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Dating New Zealand Obsidians by Resonant Nuclear Reactions

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ABSTRACT

Measurements of hydration depths of prehistoric obsidian artefacts by thin-section techniques have yielded dates of mixed accuracy in different parts of the world, but have been notably unsuccessful in New Zealand. Resonant nuclear reactions, widely employed to study surface diffusion in solids, were attempted on Mayor Island obsidian from New Zealand. It was found that artefacts of varying ages have hydration rinds of very similar overall thickness and that the relationship between the theoretical and actual character of the diffusion front is more complex than is widely assumed.

Keywords: RESONANT NUCLEAR REACTIONS, OBSIDIAN DATING, FLUORINE PROFILES, HYDROGEN PROFILES.

INTRODUCTION

In 1960, Friedman and Smith published a paper which established that the manufacture of prehistoric artefacts could be directly dated by measuring the depth of hydration which had occurred on the fresh surface cleaved by prehistoric man. Since that time no fewer than four entirely different techniques have been developed to measure this microscopic band of hydration. Friedman's method relied on the preparation of thin sections, the identification of the layer by virtue of its birefringent properties under polarised light, and its measurement with a special Vicker's image splitting microscope. There have been many variations on this basic theme since. Measurements to within ±0.2μm can be achieved with this method, corresponding to a typical dating error of ±15–±20% over the last millennium. An obvious disadvantage of the method is that it is partly destructive of artefacts. In New Zealand, obsidian chips are very common on archaeological sites, and so this is not necessarily a serious drawback.

New Zealand archaeologists were quick to take advantage of this new method, and Ambrose and Green reported encouraging results on no fewer than 100 obsidian specimens in 1962. This was followed in 1964 by a second paper giving the details of measurements ranging from 0.8–2.0μm from several archaeological sites (Green 1964). The relative dating of these sites by the hydration depths appeared to closely follow the order of age established by other archaeological means. Thus, early indications were that this technique of dating would have a rosy future in New Zealand. Ambrose and Green (1962) recognised the importance of keeping a close watch for changes in hydration rate from one source to another and for different environmental temperatures throughout New Zealand. There are about 18 sources of obsidian in New Zealand; one of these, a green variety from Mayor Island, is especially common in archaeological sites. For this reason, it was chosen for this early pilot study and also for the research reported in this paper.

After this brief initial flurry of research, very little was done in New Zealand until about 1970. In that year, the necessary thin-sectioning equipment and high quality

microscope were obtained at Otago University, and the threads of the research were again taken up. However, despite cutting up large numbers of obsidian artefacts of various ages, clear hydration bands could not be found, and therefore could not be measured. In 1976, one of us (Leach) was determined to get to the bottom of this problem and spent several weeks in Friedman's laboratory in Denver, cutting up many more artefacts spanning the prehistoric period. The results were far from satisfactory. Although what appeared to be birefringence could be seen extremely close to the surface of the Mayor Island artefacts, two problems were manifest:

(i) On the one hand, doubt was expressed as to whether what was seen in thin section was actually hydration at all. One alternative possibility was that the rapid change in refractive index at the section edge was causing a "becke-line" (Krumbein and Pettijohn 1966:386). This can easily be confused with a very thin band of hydration, especially if the microscope is slightly out of focus.

(ii) On the other hand, a sharp diffusion front could not be discerned on any of the artefacts — the small band of supposed birefringence merged imperceptibly into the background of the obsidian. Where should we measure the front of any hydration?

In the meantime, in 1974, Lee *et al.* had published a paper describing an entirely new way of measuring hydration depth on obsidian artefacts. They used a fluorine ion beam in an accelerator to perform a nuclear reaction with the hydrogen in the band of hydration at a resonant energy of 16.45 MeV. The technique is limited to depth profiling to only about 2μm. Of particular importance was their finding that tektite samples had hydrogen "distributions characterised by gently sloping exponential diffusion profiles, rather than steep diffusion fronts observed in hydrated obsidians" (Lee *et al.* 1974:46). These tektite samples did not have visible hydration bands in thin section, despite the fact that water had diffused into their surfaces. This seemed to be a possible explanation for the curious results obtained on Mayor Island obsidian.

Since 1974, there has been a resurgence of interest in applying accelerator techniques to the dating of stone tools by virtue of migration or diffusion of several species into or out of the artefact surface following its manufacture by man. Table 1 shows some of the reactions which have been attempted to document the diffusion of fluorine, hydrogen, sodium and nitrogen into artefacts.

Two new techniques have appeared since the first application of accelerators to this dating problem. Experiments have been carried out exchanging the water in obsidian with external tritiated water (Lowe 1977). Estimation of the degree of hydration is achieved either by direct measurement of β emissions from the obsidian surface (the obsidian is a natural scintillator) or by back exchanging and counting aliquots in a scintillation counter. There are several complications with this method — for one thing, some New Zealand obsidian types are quite radioactive and already exhibit a significant level of β activity (see Leach *et al.* 1978). Despite this, initial results with the method are very encouraging, and certainly warrant further research. One important advantage of the technique is that no assumptions need be made about the exact nature of the diffusion process. It is the quantity of water which has diffused rather than its depth which this technique measures. A disadvantage is that β emissions will travel up to only 1.3μm in obsidian, and this is an effective limitation on the surface counting method.

The fourth method was developed by Tsong *et al.* (1978). This involves sputtering the artefact surface at a controlled rate of about 10μm per hour, with an 18 KeV argon ion beam. The ejected species can be identified by standard optical emission spectroscopy. In the case of hydrogen, a monochromator is set at a wavelength of 6563 Å corresponding to the small hydrogen peak, and emissions are counted with a photomultiplier. This enables the hydrogen profile to be reconstructed with considerable accuracy. Ziegler *et al.* (1978) reported a refinement to the technique which eliminates the signal from the crater rim. They combined an electronic signal rejection method with scanning the ion beam over a diameter of 85μm. The absence of this refinement

TABLE 1

A SELECTION OF NUCLEAR REACTIONS WHICH HAVE BEEN ATTEMPTED ON ARTEFACTS FOR DATING PURPOSES

Fluorine	$^{19}F(p,\alpha\gamma)^{16}0$	Taylor 1975
	$^{1}H(^{19}F,\alpha\gamma)^{16}0$	Lee *et al.* 1974
Hydrogen	$^{1}H(^{15}N,\alpha\gamma)^{12}C$	Lanford *et al.* 1976, Lanford 1977.
	$^{1}H(^{7}Li,\gamma)^{8}Be$	AURA, Leach and Naylor 1977.
Sodium	$^{23}Na(p,\gamma)^{24}Mg$	Lee *et al.* 1974.
Nitrogen	$^{14}N(p,\gamma)^{15}0$	Ettinger and Frey 1976.
	$^{15}N(p,\alpha\gamma)^{12}C$	Ettinger and Frey 1976.

in the obsidian studies to date could explain the almost ideal hydrogen profiles which have been obtained. These may exhibit a smearing effect caused by information continuing to arrive from superficial depths around the crater rim. This sputtering technique is a very promising development.

THE DIFFUSION MODEL

Before describing our own experimental research, it is necessary to briefly consider the diffusion model itself. In point of fact, there is little agreement about the precise method by which water finds its way into obsidian, nor indeed what the diffusion profile really looks like. Friedman and Smith originally suggested that the diffusion
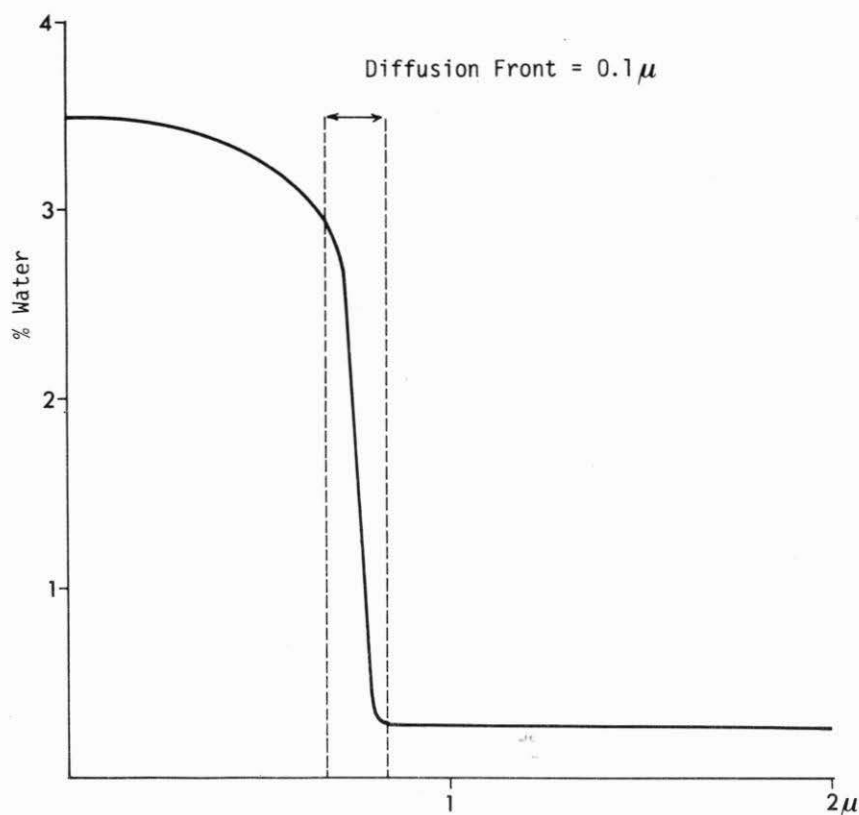

Figure 1: Friedman's diffusion model. This supposes that the diffusion front is very steep, and therefore easily observed under a microscope.

front is characterised by a very steep change in the concentration of water, and that this sharp "front" can be accurately located with thin section microscopy (Friedman and Smith 1960; see also Friedman *et al.* 1966:326). This model is illustrated in Figure 1.

Another model has been proposed by Haller (1963), and, on the whole, this is now preferred by people investigating obsidian dating. This proposes that the diffusion front is actually a wide band of progressively falling concentration of water, rather than a sharp front as suggested by Friedman and Smith (1960). The sharp change which is observed under a microscope probably corresponds to a becke-line caused by the rapid change in refractive index at the point of gradient inflection at the maximum depth of the concentration profile (Fig. 2). This difference in model is of considerable importance for two reasons: firstly, if for any reason this gradient inflection is
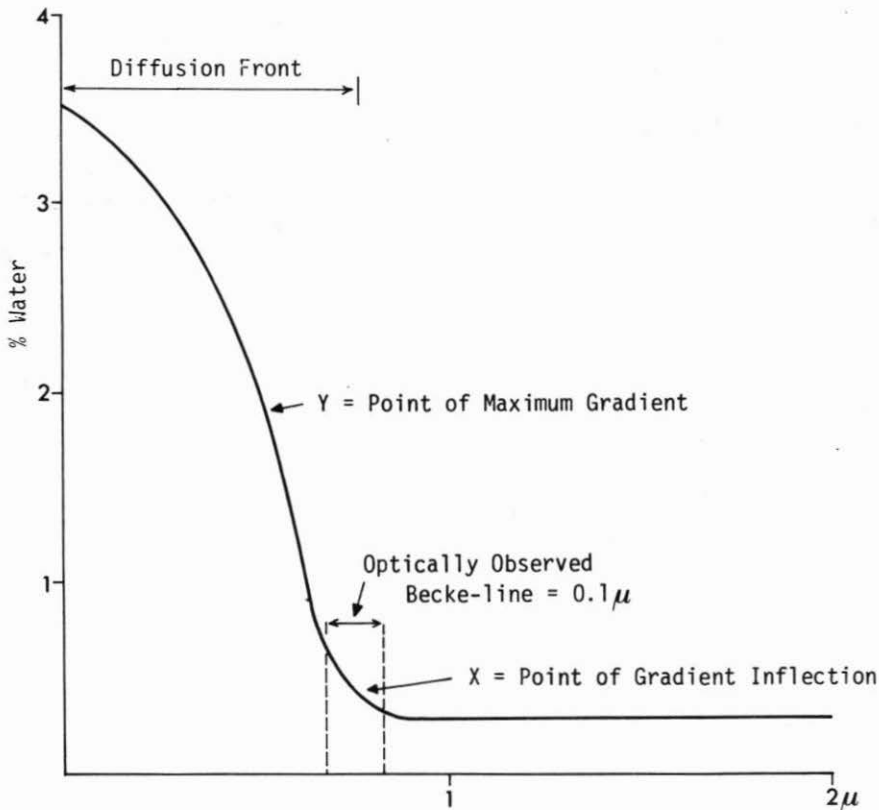

Figure 2:   Haller's diffusion model. This supposes that the front is a zone of gradual change, the maximum depth of which in some cases would be extremely difficult to identify under a microscope.

not especially marked, as in the case of tektites, the front of the diffusion profile will be difficult if not impossible to observe under a microscope. Secondly, if Haller's model is more correct, there will be a consistent discrepancy in the results reported so far for accelerator and optical techniques. People working in both fields are *attempting* to measure the same point, that is the width at half maximum (WHM), corresponding to the point of maximum gradient on Haller's figure. The optical method, however, *in practice* would be identifying a point which approximately corresponds to the width

at tenth maximum (WTM). This discrepancy between the two types of measurement could be 1μm or more, depending on the age of the sample.

Unfortunately, making such fine distinctions, irrespective of their importance, can be very difficult when it comes to interpreting experimental results from the real world. Counting errors and other uncertainties combine to blur our knowledge of the exact nature of the diffusion front in different obsidians. In our view, it would be wise at this stage for researchers in both fields of optical and accelerator methods to adopt a convention of measuring depths at tenth maximum (WTM). In this case, there is unlikely to be a consistent discrepancy, regardless of which diffusion model is more correct.

From the foregoing, it should be clear that there is an urgent need to learn something definite about the nature of diffusion profiles for Mayor Island obsidian, before considering how they might be used for either relative or absolute dating. This is what our experimental research has been aimed at.

FLUORINE PROFILES

The first type of profile reconstruction attempted was with fluorine. This element has been shown to diffuse either into or out of prehistoric artefacts at predictable rates for several rock types, including quartzite and trachyte. Theoreticians have suspected that the diffusion of fluorine and water are two related processes. For example, it
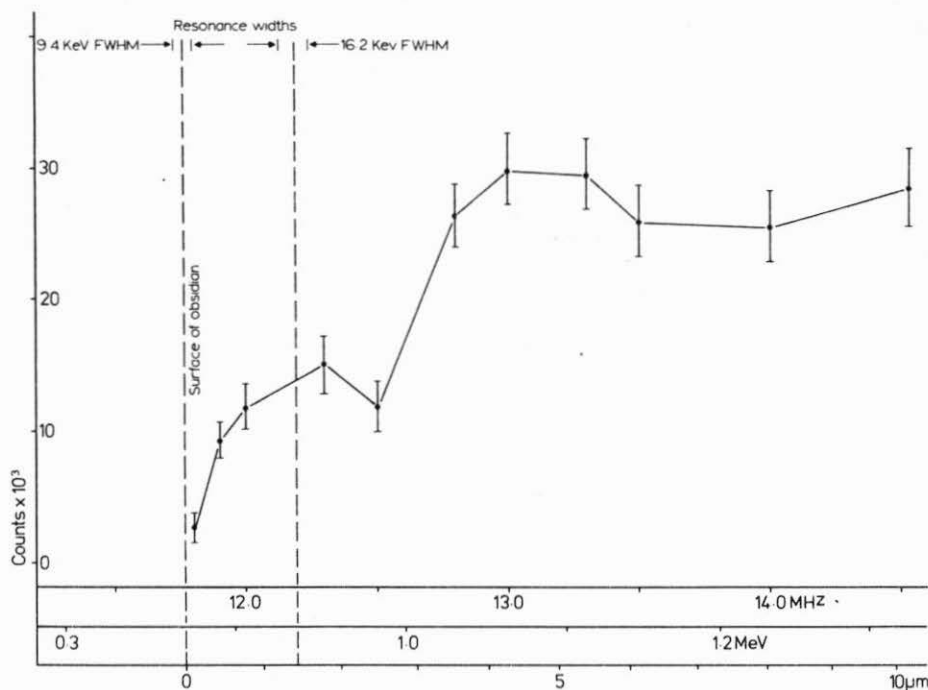

Figure 3: Fluorine profile of freshly cleaved Mayor Island obsidian using the nuclear reaction $^{19}F(p,\alpha\gamma)^{16}0$. Resonance peaks are at 872.11, 935.4, 1347.7, 1373.0, 1694.0 KeV. Stopping power was calculated to be 0.045 MeV/μm. The beam width was 4mm square and slit width 2mm square. The γ peaks counted were 6.14 MeV + two escape peaks at 5.12 and 5.63 MeV. The detector was a Ge(Li) crystal mounted 25mm from the target at 90° to the beam. Depth resolution = Resonance width (HWHM)/Stopping power = ± 0.05μm.

is well known that in hydroxyapatite structures (such as teeth) the presence of fluorine inhibits the diffusion of hydroxyl ions (Taylor 1975:128). Similarly, research in Japan has shown that in glasses there can be an inverse relationship between water and fluorine concentrations (Noshiro and Jitsugiri 1973). It seemed pertinent therefore to examine the fluorine profile as well as that of water in the study of Mayor Island obsidian.

The nuclear reaction used was $^{19}F(p,\alpha\gamma)^{16}O$, which has two useful resonance peaks at 872 and 935 KeV. The AURA II folded tandem accelerator at the University of Auckland was used for the experiments. This reaction has been extensively used by Taylor (1975) in attempts to date stone artefacts. Figure 3 shows the fluorine profile in a fresh piece of Mayor Island obsidian, cleaved immediately prior to analysis. This reaction is particularly useful because unlike many which are used for studies of water diffusion, the depth penetration can easily reach 10μm without undue complications. Depth resolution is about ± 0.05μm at the surface. The next resonance peak occurs at about 1.35 MeV (corresponding to about 11μm depth). On the whole, this reaction seems ideal for profile reconstruction of artefacts. In the case of this type of obsidian, however, other factors intervene.

The predicted gamma yield for a fresh piece of obsidian, assuming that the fluorine concentration is uniform irrespective of depth, is similar in overall shape but not in detail to that obtained for Mayor Island obsidian (shown in Fig. 3). It is sufficiently different to cast serious doubt on the all important assumption of homogeneous fluorine concentration in natural material. If the reconstructed profile in artefacts is to be at all meaningful, one must assume that the background level in fresh material is very uniform. The fluorine concentration between 2 and 4μm in this sample is not the same as further into the obsidian.
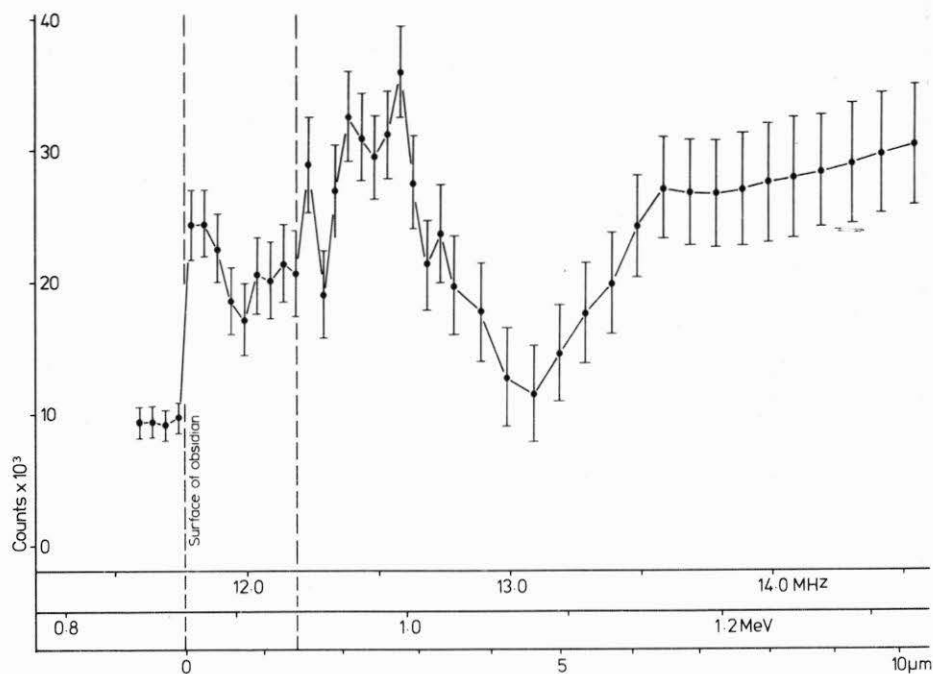

Figure 4: The fluorine profile (background subtracted) of an assumed Mayor Island artefact from under the Rangitoto ash on the Sunde site (N38/24) on Motutapu Island. The age of this sample is believed to be 600 years BP.

Figure 4 shows the net fluorine profile after the curve for fresh obsidian has been subtracted off (or unfolded from) an artefact. Firstly, this profile shows that the overall fluorine concentration is considerably higher than that of the control sample (Fig. 3). This is evident from the high gamma yield deep inside the artefact where it should be zero. Thus, one of the important assumptions in using such a nuclear reaction for dating falls by the wayside. It will be noticed that there is a rising net yield up to about 3µm in the artefact — this could reflect fluorine depletion by a process of diffusion from the surface, but this seems unlikely, given the complicated profile further into the artefact.

On the whole, the most likely interpretation is that fluorine concentration is not homogeneous in *this* type of obsidian at least, and profile reconstruction of fluorine could not form the basis of an effective dating technique. PIGME research carried out at Lucas Heights on Mayor Island obsidian (Deurden 1980: pers. comm.) has shown a moderately high concentration of fluorine compared with other New Zealand types; but more to the point, it varies by as much as 50% from one sample to another (950–1400ppm). Whether this variation in fluorine level will lead to a similar variation in hydration rate (as predicted above) is something which has not yet been investigated.

HYDROGEN PROFILES

In order to assess the hydrogen profiles in obsidian we used a nuclear reaction with a lithium ion beam, $^1H(^7Li,\gamma)^8Be$. This has two resonance peaks — one at 3.09 MeV and another at 7.21 MeV. The latter corresponds to a depth of about 6.35µm, and
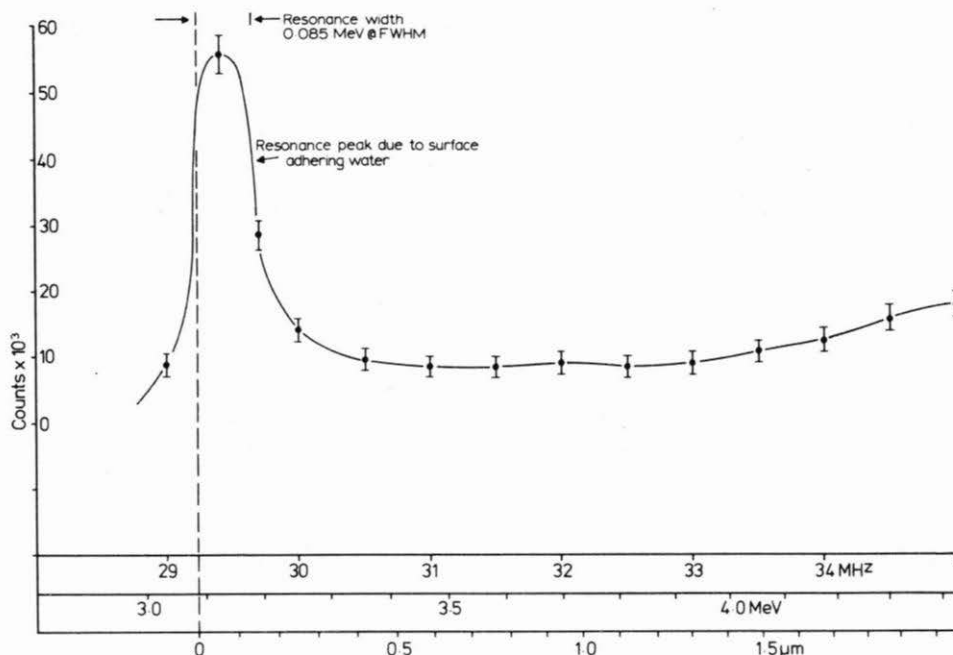

Figure 5: Hydrogen profile of freshly cleaved Mayor Island obsidian using the nuclear reaction $^1H(^7Li,\gamma)^8Be$. Resonance peaks are at 3.087 and 7.21 MeV. The stopping power was calculated as 0.65 MeV/µm. The beam width was 5mm square, and the slit width was 4mm square. The γ peaks counted were 14.7 and 17.6 MeV using a window of 10–18 MeV. The detector was a NaI(Tl) crystal 5x4 inch, mounted 25mm from the target at 90° to the beam. Depth resolution = Resonance width (HWHM)/Stopping power = ± 0.07µm.

does not complicate the profile closer to the surface. As a profiling technique, this reaction has a lot to recommend it. Depth resolution is about ± 0.07μm at the surface. The profile shown in Figure 5 is that obtained from a freshly cleaved piece of Mayor Island obsidian. The curve is almost exactly as predicted. Firstly, there is a large gamma yield at the actual surface, indicating the presence of surface bonded water. It is well known that silica-rich minerals always possess this layer of surface water; it is impossible to get rid of it even under very high vacuum at elevated temperatures. It may be noted that the full width at half maximum (FWHM) is exactly as predicted. Of equal importance, the hydrogen concentration at different depths in the obsidian is very uniform. For Mayor Island obsidian, this has been estimated at approximately 0.1–0.2% (Ewart *et al.* 1968:124). In this case, the assumption of homogeneity seems entirely justified.
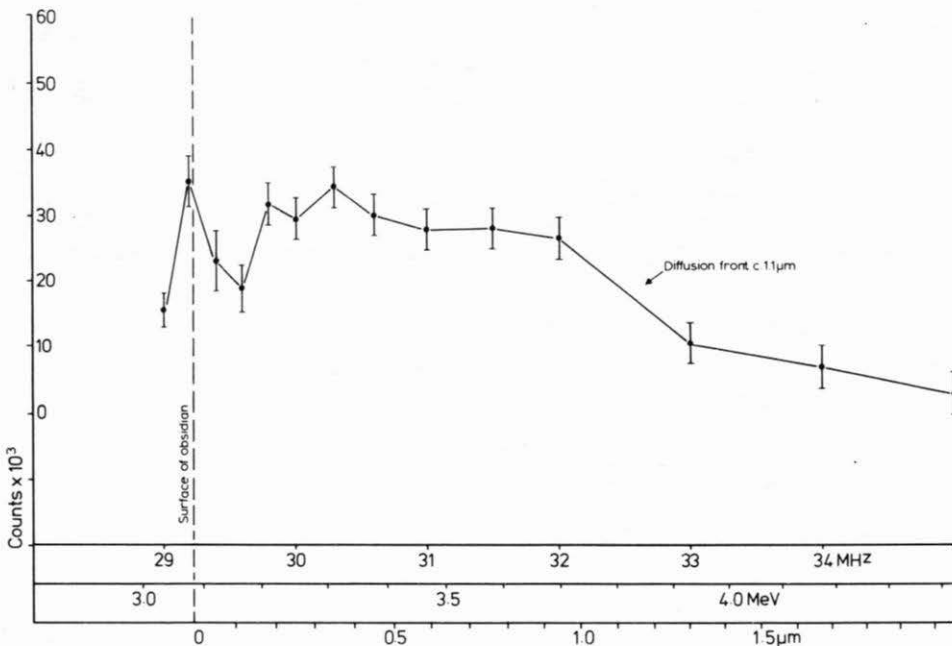
Figure 6:   The hydrogen profile of an assumed Mayor Island artefact No. AR926 from the Davidson undefended Station Bay site on Motutapu Island (N38/37), aged about 200 years BP. The background curve (Fig. 5) has been subtracted off.

Figure 6 shows the hydrogen profile for a 200-year-old artefact after unfolding off the curve for fresh obsidian. The characteristics of this curve (with one notable exception) closely follow that predicted by the Haller diffusion model. The exceptional feature is that hydrogen concentration does not seem to be highest immediately inside the surface of the artefact — the net yield in fact shows a small inverse peak. The obvious possibility is that too much of the assumed surface-bonded water has been unfolded off the artefact. As will be seen shortly this characteristic apparently increases with the age of the sample. It will be noticed that the gradient inflection is not very sharp, but probably occurs somewhere between 1.0 and 1.3μm. It is very doubtful indeed whether this hydration front could be detected under a microscope.

Figure 7 shows the unfolded profile for the same 600-year-old artefact used in Figure 4. There are two features which are notable. Firstly, the concentration gradient up to about 0.5μm is very flat, again suggesting that too much surface-bonded water has been subtracted. Secondly, the artefact has a lower bulk water content than the control
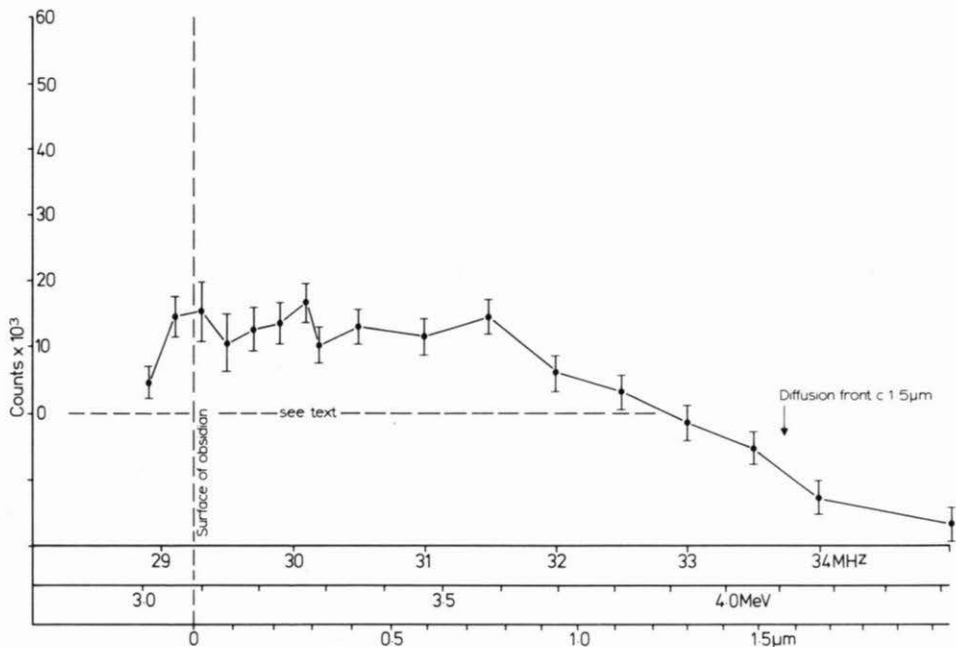
Figure 7:   The hydrogen profile for an assumed Mayor Island artefact No. A13 from the Sunde site (N38/24) under the Rangitoto ash on Motutapu Island, aged about 600 years BP. The background curve (Fig. 5) has been subtracted off. Note that deep inside the artefact the water concentration apparently falls below zero. This indicates that water concentration varies within the Mayor Island source.

sample of fresh obsidian. This is evident from the net yield falling below zero, deeper into the artefact. This shows that water content varies significantly within this one source of obsidian. According to Haller's model, the overall diffusion rate should be lower in this artefact than the one shown previously. Again, the front of the diffusion profile shows only a slight gradient inflection, and occurs at about 1.5μm.

Figure 8 shows the results for an artefact securely dated to 770 years BP, and shows even more clearly the extent to which surface-bonded water is reduced with age. In this case, after unfolding off the control profile we are left with a zone of apparent depletion inside the artefact.

From the foregoing illustrations it must be clear that identifying the width at tenth maximum (WTM) for these artefact profiles is far from easy. It is interesting to note that many of the papers written on this subject claim that surface nuclear reactions are capable of yielding more precise results than optical microscopy. This view is unduly optimistic; in point of fact, the advantages are not likely to relate to precision of overall depth measurement. In the case of the lithium ion reaction, depth resolution is, strictly speaking, the resonance half width divided by the stopping power, and corresponds to about ± 0.07μm. However, this merely tells us how accurately we could reposition the resonance reaction at a certain depth. The accuracy of measuring the depth of diffusion is an entirely different matter. In the case of the profiles illustrated here, this precision is ± 0.2μm at best, and that is directly comparable to Friedman's optical method. Of course, in the case of these particular artefacts it is very doubtful whether optical methods could reveal the diffusion front at all, since the profiles illustrate gradual changes in water
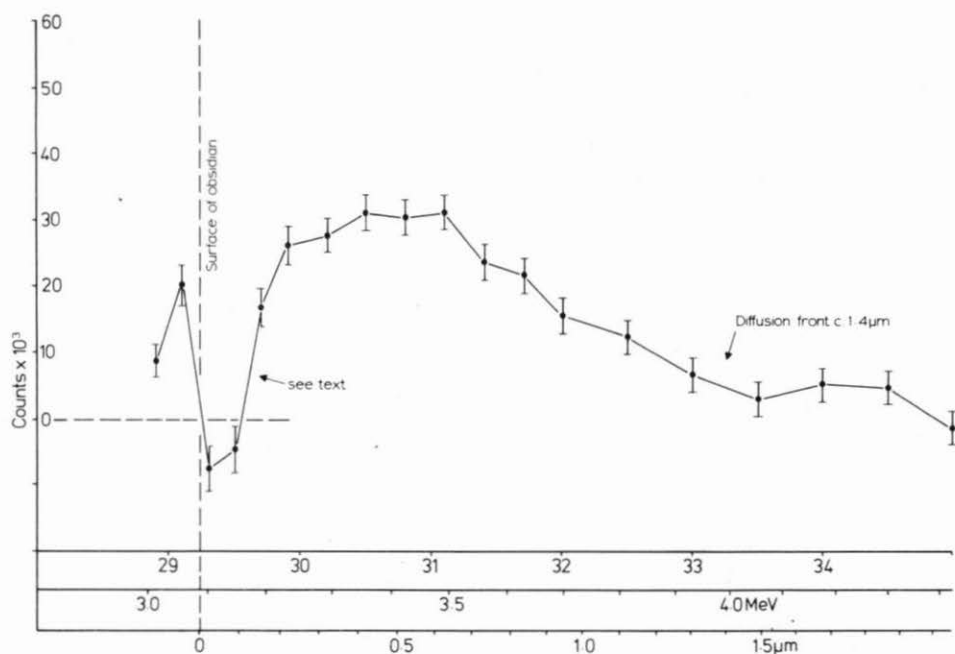
Figure 8:   The hydrogen profile for an assumed Mayor Island artefact No. AE261 from the Washpool Midden site (N168/22) in Palliser Bay, aged about 770 years BP. The background curve (Fig. 5) has been subtracted off. Note that the surface-bonded water is considerably less in this sample than others, and apparently decreases with age of sample.

concentration, rather than a sharp front. The hydration depth results for six artefacts looked at are summarised in Table 2. All but #3 are securely dated by radiocarbon determinations. Artefact #3 is a surface collected item from the Manukau area, and was included to try and establish the age of an unknown, as a test of the method. At first inspection of Table 2 there does not seem to be much of a correlation between depth of diffusion and age of artefact. A widely held model proposes that hydration depth increases arithmetically with the square root of the age of the sample. There is growing evidence that this view is simplistic.

Several authors have suggested that the rate of diffusion in obsidian is a complicated balance between at least two autocatalytic processes (Leach 1977:124), and that the rate could well vary during the life of the artefact in an archaeological site. In addition, it is known the hydration rate varies from one source to another because of internal chemical composition changes (Friedman and Long 1976). On the one hand, an increasing quantity of water in the glass lowers the viscosity and increases the diffusion coefficient. On the other hand, the presence of water in the glass places the structure under compression, and this will decrease the diffusion coefficient (Leach 1977:124; Charles 1958; Ericson 1975:154). According to the balance of these two factors, the shape of the diffusion profile will vary accordingly (for details of this, see Haller 1963). Some authors are now drawing attention to profiles in obsidian which have more than one concentration plateau, confirming the complexity of the process (see for example Ericson 1975:155).

In the case of Mayor Island obsidian, the results in Table 2 suggest that diffusion up to 1μm occurs very rapidly, certainly within the first 200 years. Thereafter, the diffusion rate appears to be considerably slower. As will be seen below, these results make more sense when viewed against their environmental temperatures.

Mean annual temperatures for the various sites were estimated from published climatological data (Robertson 1960). Sample provenances are: #1 = Motutapu undefended site (N38/37), AR926. #2 = Sunde site (N38/24), Motutapu Island, from under the Rangitoto ash, artefact Number A13. #3 = surface collected artefact of unknown age from Manukau area. #4 = Washpool Midden site (N168/22), Lens B, artefact Number AE261. #5 = Waihora village (C240/283), Chatham Islands, artefact Number AA520. #6 = Tiwai Point (S181-2/16), artefact from TW-D31-1b.

Item	Age (years BP)	Hydration depth	Temperature
#1	200	1.1μm	14.2°C
#2	600	1.5μm	14.2°C
#3	?	1.2μm	13.1°C
#4	770	1.4μm	11.9°C
#5	400	0.9μm	11.5°C
#6	700	0.9μm	9.7°C

SURFACE-BONDED WATER

Returning to the subject of surface-bonded water, the results here are most interesting. It is clear from Figures 6–8 that the assumed amount of surface adhering water is not a constant but apparently decreases with increasing age. This phenomenon could be of use in dating relatively young samples. It is unlikely, however, to be a linear process throughout the total life of an artefact, although these few results may suggest this for the first millennium.

It makes sense that as the water content inside the glass rises with age, so the degree of attraction to additional water should fall. It is also possible that surface oxidation may be inhibiting the water attraction. It must be remembered that glass is not a static medium. On the one hand, it is strictly speaking a supercooled liquid and the surface is progressively deforming with time. On the other hand, the acquisition of water into the surface, is itself the cause of a swelling process — this is readily observed with an interference microscope. Given these changes at the surface of an artefact, it is hardly surprising that the amount of water actually attached to the surface should change with time.

ENVIRONMENTAL TEMPERATURE

The thermal history of an artefact since it was manufactured is known to have a marked effect on the diffusion coefficient (Ambrose 1976), and, although too few data are available to be certain, this factor could explain the apparent lack of correlation of hydration depth with age for the samples studied.

Insufficient work has been done on establishing the relationship between thermal activity and the diffusion rate constant for Mayor Island obsidian. Some information is available, and this could be used for examining the relationship between age and hydration depth for these artefacts. It must be stressed that there are considerable uncertainties in pressing forward with such calculations, but the attempt is worthwhile if it only serves to point to areas where refinements in methods are needed. With this caveat clearly in mind, closer examination of the results does seem to indicate that the older artefacts from cold environments have hydrated a similar amount to young artefacts from warmer environments.

The relationship between the diffusion rate constant and environmental temperature can be expressed as:

$$k = A\,e^{[-E/RT]} \quad \text{...} \quad (1)$$

where k = the diffusion rate constant at temperature T (per thousand years)
   A = a constant, related to the type of obsidian

E = the activation energy in cal/mole
R = the gas constant = 1.987 cal/mole/°Kelvin
T = the absolute temperature (°Kelvin).

Experiments carried out by Friedman *et al.* (1966), Friedman (1976), and Ambrose (1976) have resulted in reasonably uniform estimates for the activation energy of obsidian. For instance, artefacts from Gardiner, Montana, have yielded an estimate of 1.9580×10^4 cal/mole,[1] and others from Pine Mountain, Oregon, yield a figure of 1.9220×10^4. Obsidian from Whangamata, near Taupo in New Zealand, has been investigated, and the equation parameters can be estimated from the Arrhenius plot given by Ambrose (1976:98) by fitting an exponential curve of $y = ae^{bx}$ to his line, where E is the slope (b). This yields a value of $E \simeq 1.6913 \times 10^4$, and is a reasonable initial estimate for Mayor Island, until further information is to hand. The real difference between one type of obsidian and another is expressed by the constant A. This is the intercept at $1/T = 0$. Estimates for A vary considerably and express variation of factors such as the chemical composition of the different types of obsidian. For instance, the Gardiner artefacts produced a value of 6.457×10^{15}, Pine Mountain of 1.429×10^{15}, and Whangamata of 3.2087×10^{13}. Ambrose, in attempting to estimate the age of an artefact from Tokoroa (N84/1), made from Mayor Island obsidian, suggested a tentative curve for Mayor Island obsidian, from which A was estimated as 1.0469×10^{13} by us. However, this yields a base hydration rate for Mayor Island obsidian which is far too fast in our opinion. The data obtained in this study were examined by the same curve fitting procedure to give a tentative estimate of $\simeq 3.9761 \times 10^{13}$, which is about one third the rate. The various lines for equation (1) are plotted out in Figure 9. It is hoped that these will serve to promote further research into these constants. At the moment, our knowledge in this area is sadly deficient.

Establishing the age of an artefact from hydration depth, assuming constant environmental temperature, involves solving the equation:

$$M = kt^\lambda \qquad\qquad\qquad (2)$$

where M = the depth of hydration in μm
    k = the diffusion constant at fixed temperature
    t = the lapsed time in years
    λ = the diffusion exponent.

The question of what is a suitable value for the diffusion exponent has been recently reviewed by Ericson *et al.* (1976:39), and estimates were cited of 0.5, 0.75, 1.0, and even as high as 3.0 in one instance. Although a value of 0.5 is widely assumed, there is no reason why this should be the same for different types of obsidian. As Ericson *et al.* (1976) point out, the major differences between different estimates probably reflect a combination of several systematic variables at work, both intrinsic and extrinsic. The question of what this exponent is for Mayor Island obsidian is one which needs proper examination in New Zealand.

If we assume for a moment that the archaeological age estimates in Table 2 are reasonable, the value of λ can be estimated using the values for k derived from equation (1), with values for $E = 1.6913 \times 10^4$ and $A = 3.9761 \times 10^{13}$. This yields estimates of $\lambda = 1.001, 0.878, 0.871, 0.899$, and $0.851(\bar{x} = 0.900 \pm .026$ SE). These are satisfyingly consistent results, but uncomfortably different to the assumed value of 0.5.

This is a very interesting result and, if the value for λ is anywhere near the mark, may well explain why optical examination of Mayor Island artefacts has failed to show convincing hydration fronts. An exponent close to unity will result in hydration bands with fronts with a weak gradient inflection, which would be difficult to distinguish from the background water level.

Equations (1) and (2) can be combined to give a formula which relates time to the various terms mentioned above:

$$t = e^{[(\ln((M \times 10^3)/Ae^{[-E/RT]}))/\lambda]} \qquad\qquad (3)$$

By inserting the values $E = 1.6913 \times 10^4$, $A = 3.9761 \times 10^{13}$ and $\lambda = 0.9$, the ages of the various artefacts studied here and that from Tokoroa cited by Ambrose (1976:97)
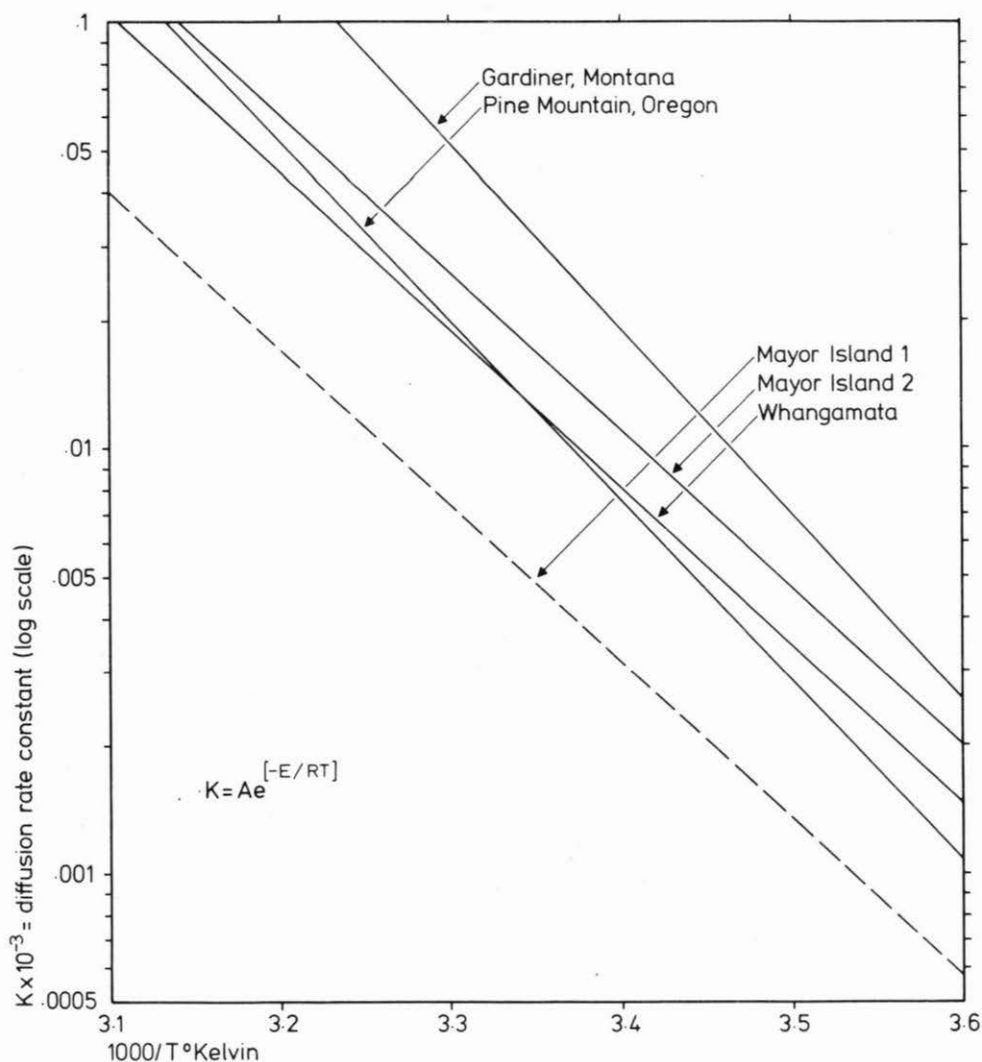
Figure 9: The relationship between diffusion rate constant and environmental temperature for different types of obsidian. Mayor Island 1 is the curve suggested by Ambrose (1976:98) after extrapolating from that established for Whangamata. Mayor Island 2 is suggested by the present work. See the text for details relating to the constants A and E for these curves.

can be estimated. The results are given in Figure 10 and Table 3 (rounded to the nearest 10 years). An experimental error of ± 0.2μm was used to assess the error of the age estimate.

These errors are clearly quite large, and illustrate the need to refine profile reconstruction if at all possible. Equation (3) is very sensitive to environmental temperature; for instance, for item #1 a value of ± Δ 1°C alters the age estimate by about 40–50 years, and this is clearly one of the most important considerations in obsidian dating.
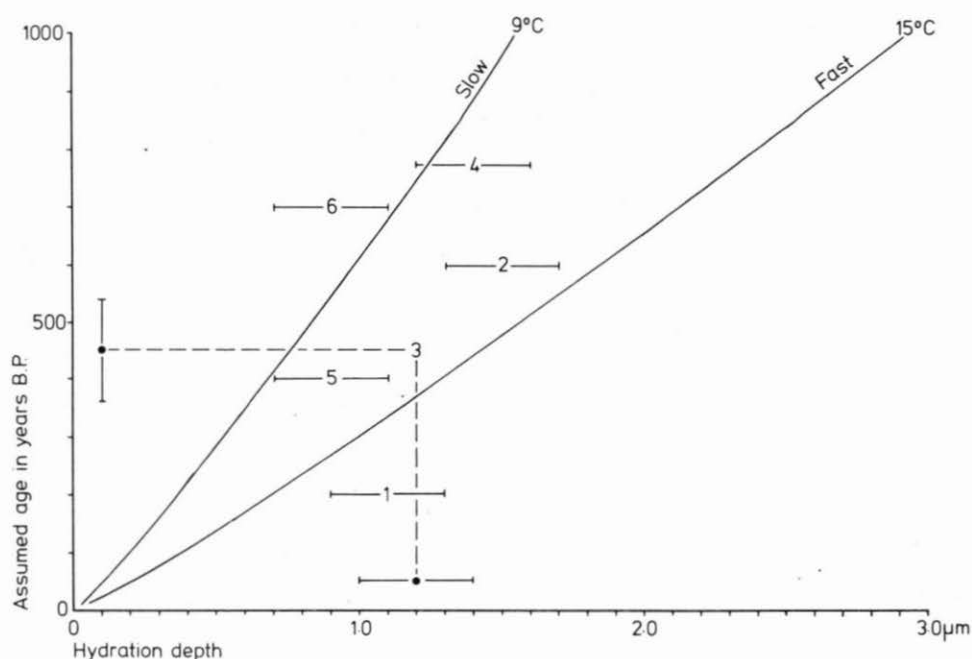
Figure 10:   The hydration depth curve of Mayor Island obsidian plotted against age for the range of mean annual temperatures in New Zealand. The curve follows the general formula $M = kt^{0.9}$. Various artefacts are also plotted with error ranges of $\pm$ 0.2µm, following the ages assumed on archaeological grounds. Details are given in Table 2. The age of artefact No. 3 is not known, and has been estimated from equation (3).

TABLE 3

DIFFUSION RATE CONSTANTS FOR THE VARIOUS ARTEFACTS STUDIED USING EQUATION (1)

The sample ages were estimated using equation (3) using a diffusion exponent of 0.9. Sample #7 is the Tokoroa artefact studied by Ambrose (1976:97) from site N84/1. The details for samples #1 to #6 are the same as in Table 2.

Item	M	T°K	$k \times 10^{-3}$	Estimated Age years BP	Assumed Age years BP
#1	1.1µm	287.4	5.459	360 ± 70	200
#2	1.5µm	287.4	5.459	510 ± 80	600
#3	1.2µm	286.3	4.872	450 ± 90	?
#4	1.4µm	285.1	4.299	620 ± 100	770
#5	0.9µm	284.7	4.122	400 ± 100	400
#6	0.9µm	282.9	3.408	490 ± 120	700
#7	1.22µm	286.1	4.772	470 ± 90	?

Friedman (1976:178–9) has shown how obsidian artefacts exposed to the sun on the surface of archaeological sites can hydrate at five times the rate of buried artefacts. On the whole, the results in Table 3 are not very promising at this stage, and, with the exception of #5, the assumed ages are outside the estimated ranges. Rather than be discouraged by this, the results are seen as highlighting areas where further work is needed.

CONCLUSIONS

Obsidian dating has a long and respectable history, particularly in America and Japan. The application of surface nuclear reactions to obsidian artefacts has revealed that the process of obsidian hydration is nowhere near as simple as previously thought. This particular study of Mayor Island obsidian yields several specific conclusions:

Firstly, the profiles obtained confirm that Haller's diffusion model is closer to reality than that of Friedman's. The gradient inflection approximately at tenth maximum (WTM) is not as sharp as that found in some other types of obsidian for which there is published information. This in part may explain why no becke-line could be observed in thin sections of Mayor Island artefacts at the front of the diffusion band. Optical assessment of hydration depth in this type of obsidian is all but impossible for the very thin bands which occur in the short duration of New Zealand prehistory of one millennium. The encouraging optical results published by Ambrose and Green (1962) and Green (1964) were, in our view, an over-enthusiastic interpretation. Despite the absence of a sharp front to the hydration bands for Mayor Island artefacts up to 1000 years old, it is suggested that measurement of hydration depth by nuclear methods should be made at a point corresponding to the width at tenth maximum (WTM). This approach more closely approximates the widespread practice in optical microscopy on other obsidian types.

Secondly, if these nuclear techniques are to be employed, it is important to establish that the particular obsidian type is in fact homogeneous at the microscopic level. This study has shown that Mayor Island obsidian is not homogeneous in terms of its fluorine content, although the background level of water does appear to be relatively uniform. Other types of obsidian may well have different characteristics. Despite this microscopic uniformity of water, there is clearly macroscopic variation — that is, water content seems to vary significantly from one piece to another from the Mayor Island source. This phenomenon can be predicted on geochemical grounds (see Friedman *et al.* 1963). This does not pose a serious problem in reconstructing the concentration profile shape, but it may result in a variable diffusion rate within the one source (however, for a contrary view see Leach 1977:124). Since fluorine is known to inhibit hydration, it follows that intra-source variation in fluorine content could be the cause of variability of hydration rate also. Mayor Island fluorine content apparently varies by 100% from one piece to another, and this is a disquieting feature. At this stage, it is not known how significant either of these two factors is in practice.

Thirdly, the amount of surface-bonded water does not appear to be a constant with artefacts of different age. It is possible that for relatively young samples, this change could be detected by some relatively simple method of measuring surface electrical properties. More to the point, this feature complicates profile reconstruction at shallow depths of up to 0.5μm. It also implies that surface nuclear reactions are not really viable for dating samples of Mayor Island obsidian with hydration up to this depth. This corresponds to between 130 and 250 years, depending on the environmental zone in New Zealand.

Fourthly, there is an urgent need to carry out basic research into the values for the three constants in equation (3). This can be done by a combination of controlled physical experiments and measurements on reliably dated artefacts from archaeological sites.

Finally, it has to be admitted that after 18 years of trying in New Zealand, we still do not have a reliable method of obsidian dating, either relative or absolute. This present study has at least revealed the reasons why optical measurements have been so difficult and unreliable in the past. This should not be seen as a counsel for despair, but merely a cautionary tale. With perseverance we may yet crack the nut.

Notes
1. The values for A and E from this experiment are incorrectly cited by Friedman (1976:178), but it is perfectly clear that $E = 1.9580 \times 10^4$, not 6.457×10^4, and $A = 6.457 \times 10^{15}$, not 1.9580×10^{15}.

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