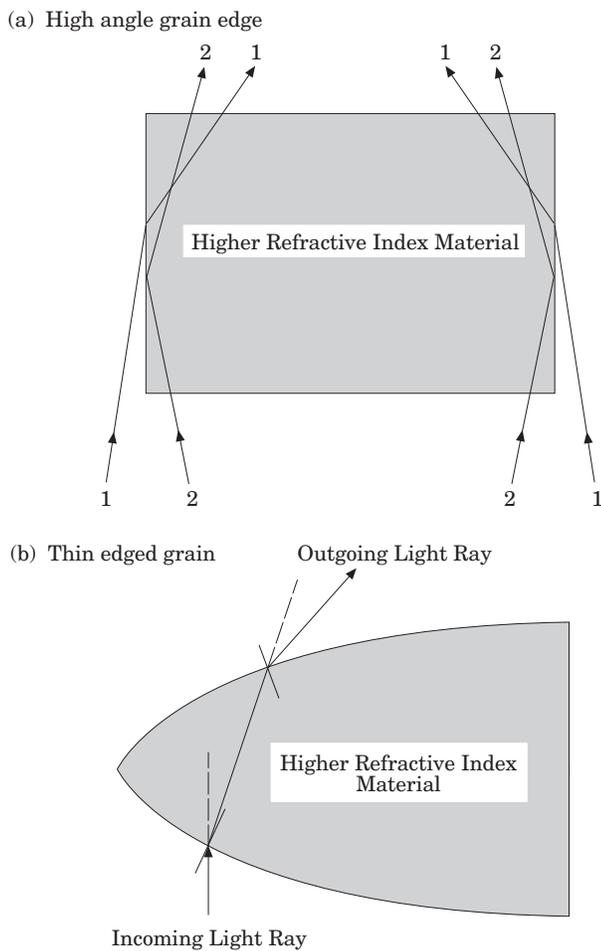
Higher Refractive Index
Material

Incoming Light Ray

Figure 5. Origin of Becke lines. (a) Becke line formation at a high-angle grain boundary for a material with a higher refractive index than its surroundings. Light rays encountering the grain boundary from the low refractive index side are bent inwards, those encountering the boundary at a low angle from the high refractive index side are totally reflected. (b) Becke line formation for a thin-edged grain. An initially axis-parallel light ray is bent towards the centre of the higher refractive index material at both the upper and lower surfaces.

that, in both vibration directions the refractive index of the mounting medium is higher than that of the hydrated rim, and the refractive index of the rim is higher than that of the unhydrated glass. In addition, insertion of a gypsum accessory plate shows that the rim is length fast, and the interference figure observed on the rim is a flash figure.

Optical anisotropy in glass is typically caused by the presence of unrelieved stress. In hydrated obsidian, this is probably caused by an increase in molar volume during hydration. This can only be accommodated in a direction perpendicular to the glass/mounting medium interface. Expansion parallel to the interface can only be partially relieved to the extent the glass is compressible. The resultant unrelieved stress field should therefore have a principal axis perpendicular to the glass/ mounting medium interface, and be similar in magnitude in all directions perpendicular to that interface. Therefore, the optical indicatrix should have similar properties, suggesting a nearly uniaxial system with the optic axis in the perpendicular direction. While not proven, the observation of a flash figure in this section is consistent with this hypothesis. If this is the case, we can conclude further that, for this sample, the hydrated material is uniaxial positive, as the rim is length fast (light vibrating parallel to the glass/mounting medium interface moves faster, thus has a lower refractive index, than light vibrating perpendicular to that interface).

Finally, while the Becke line observed in plane polarized light suggests that the interface is sharp, when the analyser is in place the boundary between the isotropic glass and the anisotropic rim is clearly gradational (Figure 6(d)). This has been observed experimentally as well. Sheetz & Stevenson (1988) noted that hydration rims developed in excess of 180°C often exhibit "fuzzy" edges, or cannot be optically defined. Both observations are in good agreement with the water concentration depth-profiles measured in this study using SIMS.

It remains to be seen whether the observations described here are universal for hydrated obsidian rims. For instance, optical examination of a number of hydrated obsidian artefacts shows that some have an additional dark line near the isotropic/anisotropic transition. Accumulated stress may cause the formation of a grain boundary within the glass in some samples which, eventually, may cause the exterior surface to exfoliate. The extent of this effect, and its relationship to the optical measurement, however, remains uncertain. Where it is a Becke line which is being observed, however, its deleterious effect on the potential accuracy of the measurement is significant. Because the Becke line moves with the focus position, the result depends on the subjective choice of where the image is in focus. The SIMS method is especially advantageous in comparison, as this uncertainty is completely removed. These observations clearly suggest that the limitations of optical observation are so great, and the relationship between what is being observed and the actual hydration process so variable, that optical observation is unlikely to ever be an accurate method of characterizing obsidian hydration and, therefore, to be an accurate source of hydration dates.

Modelling

The data presented above demonstrate that SIMS provides a method of measuring the depth versus concentration profile for water in hydrated glasses. In order to use these data to date obsidian and other glass artefacts effectively it is next necessary to develop a mathematical model of the processes involved.

Examination of the general shape of the diffusion profile shows that it resembles profiles obtained from
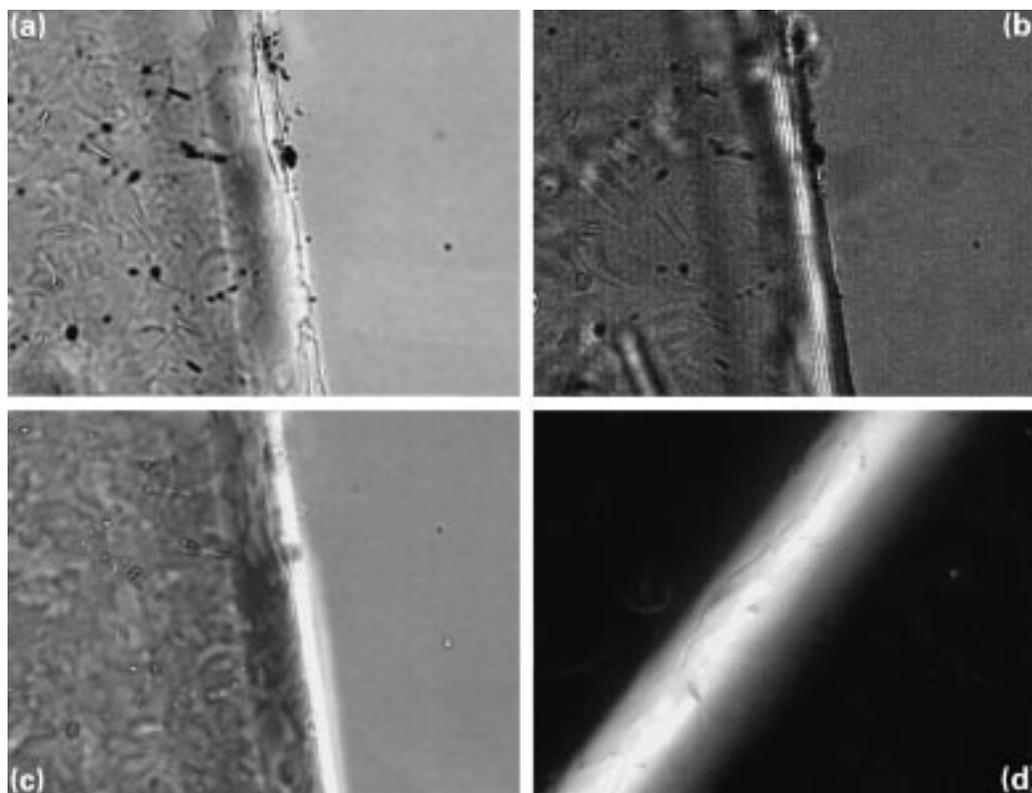
Figure 6. Photomicrographs of the hydration rim on sample ETH-72-6-C3-Ph-8, a 149,000-year-old obsidian tool from Gademotta Ridge, Ethiopia. The optically measured width of the hydrated rim is 17·4 μm (Wendorf *et al.*, 1975; C. V. Haynes, unpubl. data). Each image is 0·125 mm wide. (a) The hydrated rim in optimum focus. Note that the boundary between the hydrated and unhydrated regions is marked by a line which is light on the rim side, and dark on the unhydrated side. (b) The same image as (a). The light has been reduced to enhance the interference fringes probably caused by the glass/mounting medium boundary. (c) The same image as (a) with the stage dropped 9 μm. Note that the Becke lines at both the rim/mounting medium and rim/unhydrated glass boundaries have moved to the right. (d) Image with crossed polars, rotated ∼45 deg. to the analyser/polarizer direction. The mounting medium is to the upper left, the unhydrated glass to the lower right. Note that the hydrated/unhydrated glass boundary is gradational, not sharp.

solid–solid or liquid–liquid diffusion couples in which a component is allowed to diffuse between two materials of initially different compositions (Figure 7). Such a boundary is sometimes referred to as a Matano interface. Unfortunately, as discussed above, hydration of obsidian appears to primarily involve the diffusion of a water (in some form) into the glass, and not exchange or interdiffusion. Thus, obsidian hydration cannot be modelled in this manner. In addition, because diffusion of water in the soil next to the interface can reasonably be expected to be much faster than diffusion of water in the glass, a constant composition boundary value is appropriate.

A common cause of complexity in diffusion profiles is the effect of cross-terms (off-diagonal elements in the diffusion coefficient matrix needed when more than one element is diffusing) during multi-component diffusion. Diffusion is mass transport in response to a chemical potential gradient. Thus changes in the chemical potential of a diffusing species due to variations in the concentrations of other diffusing species can strongly affect its diffusion behaviour, even to the extent of causing flow "uphill" against a composition gradient (cf. Crank, 1975; Kirkaldy & Young, 1987). While this may be a factor in man-made glasses, our data show that, except in the near-surface region (less than approximately 1 μm from the surface), the concentrations of major elements other than water are nearly constant in the hydration rims of obsidians, and thus the effects of cross-terms can probably be ignored.

If the boundary between the two substances moves during the diffusive processes this can also complicate the diffusion profile and may, in some cases, yield profiles similar to those observed in obsidians. The classic example of the moving boundary problem is the diffusion of heat between melting ice and water (assuming no convective flow of the liquid). As heat is transferred from the water to the ice, the ice melts, and the ice/water boundary moves. A similar situation may occur in obsidian hydration if dissolution of the obsidian is significant. For the purposes of this paper, however, dissolution will be ignored, and the obsidian boundary will be considered to be fixed in space. We will consider the effects of dissolution in future work.
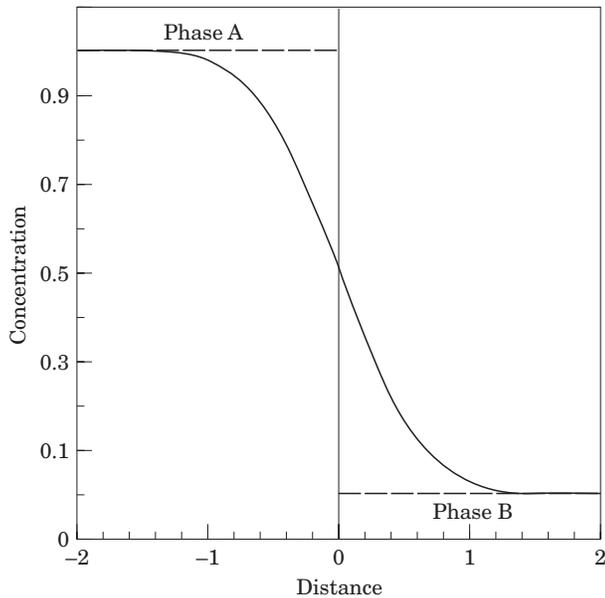
Figure 7. Typical Matano interface for exchange of a single compound between two phases (or materials which form a single phase after the diffusion couple is formed) with initially different, constant compositions. The dashed lines show the initial compositions in each material. The vertical line is the initial boundary between the two phases, and the curve was calculated assuming D=1E−9, t=1·28E+8 (arbitrary units).

The three factors most likely to explain the observed concentration versus depth profiles are: (1) changes in the diffusion coefficient due to changes in the water concentration (compositionally-dependent diffusion); (2) the effect of unrelieved stress due to volume changes caused by water uptake (non-Fickian diffusion) and; (3) reaction of water with the glass. The effects of these processes can correlate with one another, as they are all dependent on water concentration, and it may therefore be difficult to deconvolute them in natural samples.

Compositionally-dependent diffusion is probably the least complex of these phenomena. Water initially entering dry, silica-rich glass reacts to form silanols (Si–O–Si bonds break, forming Si–O–H H–O–Si pairs, cf. Scholze, 1959; Ernsberger, 1977; Bartholomew et al., 1980; Stolper, 1982; Yanagisawa et al., 1997). As this disrupts the silicate framework, the viscosity of the glass is lowered. In liquid systems, the viscosity of the matrix can be related to the diffusion coefficient by the Stokes–Einstein equation:

$$D_{12} = \frac{kT}{6\pi\Gamma_2 r_1} \frac{\partial \ln a_1}{\partial \ln m_1} \qquad (11)$$

where k is the Boltzmann constant, T is absolute temperature, r is the radius of the diffusing substance, Γ is the viscosity, a is the thermodynamic activity, m is the molar concentration, subscript 1 refers to the diffusing substance, and subscript 2 to the solute

(Kirkaldy & Young, 1987). This equation strictly refers to a large molecule diffusing in a low molecular weight solvent, and it has been shown that the viscosity must often be raised to a power other than 1 (Davies et al., 1967; Hiss & Cussler, 1973; Reid et al., 1977; Evans et al., 1981; Kirkaldy & Young, 1987). Nonetheless, equation (11) shows qualitatively that the diffusion coefficient should be an inverse function of viscosity and change with the water content of the glass. Therefore, a model of water diffusion in obsidian based on a compositionally-dependent diffusion coefficient is theoretically justifiable.

An alternative, or perhaps additional, approach is to treat water diffusion as diffusion with reaction due to the formation of silanols. In this case, a sink term (describing a portion of the diffusing species which, after reaction, becomes immobile) is added to Fick's Law as:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right) - \frac{\partial S}{\partial t} \qquad (12)$$

where S is the concentration of the diffusing substance immobilized. This has been shown to generate curves similar to those we have observed for water diffusing in obsidian (cf. Crank, 1975; Doremus, 1995). This approach should be related to that using a compositionally-dependent diffusion coefficient because the reaction forming the silanol is also the likely cause of the change in the diffusion coefficient. A combination of the two approaches may therefore prove useful.

Finally, the possibility of non-Fickian diffusion may be considered. The fact that the hydrated rim is not crystallized, yet is optically anisotropic indicates that the rim contains significant unrelieved stress. Crank (1975) notes that if the rate of stress relief is significant relative to the rate of diffusion this can significantly affect the diffusive process. This has been observed in glassy polymers, where optical fronts are commonly observed, and the rate of movement of these fronts has been shown to be a variable power function of time. The appearance of an optical front which moves as a variable power function of time has also been observed for obsidians (Findlow et al., 1975; McGrail et al., 1988), and thus the possibility that diffusion in obsidian, and possibly other glasses, is non-Fickian should be considered.

The most recent models for diffusion of water in high temperature (400–1200°C) glasses and melts (cf. Zhang, Stopler & Wasserburg, 1991a, b; Behrens & Nowak, 1997; Nowak & Behrens, 1997) are based on transport of both OH^- and molecular water, which in turn requires that concentration of each be measured as a function of depth. Such models are difficult to apply to obsidian hydration, however, as typical hydration rims are too narrow to allow accurate measurement of speciation profiles using commonly employed techniques. Infra-red spectroscopy, for

instance, the most common method of measuring water speciation, uses wavelengths from approximately 10 to 10,000 cm^{-1}, and the absorption frequencies for OH^{-} and molecular water are approximately 4515 cm^{-1} and 5230 cm^{-1}, respectively (Zhang, Stolper & Wasserberg, 1991*a*). Thus, the minimum spot size (approximately 10 μm for micro-infra-red techniques; see McMillan & Hofmeister, 1988) is limited to a range greater than the width of the average profile in this study.

An alternative approach has been presented by Nowak & Behrens (1997) who based their model on an effective diffusion coefficient for total water. Given the current analytical limitations, such a ''total water'' technique is necessary. Similarly, for the purposes of this paper, the effects of reaction and non-Fickian diffusion will not be considered explicitly. However, as noted above, the similarity between the effects of these processes and that of compositionally-dependent diffusion may mean that they have been *de facto* incorporated in the solution obtained. The availability of a larger data base in the future may, however, make a more specific approach feasible.

The model presented in this paper relies solely on compositionally-dependent diffusion. In most cases there are no known analytical solutions to Fick's Laws for cases in which the diffusion coefficient depends on the concentration of the diffusing element. Because of this limitation, numerical solutions (finite difference or finite element) are needed. Many scientific problems exist for which the appropriate differential equations are too complex to be solved analytically (e.g., groundwater flow, aircraft design), and for which computer-based numerical techniques are used to obtain the solution. The same techniques can be applied to the differentials in Fick's Second Law. In the explicit finite difference method, which is the simplest but least stable approach, the values at the next time-step are based solely on those at the current time-step. In the fully implicit method, which is more numerically stable, the values at the next time-step are based on the differentials at that time-step. Because the values at the next time-step are not known, however, the solution must be obtained by iteration. The Crank–Nicholson approximation, which also must be solved iteratively, uses an average of the two approaches, which has theoretical advantages (Crank, 1975).

In order to solve the diffusion equation, values for the diffusion coefficients are required and, in the case of concentration-dependent diffusion, a mathematical form of that dependence must be determined. As there is no a priori reason to predict the appropriate form of this function, a number of different equations were tested. Figure 8 shows the results of using such a model to fit the SIMS data from a sample of Pachuca obsidian, recovered from Operation G, Level 17 at the Xaltocan site in the Basin of Mexico. There is a radiocarbon age of 1070 ± 60 BP from Level 16 that
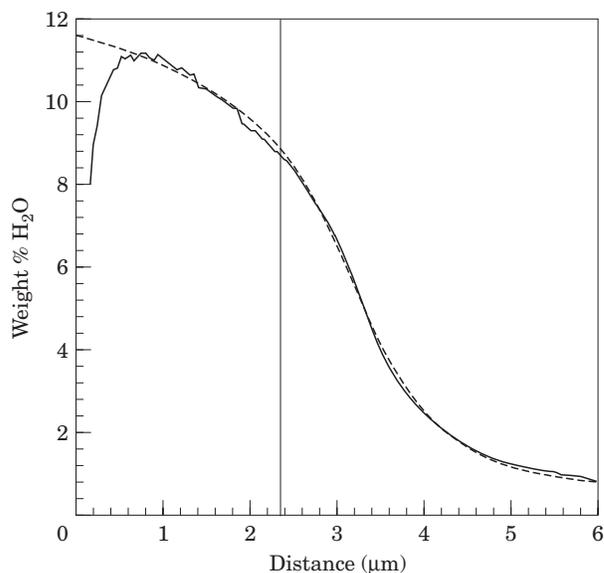

Figure 8. Comparison of the results of a finite difference model of composition-dependent water diffusion in obsidian with the SIMS results from sample 93–129 from the Xaltocan site in the Basin of Mexico. The diffusion coefficients have been adjusted to provide the best possible fit. The optically measured hydration depth, $2\cdot38 \pm 0\cdot07$ μm is also shown.

calibrates to CE 890–1026 with an intercept of CE 989 (Stevenson *et al.*, 1998), but no absolute age is currently available from Level 17. The age of this piece is therefore somewhat uncertain, but it is sufficiently well-constrained to test the ability of the model to fit the shape of the concentration/depth curve. As the purpose of our current efforts is to develop a preliminary model which will reproduce the observed hydrogen concentration profiles, this age was used for the modelling, but it is, in fact, only a *terminus post quem* limit.

The closest fit to the measured profile, shown in Figure 8, was obtained using a fully-implicit, finite difference solution with variable distance and time-steps. This has proven to be the most stable solution to date, and used the following equation:

$$D = D_0 \cdot (1 + (x \cdot (C/C_0))^y) \qquad (13)$$

where $D_0 = 5\cdot2\text{E-}11$ (μ^2/s), $x = 1\cdot5$, and $y = 6\cdot8$ to describe the variation of the diffusion coefficient with water concentration. The resultant fit is very good. A chi-squared goodness-of-fit test on the entire range of SIMS data yields a test value of $7\cdot0$. The critical value at the $\alpha = 0\cdot05$ level is $124\cdot3$. Therefore, the hypothesis that the model and the measured H$_2$O concentration versus depth profile are equivalent is supported. In reality, however, there was no attempt in this model to fit the SIMS data in the near-surface region. Excluding the data for the first $0\cdot5$ μm yields a test value of $2\cdot5$, and a critical value at $\alpha = 0\cdot05$ of approximately $113\cdot1$, also supporting the suitability of the model.

While this form of the concentration-dependence equation fits the data for this sample, and reproduces the shape of other profiles, it has not been calibrated to experimental or time series data, and the effects of regional environmental variations have not been taken into account. Therefore, it should not be used for dating applications until refined. The effect of the near-surface changes in water concentration, not considered in this model, may also strongly effect the final result.

Despite these current limitations, our initial efforts show that, by allowing the diffusion coefficient to vary with the water concentration, a good fit to the data can be achieved. Although this preliminary model is not yet capable of reproducing the near-surface changes correlated with Na/K diffusion, the success of the model clearly demonstrates the potential of such modelling to reproduce the real concentration/depth data and thereby to produce more accurate chronometric results.

Conclusions

The results of our work to date have shown that there are serious difficulties with the current methodology used for obsidian hydration dating. Until these are corrected, it is unlikely that OHD will become a reliable chronometric tool. We have shown that the optical technique employed for standard OHD measurements is unsuited to providing data with the needed precision, and that the theoretical basis on which these data have been evaluated is incorrect. Together, these effects probably account for much of the unreliability of OHD analyses. Our work has suggested further, however, that these limitations may not be unavoidable, and with suitable changes in both the measurement and modelling procedures it is possible that obsidian hydration may be useful for chronometric purposes.

In addition, preliminary results suggest that analysis of the hydration rims on obsidian artefacts may have more than chronometric potential. Available data have shown that diffusion of water in obsidian is a function of time, temperature, and relative humidity. For archaeological and geological samples, each profile provides data on changes in water and Na/K content with depth. Preliminary data also suggest that it may be possible to measure changes in the deuterium/hydrogen ratio as a function of depth by SIMS. Simultaneous solution, using these data to constrain all three variables, therefore, may provide palaeoclimatic, as well as chronological data. In cases where radiocarbon ages, or other independent chronometric data are available, forward modelling of water profiles may also provide such constraints. This possibility has already been foreshadowed by Garcia-Barcena (1976) who proposed using independently dated obsidian artefacts to extract an integrated temperature by solving

equation (2) for T, and by the work of Friedman, Gleason & Warden (1993) and Friedman et al. (1993) who investigated the possibility of using deuterium/hydrogen ratios in volcanic ash to monitor the isotopic concentrations of ancient waters for palaeo-climatic reconstructions. If successful in obsidians, such modelling would greatly enhance the utility and importance of glass hydration analysis. First, however, similar analyses of well-designed experimental and well-dated archaeological samples are needed to constrain the dependence of the diffusion coefficient on water concentration for individual glasses, and regional studies are needed to ascertain the extent to which a model, calibrated in one location, may be applied in another.

The utility of OHD as a model of the degradation of nuclear waste glasses also needs to be re-evaluated. Following intrinsic-rate OHD protocols, waste glass studies have employed elevated temperature, short duration experiments to rapidly hydrate and degrade man-made glasses, and have used the standard OHD equations (equations (1) and (2)) to model the results and to make predictions concerning waste-glass degradation (Bates, Jardine & Steindler, 1982; Byers, Jercinovic & Ewing, 1987; Abrajano, Bates & Mazer, 1989; Mazer et al., 1992). Our results indicate that this approach may, in fact, not be adequate. Short duration experiments may not realistically model long-term processes even if simple diffusion can describe the initial process. Therefore, some revision of the conclusions of these studies may be necessary.

Despite the difficulties described above, this study suggests that OHD can be made more reliable by placing it on a more analytically and theoretically rigorous footing. The recognized potential of OHD for archaeology, especially in key loci of early civilization (e.g., Mesoamerica and the Middle East) make such an effort worthwhile. Although it may never be the inexpensive, simple method envisioned by early researchers, the hydration process may be understood and generalized to natural and some man-made glasses, and OHD may yet become a reliable chronometric tool. The possibility that obsidian hydration and exchange data may yield important palaeoclimatic data further illustrates the importance of continued refinement of the method.

In order for obsidian hydration dating to become reliable, several avenues of research need to be pursued. To begin with, the evolution of an obsidian hydration rim with time needs to be understood. This is best done by combining analysis of short-term, high-temperature experiments with similar observations on archaeological specimens, all from the same obsidian source, from a variety of ages and environments. A similar approach can be used to quantify the effect of obsidian chemistry and environmental variables, particularly temperature and relative humidity. In addition, the effects of the various processes outlined above (e.g., dissolution, compositionally-

dependent diffusion, reaction, non-Fickian diffusion) need to be considered in more detail and the sources of the observed near-surface perturbations understood. Finally, the possibilities of using either temperature–humidity–time variations or stable isotopic measurements to constrain paleoclimates needs to be fully explored. Such a multi-focus approach is necessary if the potential of hydrated obsidian to provide high-precision chronometric and/or palaeoclimatic data is to be realized.

Acknowledgements

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