



## POWDERED OBSIDIAN FOR DETERMINING HYDRATION RATES AND SITE THERMOMETRY

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### ABSTRACT

Obsidian hydration dating shares the disadvantage of all the chemical reaction dating systems in its reliance on experimentally determined short-term rate constants for long-term age extrapolation. In archaeological applications the extrapolation may need to encompass local edaphic variation and longer range environmental changes. Before the contribution of these varying field related rate determinants are considered the initial trajectory of the extrapolation needs to be determined. In many studies the extrapolation is circumvented by adopting radiometric systems that provide reference-age frameworks that are then used to calibrate hydration depth readings. The relative hydration ages that are attached to the reference age still require -that the hydration rate constants be experimentally determined. This is to ensure that any discrepancies between the observed artefact hydration readings and the experimentally found hydration rate can be identified and, if possible, explained. Given that deposit perturbation and artefact weathering are factors in many archaeological sites it is therefore still necessary to know the inherent hydration rate of the obsidian being dated. This paper seeks to develop obsidian powder systems to derive short-term rate constants that can apply to ambient conditions at archaeological sites. Three cases employing obsidian powders for hydration dating research are

presented here in pursuit of this aim. The first case employs rate constants estimated from the powder data and optically measured hydration; the second combines obsidian powder data and SIMS measurement on solid flakes; the third case attempts to apply simple powder diffusion data to determine effective hydration rates at two sites near Talasea in Papua New Guinea (Figure 1). The results of the powder experiments support the view that 'water' rather than H alone is responsible for the hydration process.

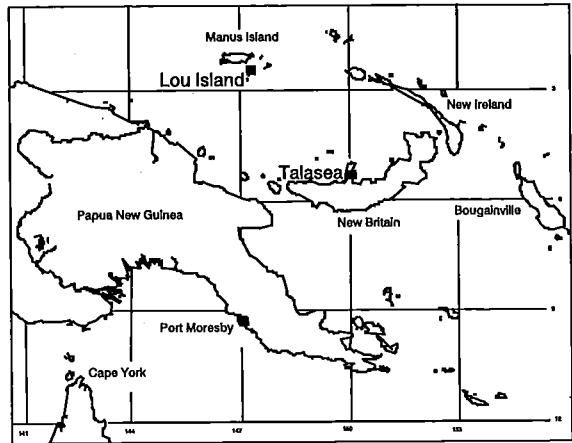


Fig. 1: Location of the two obsidian source regions providing the material used in the powder experiments at Lou Island and Talasea.

**KEYWORDS:** obsidian, hydration, thermometry, SIMS

## INTRODUCTION

### *Measurement of hydration rates*

For most archaeological applications microscopy remains the standard measurement tool for obsidian hydration studies and, to a large extent, this has influenced the experimental methods used to determine relative hydration rates. The most direct method to extract rate constants would be to expose obsidian flakes for finite periods, at known temperatures, to produce sufficient hydration for measurement with standard optical microscopy. Unfortunately this is not a feasible procedure at normal ground temperatures due to the long exposure times necessary to induce clearly measurable hydration. For example, the experimental laboratory exposure of obsidian flakes from several southwest Pacific sources, to temperatures of 10°C, 20°C, 30°C and 40°C for about twenty years, has induced hydration of around 0.3µm, 0.5µm, 0.7µm, and 1.0µm respectively. Only the 30°C and 40°C specimens developed sufficient hydration to be measured by standard microscopy. A different

widely adopted procedure is to use high temperature exposure (>90°C), in order to induce an optically measurable hydration effect over a shorter period of days or months, that can then be extrapolated to normal terrestrial temperatures (Michels *et al.* 1983).

Doubt about the limits of optical microscopy has encouraged the alternative measurement system of secondary ion mass spectroscopy, SIMS, that is able to define hydrogen diffusion depth profiles in the sub-micrometre range (Anovitz *et al.* 1999). The optical effects identified as hydration in microscopy, and the hydrogen profiles shown in SIMS, raise the question of whether H<sup>+</sup>, OH<sup>-</sup>, H<sub>2</sub>O, or H<sub>3</sub>O<sup>+</sup> is diffusing into obsidian. Many studies that report molecular H<sub>2</sub>O diffusion base their evidence on infra-red spectroscopy of silicate glasses (Doremus 2000, 1999; Hepburn & Tomozawa 2001; White 1988). As pointed out by Riciputi *et al.* (2002) SIMS analyses exhibit characteristic hydrogen related diffusion profiles, whereas within the SIMS experimental error of <0.1wt% the oxygen content remains constant across the same depth and that

therefore hydrogenation is a better term than hydration for the observed effect. The reaction of diffused hydrogen within the obsidian could produce hydroxyl and water identified in IR absorption bands but the presence of these does not necessarily indicate how they are formed. On the other hand White (1988) considers that the few if any non-bridging oxygens in obsidian leads to the conclusion that hydration is a process of replacing alkali ions by hydronium ions. Since the main archaeological purpose of any hydration measurement is to determine its depth for dating purposes, the identity of the diffusing material is usually of minor importance. However, this becomes an essential factor when calculating diffusion depths from experimentally derived diffusion rates calculated from the mass increase of obsidian powders during controlled time and temperature exposures.

The basic equation used to find the hydration age of an obsidian artefact requires the measurement of the hydration thickness  $L$ , and the rate of its growth  $k$ , into an obsidian surface. Another necessity for determining hydration rates on both powder and solid flakes is a series of measurements at different time intervals that allow the time dependence  $t^n$ , of the rate  $k$  to be calculated. The conventional time exponent is 0.5 giving the equation:

$$k = L / t^{0.5} \quad (1)$$

As well as yielding data on hydration depth SIMS analyses have been used to question the conventional square root time ( $t^{0.5}$ ) dependence of the hydration growth rate by Riciputi *et al.* (2002) who arrive at a high value of  $t^{0.757}$  in their study of artefacts from the Chalco Mound archaeological site, Mexico. Their time dependent growth rate calibration is calculated from SIMS measurements on archaeological obsidians from radiocarbon-dated contexts. The acceptance of the radiocarbon dates as a precise chronometric for the related hydration in the obsidian specimens is problematic and an un-

sure calibration system on which to establish the essential  $t^n$  constant. The careful excavation and depositional integrity of the Chalco site has not escaped the usual misalignments of radiocarbon dates and stratigraphy that most archaeologists are familiar with. For example an inversion in calibrated radiocarbon dates is explained as a result of rodent burrowing. This misplacement is not an unusual occurrence in archaeological sites but it does call for caution in the general practice of using radiocarbon determinations as proxy calibration points for the obsidian dating system. The problem of obsidian surface dissolution should also be addressed when hydration rates are derived from archaeological obsidians without any supporting experimental data. The juxtaposition of a radiocarbon dated deposit and an obsidian hydration thickness depleted by surface loss would require a decrease in the rate constant  $k$  or an increase in the exponent of time ( $t^n$ ) to match the hydration chronology to the radiocarbon age. A value of  $t'$  could indicate a high surface loss rate, while the precision of the SIMS method would be irrelevant for determining hydration rate constants from the reduced hydration depth.

#### *Powder based rates*

The calculation of hydration rates for multiple obsidian sources at normal site temperatures could be ideally achieved with greater access to SIMS, although this would still require multi-year experimental exposure of obsidian flakes in controlled temperature conditions. Reduction of glass to powder is an alternative system used in hydration (Haller 1960) and surface reaction rate experiments, for example in studies of ion exchange in glass-water surface interaction of nuclear waste glasses (McGrail *et al.* 2002). In the case of obsidian the weight gain of a powder, exposed to normal temperature and humidity, can give an indication of the diffusion velocity and the nature of the diffusing material. The working

assumptions behind this procedure are, that the weight gain of a powder exposed to saturation vapour pressure is directly attributable to diffusion of molecular water, hydroxyl or hydrogen, and that their density  $d_h$  in the obsidian does not alter significantly within the temperature range experienced in most soil environments. An additional assumption is that ion exchange of the diffusing material with mobile cations in the hydration zone does not remove them from the powder system. If the conventional assumption correctly identifies molecular water as the diffusing species in the low temperature hydration of obsidian, then the powder-based system could rely on the fact that  $1\text{g H}_2\text{O/m}^2$  is equal to a water film  $1\mu\text{m}$  thick. Calculating this as a depth of hydration is straightforward using the following relationship:

$$L = \Delta m / (A d_h) \quad (2)$$

Where  $L$  is hydrated layer thickness,  $\Delta m$  is the percentage weight gain due to hydration,  $A$  is powder surface area in  $\text{m}^2$ , and  $d_h$  is the density as a percentage weight of 'water' in the hydrated zone. Alternatively the dominance of hydrogen as the diffusing element would reduce the value of  $d_h$  and as a corollary increase the estimate of  $L$ . In either case the relative hydration velocity can be measured over a short period of several months, at normal terrestrial temperatures, so long as the exposure time, surface area and relative density of the diffusing agent in the hydration layer are known. The hydration depth  $L$ , of experimentally hydrated solid obsidian flakes when known from either optical or SIMS measurement, can give the value of  $d_h$  in equation 2 and help to determine the nature of the diffusing material.

### Case 1.

#### *Umleang source (ANH 3885)*

The first of the three experiments presented here is from the Umleang source on Lou Island in the Manus Group of Papua New

Guinea. Obsidian flakes were crushed in a dry airflow with a dew point of  $-60^\circ\text{C}$ , then reduced to powder in a rotary hammer mill and sieved to produce 45-63 $\mu\text{m}$  powder fractions. These were weighed then exposed to 100% relative humidity in thermostatically controlled tanks to within  $\pm 0.05^\circ\text{C}$  (Appendix 1). The powders were used without further treatment such as acetone washing to remove finer colloidal size particles adhering to the larger particle sizes in the sieved fraction. Tailing of finer fractions can be seen in the size distribution of similarly produced powder nominally within the 38  $\mu\text{m}$  to 45 $\mu\text{m}$  range (Fig. 2). The effect of the smaller fraction will be to increase the surface area and the apparent hydration velocity over the short term, but it will also reduce the rate as the relative surface area of the diffusion front diminishes geometrically over time (Fig. 3). For this reason the experimental powder sets used in this study have been limited to one year or less.

The weight gain was recorded at 4 points in the first 6 months for powders held at temperatures of  $10^\circ\text{C}$ ,  $20^\circ\text{C}$ ,  $30^\circ\text{C}$ , and  $40^\circ\text{C}$  and calculated as one-year gains. The regression of % weight gain ( $\Delta m$ ) over time ( $t^{0.5}$ ) gave  $r^2$  values of 0.997, 0.996, 0.995 and 0.997 for the four respective temperature conditions. Powder surface areas were determined by BET nitrogen analysis from the 45 - 63  $\mu\text{m}$  sieve fraction and gave a value of  $0.58\text{m}^2 \pm 0.03$ . The hydration thicknesses of four of the same source solid obsidians exposed at 100% rH for between 11 and 15 years at  $40^\circ\text{C}$  were optically measured using digital scanning procedures (Ambrose 1994). The mean hydration in depth in  $\mu\text{m}$  calculated for one year, from the solid  $40^\circ\text{C}$  samples, was then used to find the water content  $d_h$  from the one year powder weight gain and area from equation 2. The relevant values are set out in Table 1.

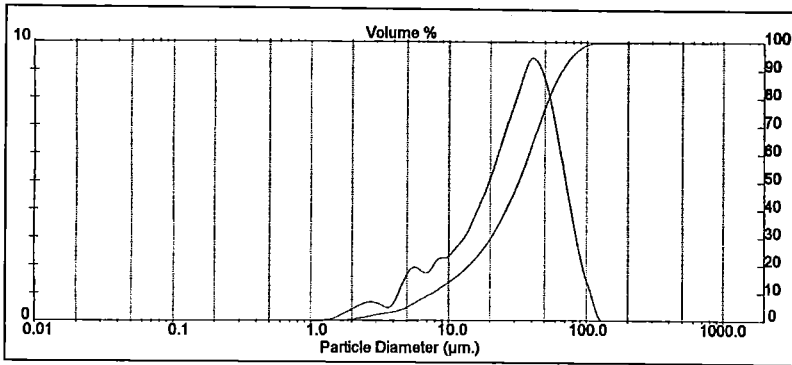


Fig. 2: Small particle size straggling in an unwashed 38 - 45 mm sieved fraction. The effective surface area will be higher than that calculated for the indicated size range. The spread of size diameters above the sieve range assumes a spherical particle whereas the crushed obsidian will have irregular axes some being longer than the limiting sieve sizes. A laser system was used to generate the powder particle size data.

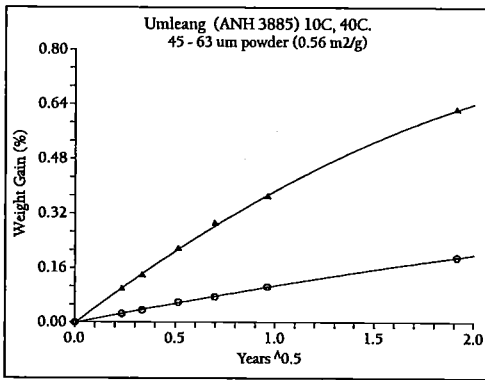


Fig. 3: Comparison of the fall-off in diffusion rate over time between the 10°C (●) and the 40°C (▼) powders inferred to be due to the diminishing geometric surface area of very small grains in the unwashed sample below the limiting sieve size.

	T (°C)	$\Delta m$ (g/g)%	A(m <sup>2</sup> )	$d_h$ (g/g)%	L (µm)	k (L/yr <sup>0.5</sup> ) predicted
<i>Powder</i>	10	0.1091	#	#	0.063	0.0639
	20	0.1808	#	#	0.104	0.1042
	30	0.2995	#	#	0.173	0.1645
	40	0.4237	0.58 ± 0.03	2.94 ± 0.10	0.244*	0.2523
<i>Solid</i> (n4) 40					0.244 ± 0.010	0.2440 ± 0.0063

Table 1: Powder weight gains and thin section hydration depth calculated as a one year exposure, to provide the hydration rate constant k for the Umleang (2883) obsidian deposit from Lou Island, Papua New Guinea. The optically measured hydration thickness derived from 4 flakes held at 40°C for periods of between 11 and 15 years gives a one year value of 0.244 ± 0.010 µm. The predicted k values are found from the regression equation of the one-year hydration thickness ln L vs reciprocal temperature Kelvin (equation 3). # indicates an assumed value. \* the hydration depth of the powder is inferred from optical-digital hydration measurements on the 4 solid flakes held at 40°C.

The relationship of hydration rate  $k$  to temperature can be expressed by an Arrhenius type regression equation:

$$\ln k = a + -b * 1/T \quad (3)$$

where  $a$  and  $b$  are intercept and slope constants and  $T$  is temperature (Kelvin).

Intermediate hydration rate values of  $k$ , from equation 3, and the temperature  $T$ , can be found from a least squares regression of the four predicted hydration values to give:  $k = \exp 11.58306 + -4058.487 * 1/T(\text{Kelvin})$ . Although the correlation between temperature and hydration depth calculated for the powder weight gain produced  $r^2 = 0.998$ , the regression produces some error when calculated as predicted values, particularly for the higher temperature 30°C and 40°C samples. The result is nevertheless within experimental error when preparation of the powder without washing out of fines is considered. The results show the feasibility of using obsidian powder for determining the hydration rate constant  $k$ , except that the data lack information on 'water' density  $d_h$  for the lower temperature exposures. Therefore it is not appropriate to simply assume that the same 40°C  $d_h$  value is applicable to the lower temperature powders for deriving the  $L$ , the hydration depth.

The data in Table 1 for the 40°C example show that the value for  $d_h$  in the hydrated obsidian powder at around 3% by weight is consistent with a form of molecular water. The figure can be compared with the original water content in the non-hydrated obsidian ranging between 0.07 - 0.10% as determined by IR spectroscopy on the Umleang obsidian, according to the protocol of Stevenson *et al.* (1993). In this case only the optically measured 40°C solid flakes were available to provide the hydration depth. The approximately 2.9% by weight of "water"  $d_h$  in the hydrated layer has been equally applied to the lower temperature powders for the purposes of this exercise, but further results outlined below indicate that "water" density may be higher in

the case of lower temperature hydration. Importantly the results indicate that the hydration is a result of  $H_2O$ ,  $H_2O$  or  $OH$  diffusion and not  $H$  alone. This is in contrast to recent SIMS analyses of Chalco obsidian where an invariant oxygen content across the hydrated zone from its surface to the non-hydrated bulk, is cited in support of the view that hydrogen alone is responsible for the development of hydration (Riciputi *et al.* 2002,1063). In order to further investigate this apparent contradiction it is informative to combine hydration depth readings provided by SIMS, and powder weight gain data on samples prepared from the Wekwok source in Case 2.

## Case 2.

### *Wekwok source (ANH 2000)*

Many studies of hydration in glasses, including obsidian, are undertaken at elevated temperatures where optically measurable diffusion profiles can be generated in a short period of days or weeks. These experimental exposures are usually well above the range of normal archaeological site temperatures but the advent of SIMS profiling introduces the prospect of experimentally exposing obsidians to shorter term normal terrestrial temperatures where hydration below the limits of optical microscopy can be measured. Even so the required exposure time of one to two years at around 20°C may be necessary to induce sufficient hydration depths of 0.1µm - 0.2µm for SIMS measurement.

Fortunately we have obsidian flakes with up to 15 years exposure at 10°C, 20°C, 30°C and 40°C that have been analysed by SIMS for their respective hydration depths. The obsidian is a sample from a single ~10 Kg boulder from an eroding pyroclastic breccia at the locally named Wekwok site on Lou Island in the Admiralty Islands of Papua New Guinea. Flakes struck from the boulder were placed in 10ml borosilicate beakers and housed in the same thermostatically controlled temperature

and humidity enclosures as the powders, as shown in Figure 12. The boulder is also used as a local secondary chemical reference standard for its homogeneity and glassy quality (Appendix 2). The SIMS data provide baseline hydration characteristics for the Wekwok source.

The SIMS hydration depth measurements made by Evans East (Figure 4), were reduced to rate constant  $k$  values using equation 1 (Table 2). An Arrhenius type curve fitted to  $k$  versus temperature has  $r^2 = 0.999$ .

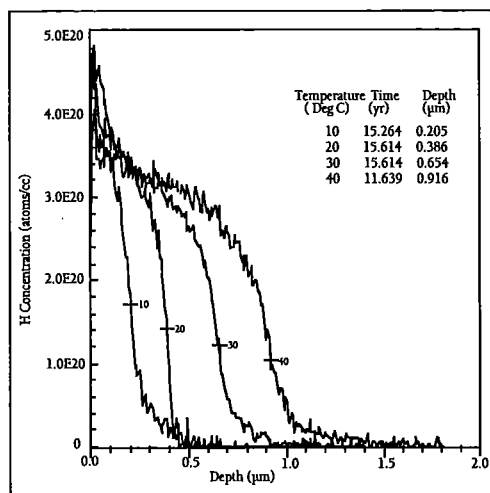


Fig. 4: SIMS hydrogen profiles on obsidians hydrated for 15.2y, 15.6y, 15.6y, and 11.6y at 10°C, 20°C, 30°, and 40°C respectively.

Powders from the same Wekwok source were exposed at 20°C, 30°C, and 40°C to complement the SIMS measurements. An estimated constant for a 10°C sample is calculated from the three measured powder samples. The powders used in these experiments were hand-sieved in closed nested sieves in air dried to -60°C dew point as with the Umlang case above. The effect of not washing out the < 44µm fraction can be seen in the case of powders held at fixed temperature for up to 43 months when there is a clear reduction in the weight increment, particularly with the higher

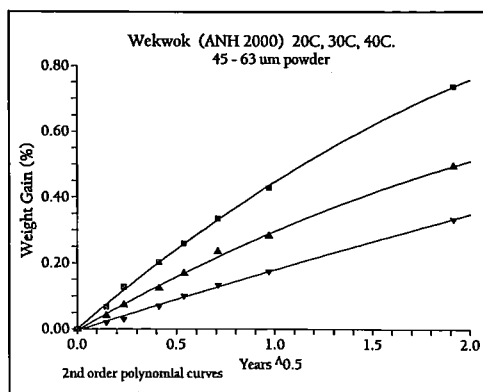


Fig. 5: Fall-off in diffusion rate due to the diminishing geometric surface area of powder below the targeted sieve fraction. The unwashed small particle size attached to the sieved fraction has a significant effect in diminishing the growth rate of the powders over time. For this reason the rates of weight gain is limited to a shorter time span of less than six months.

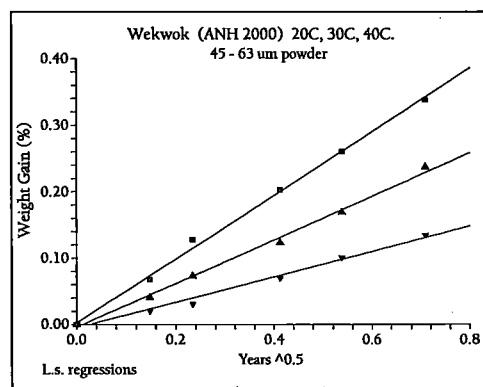


Fig. 6: The same powder data as presented in Figure 5, but limited to increments of less than 6 months. 40°C (□), 30°C (▲), 20°C (▼).

temperature conditions. (Figure 5). For this reason analysis for this series was limited to less than six months (Figure 6). SIMS measurements for the four temperature exposures, and the weight gains  $\Delta m$  of three powders were used to determine 'water' concentration  $d_h$  using equation 2 (Table 3).

T (°C)	t(yr)	SIMS L (µm)	k(µm/yr <sup>0.5</sup> )
10	15.264	0.205	0.0525
20	15.614	0.386	0.0977
30	15.614	0.654	0.1655
40	11.639	0.916	0.2685

Table 2: SIMS hydration depth measurements on four obsidian flakes exposed for the indicated periods and temperatures. The rate constant  $k$  is calculated from equation 1. The relationship of the hydration rate constant  $k$  and temperature for these data is given by the regression equation 3:  $k = \exp(13.9801 \pm 4787.04 \cdot 1/T)$  (Kelvin).

To this point the results have been presented as 'water' ( $d_h$ ) in the hydration layer without considering the relative density  $R$  that expresses  $d_h$  in g/g of the obsidian density  $\rho$ . This can be calculated from equation 4 with the results presented in Table 3. The density  $\rho$  of the Wekwok obsidian is 2.38 g/cm<sup>3</sup>.

$$R = m / (A L \rho) \quad (4)$$

The results from equation 4 show that around 1% of mass as an increase in the relative density of the obsidian has been gained through hydration of the powders.

The apparent inverse relationship between water content  $d_h$ ,  $R$  and temperature and/or hydration depth is masked by significant error margins and requires further investigation in

controlled experimental conditions. These Case 2 data indicate that in the previous Case 1 example of Umleang obsidian, the 'water'  $d_h$  or  $R$  is likely to be higher, and hydration thickness less, in temperature exposures below the values calculated on the basis of 40°C alone. It is also possible that the amount of adsorbed water on the powder surface is affecting the results, although the powders were dried under vacuum and brought to air pressure with dry nitrogen before each weighing event. The instantaneous attraction of water to a newly fractured glass surface (Poggemann *et al.* 2001) reduces over time as diffusion and sub-surface chemical changes alter the air-glass interface reactions (Feng 1994). This time dependent effect would be hastened by the increasing hydration rate at higher temperatures. Silica surface chemistry in the ambient temperature range of interest is sensitive to temperature (Brady 1992) and can be expected to similarly affect water adsorption, as measured by surface conductivity (Boksay *et al.* 1975). A test of the proposition that water density increases in lower temperature conditions could be expected on vapour pressure considerations alone. However Doremus (1999) shows a positive relationship between water content and temperature above ~400°C, but a comparison of the relative powder  $d_h$  and the solid SIMS temperature hydration responses is informative in pointing to an inverse relationship. In Figure 7

T (°C)	$\Delta m$ (g/g)%	A (m <sup>2</sup> /g)	$d_h$ (g%)	R(g/g%)	k (µm/yr <sup>0.5</sup> )
	<i>Powder</i>				<i>SIMS</i>
10*	0.1084*	0.82*	2.52*	1.06*	0.0525
20	0.1847 ± 0.0044	0.82 ± 0.03	2.31 ± 0.04	0.97	0.0977
30	0.3111 ± 0.0067	0.83 ± 0.03	2.26 ± 0.04	0.95	0.1655
40	0.4892 ± 0.0167	0.83 ± 0.03	2.20 ± 0.05	0.92	0.2685

Table 3: Percent powder weight gain, with standard error, based on 1 year values for Wekwok (2000) obsidian.

The estimated values for a 10AC powder are shown with an asterisk\*. The  $k$  values are equivalent to the hydration thickness  $L$  for one year.



the weight uptake of Wekwok powder with an assumed constant 2.5%  $d_h$  water content in the 10°C hydration layer is projected to 40°C and compared with the SIMS measurement of hydration thickness on solid flakes. There is a divergence that could be accounted for by an unallowed difference in the water density  $d_h$  in the powder hydrated layer with its less responsive reaction reflecting this, but the error margins are too great to give a clearer definition of this effect. These data also reflect on the calculated hydration rate of the Case 1 exercise where  $d_h$  is taken to be constant so that the depth of hydration  $L$  for the lower temperature examples will be less than those calculated on the basis of the 40°C powder alone. Another reported case of measurement divergence is between optically measured hydration and hydration depths derived from SIMS (Stevenson *et al.* 2001).

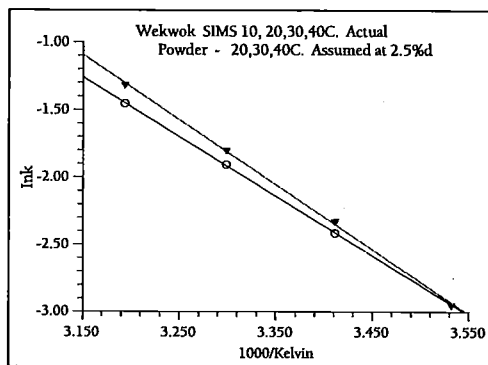


Fig. 7: The hydration rates calculated from SIMS ( $\blacktriangledown$ ) at the 4 temperature exposures between 10°C to 40°C diverge from rates calculated on the powder alone  $\circ$ . In this case the water density at 10°C is assumed to be constant at 2.5% over the temperature range of the experimental powders. The divergence would be expected if the water density was increasing in the lower temperatures, producing an apparent less responsive temperature related hydration rate.

The Wekwok results do indicate some support for the view that water content in the hydrated layer could provide a means for determining the relative temperature conditions

experienced by the obsidian. This should therefore encourage further development of the system proposed by Liritzis and Diakostatiou (2002) where their SIMS-SS dating project relies on the "surface saturation" of hydrated obsidian as a key variable in defining the rate constant of an intrinsic hydration dating system (see also, Liritzis *et al.* 2004).

### Case 3

#### Site thermometry

As shown above, hydration rate determination by gravimetric analysis of obsidian powders exposed to fixed temperatures is feasible over the short period of a year or less. Following the same procedure it should be possible to use obsidian powders to derive effective hydration rates at archaeological sites. An additional attraction of using obsidian powder for this purpose is that it will respond as a combined vapour pressure and temperature monitor when exposed at an archaeological site and obviate the need for separate temperature and humidity monitoring. Previous monitoring of relative humidity has been accomplished with the use of polycarbonate diffusion cells (Ambrose 1984; Stevenson *et al.* 1993; Friedman *et al.* 1994). A test of the use of obsidian powder was carried out at two sites in Talasea, West New Britain, Papua New Guinea, through the cooperation of R. Torrence who was conducting archaeological field studies in the area. The transfer of laboratory type powder analysis to a field site required special consideration of the equipment to be used, and the manner of its emplacement within the soil profile.

#### Procedure

Obsidian flakes from the plentiful Bitokara source at Talasea (Torrence and Summerhayes 1997) were reduced to powder in a rotary mill with the 44 - 63 $\mu$ m range being separated in nested sieves that were flushed with a stream of heatless dried air as described above. Ace-

tone, dried in type 4A molecular sieve, was used to wash finer powder from the selected size range. The bulk powder was divided into twenty fractions of about 2g, four for the calibration set at 10°C, 20°C, 30°C and 40°C, the remainder to provide material for the field cells. The prepared cells were stored in containers over type 4A molecular sieve desiccant.

As the experiment was intended for the humid tropics of Papua New Guinea where very active microbiological growth occurs, the cells were designed to exclude this problem while allowing access of water vapour. The outer casing of each cell is stainless steel with a removable cap that secures the cell contents. A borosilicate dish within the stainless shell containing around 2g of obsidian powder is sealed in place with a series of filters intended to exclude soil micro-organisms. A Millipore Type GV 0.22µm pore diameter membrane is directly exposed to the powder with a second layer glass fibre filter above the membrane. The outermost guard against termites or other insects is a stainless steel 50µm mesh. The contents are securely held in place by a screw-fitting ring (Figure 8).

For this exercise it is not necessary to calculate the diffusion depth or the other parameters outlined in the first two cases. The calculation of effective hydration temperature, EHT, is straightforward once the calibration of the laboratory powders is complete.

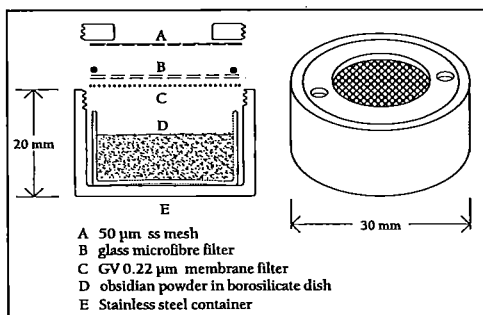


Fig. 8: Cross section of the field cells used to measure effective site hydration rates.

## Results

The laboratory powders were exposed for 403 days at 10°C, 20°C, 30°C and 40°C. Six measurements of weight gain were recorded over the period. The % weight gains calculated as a one year increment give the following result:

T °C	1/Kelvin <sup>-3</sup>	(Δm) %gain	ln gain
10	3.53170	0.0423	-3.162968
20	3.41122	0.0717	-2.6352645
30	3.29870	0.1177	-2.139616
40	3.19336	0.1842	-1.691733

Table 4: One year powder weight gains from thermal cells exposed at four fixed temperatures as a calibration set for calculation of site effective hydration rates from field exposed powder cells.

The correlation between T (1/Kelvin) and Δm (ln gain) gives  $r^2 = 1.000$  so that prediction of temperature within the experimental range should be within an error of no more than  $\pm 0.1$  °C (Figure 9). The least squares regression for these data is  $\Delta m = \exp 12.21944 \pm 4354.853 \cdot 1/(\text{Kelvin})$ .

The laboratory results were satisfactory and contrasted with those from the field trials.

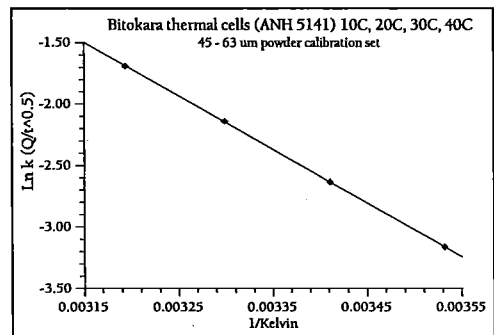


Fig. 9: Plot of the hydration velocity  $\ln k$ , versus absolute temperature  $1/T$  giving the calibration factors for the associated field cells shown in Figure 8. The correlation between the hydration rate  $k$  of the four laboratory exposed powders and temperature gives  $r^2 = 1.000$ .

The field cells were the same as those used for the laboratory set and used fractions of the same powder. Whereas the laboratory cells were oriented with the filters uppermost, each field cell was inverted to ensure that free ground water could not accumulate with the powder in the borosilicate dish. This difference probably contributed most to the very unsatisfactory results from the field cells compared with those from the laboratory set.

Site A is a hilltop position in open sunlit ground in heavy clay Pleistocene sediments at Numundo Plantation (FABM in the Papua New Guinea archaeological site register). Site B, (FACD) is in garden land, less exposed to sunlight and could be less well drained (R. Torrence *pers com.*). The experiment aimed to measure site-specific effective hydration rates over the 1.5m depth at each site.

The prepared field cells were stored in airtight cans over type 4 molecular sieve desiccator. At each of two field locations an augured hole was sunk to a depth of 1.5m to accommodate a 40mm diameter PVC tube that housed a series of six cells fixed at predetermined depths. After the field exposure the cells were replaced in the desiccator storage cans for transport to the laboratory. The release of the glass containers with their powder contents prior to weighing indicated that the field cells had experienced different conditions at the two sites. Cells from site A had some powder adhering to each sealing membrane but the powder was otherwise free. In contrast the powders from site B were clumped indicating that moisture had entered the cell at some stage. This clearly had a more serious effect on the results that the conditions experienced at site A.

Earlier work using polycarbonate cells in the Talasea area shows that an expected annual mean temperature would be around 26 to 27 °C. Site A produced only two temperature values within the expected range, the rest being unacceptably low. It can be argued that the rela-

tive humidity beneath the ground surface would be 100% at all levels in the measured 1.5m column so that this could not have depressed the results. The sensitivity necessary to accurately determine weight gain can be gauged from the result of cell #6. The 2g of powder in this cell produced a hydration weight increment of around 0.00225g over a year so that even a very small mass loss will have a major effect on the calculated temperature.

Depth (cm)	Site A		Site B	
5	11	4.8	7-	
10	2	22.2	8	18.9
25	3	24.9	9	-
50	4	24.0	10	-
100	5	26.2	11	18.5
150	6	27.8	12	20.1

Table 5: Effective hydration temperature rates from two field series depth profiles at Site A Numundo Plantation hilltop position in open sunlit ground in heavy clay Pleistocene sediments, and Site B in garden land, less exposed to sunlight and possibly less well drained. Site B had powder weight loss for cells 7, 9, and 10.

Site B produced quite unexpected results with three of the powders weighing less than their original weights. The powders in most cells were clumped, indicating that moisture had permeated the powder, possibly as free water passing across the membrane filter or as condensation. In either case there is the likelihood of soluble ions diffusing out of the sealed cell to the moist external filter system or the surrounding soil. Leaching is a problem in other glass weathering situations such as the storage of nuclear waste glasses (Feng 1994). The recent re-analysis of silicate dissolution experiments based on powder measurements in aqueous solution shows that rapid loss through alkali ion exchange can occur within hours or days of exposure (McGrail *et al.*

2002). This strongly indicates that the cell orientation has permitted the dissolution and transfer of ions from the hydrating obsidian powder surface to the external medium.

The final result from the powder thermometry field exercise is disappointing. It is clear that the validity of the laboratory phase is confirmed by these data, but the failure of the field cells shows that modification of the obsidian powder cell is necessary to prevent the transport of soluble ions into the external filters and to bring the field cell response up to the quality of the laboratory results. The emplacement of inverted field cells probably contributed to their failure due to solution effects across the membrane and although these effects would still occur under moist conditions with an upright cell, the contents would not be depleted.

## CONCLUSIONS

The feasibility of using powders to determine hydration and other surface reactions has a long history in glass studies (Tooley & Parmelee 1940). In the case of obsidian the preferred method among most practitioners for determining hydration rates is the use of proxy rate determinants such as radiocarbon dating. The development of high precision SIMS for measuring hydration profiles over short time spans offers a release from these secondary reference standards including recourse to a powder based rate-defining system. In the case of SIMS-SS dating shallow or short-term hydration depths are presently within measurable dating range. (Liritzis, 2004 pers. communication). Coupling SIMS with short-term powder hydration shows that consistent values can be achieved when the "water" concentration  $d_h$  in the hydrated layer is found. The data presented here indicates that a form of water is involved in the hydration process. Although these data do not show whether OH, H<sub>2</sub>O, or H<sub>3</sub>O is responsible, it should be noted

that hydrogen alone cannot account for the weight increment of the obsidian powders.

The problem of hydration depth reduction from surface erosion is not simply solved by employing SIMS analysis. Optical examination of an obsidian's hydrated surface characteristics remains a viable procedure for detecting and measuring errors due to surface loss. Digital microscopy has also improved its reading error margin to within the SIMS range (Jones 2002) and is more suited to the large number of obsidian hydration measurements that are necessary to provide information on possible site deposit perturbation.

The initial results of the site thermometry trial were promising for the laboratory phase but greatly improved cell performance at site locations will be necessary if this is to be a useful addition to obsidian hydration dating procedures.

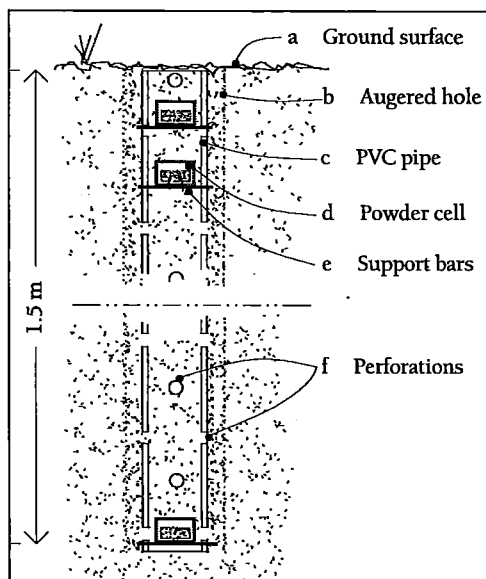


Fig. 10: Field profile array for effective hydration rate measurement. A 75mm diameter hole augered to 1.5m depth houses powder cells at 5, 10, 25, 50, 100 and 150 cm depths. The pvc pipe is filled with the same material as the surrounding deposit.

## APPENDIX 1

### Experimental

For the first two cases of Umleang and Wekwok, flakes struck from boulders were placed in 10ml borosilicate beakers for hydration at 100% rH, at 10°C, 20°C, 30°C and 40°C. The beakers were placed in four rectangular stainless steel cases, each being immersed in a temperature controlled water bath controlled to within  $\pm 0.05^\circ\text{C}$ . Each case has a 2-3mm depth of water on its floor where the 10ml beakers are placed and where the flakes are exposed. The base level of each case is 14cm below the water bath surface so that the temperature of the circulating water is transferred to the stainless case through the base and side walls. Each case has a stainless internal liner that sheds any condensation to the sidewalls and away from the enclosed samples. A covering lid is capped by insulation (Figure 11).

The same enclosures are used for the powder specimens where they were exposed in 5cm diameter shallow evaporating dishes. Obsidian raw material was struck from the same

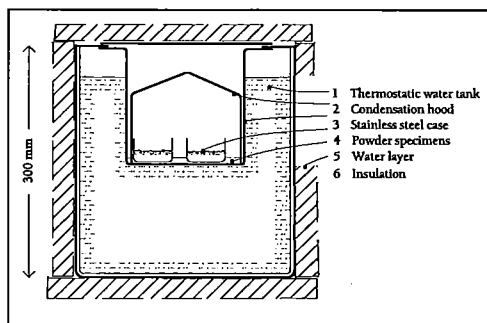


Fig. 11: Diagrammatic cross section of one of the four thermostatic water baths for temperature controlled exposure within  $\pm 0.05^\circ\text{C}$  of obsidian flakes and powders.

boulders to provide a range of fresh flakes that were crushed in a rotatory mill in air directly connected to a nest of sieves, in air dried to a  $-60^\circ\text{C}$  dew point with a heatless air-dryer. The separated sieve fractions provided samples of about 20-30g within the 44 - 63 $\mu\text{m}$  size range that were then divided into around 3-4g fractions for the four temperature controlled baths, where they were to be exposed for about 3.5 years in the case of the Umleang and Wekwok specimens. The 2g field trial powders were exposed for 403 days. The starting weights of all fractions were measured in a 5 place Mettler balance after they were placed under rough vacuum at  $\sim 0.13\text{Pa}$  for three hours at room temperature before being brought to air pressure with dry nitrogen. After weighing the dishes were again placed under vacuum to remove nitrogen before being brought to air pressure with air bubbled through a water trap to restore surface moisture levels. Over the period of exposure the same procedure was repeated to provide a record of the powder weight increments at the four temperatures. The surface area measurements of selected powders were made by the BET nitrogen system at the Chemistry Department, University of Melbourne. Optical measurement of hydration widths on obsidian thin sections were performed with oil immersion magnification at  $\times 1000$  and recorded digitally for pixel arithmetic and statistical treatment.

## APPENDIX 2

The major chemical composition of the ANH 2000 Wekwok source from 10 XRF determinations.

	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	MgO	CaO	NaO <sub>2</sub>	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	density ( $\rho$ )
mean	72.37	0.283	13.68	2.09	0.056	0.270	1.12	5.05	3.98	0.208	2.379
	$\pm 0.33$	0.005	0.10	0.01	0.003	0.015	0.01	0.11	0.02	0.152	0.003

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## REFERENCES

- Ambrose, W. R. (1984) Soil temperature monitoring at Lake Mungo; implications for racemisation dating. *Australian Archaeology*, vol. 19, 64-74.
- Ambrose, W.R. (1994) Obsidian hydration dating of a Pleistocene age site from the Manus Islands, Papua New Guinea. *Quaternary Science Reviews*, vol. 13, No 1 37-142.
- Annovitz, L.M., Elam, J.M., Riciputi, L.R. and Cole, D.R. (1999) The failure of obsidian hydration dating: sources, implications and new directions. *Journal of Archaeological Science*, vol. 26, 735-752.
- Boksay, Z., Varga, M., Wikby, A. (1975) Surface conductivity of leached glass. *Journal of Non-Crystalline Solids*, vol.17, 349-358.
- Brady, P.V. (1992) Silica surface chemistry at elevated temperatures *Geochimica et Cosmochimica Acta*, vol. 56,2 941-2946.
- Doremus, R.H. (1999) Diffusion of water in crystalline and glassy oxides: Diffusion-reaction model. *Journal of Materials Research*, vol. 14, No 9, 3754-3758.
- Doremus, R.H. (2000) Diffusion of water in rhyolite glass: diffusion-reaction model. *Journal of Non-Crystalline Solids*, vol. 261, 101-107.
- Feng, X. (1994) Surface layer effects on waste glass corrosion. *Material Research Society Symposium Proceedings*, vol. 333, 55-68.
- Friedman, I., Trembour, F.W., Smith, F.L. and Smith, G.I. (1994) Is obsidian hydration affected by relative humidity? *Quaternary Research*, vol. 41, 185-190.
- Haller, W. (1960) Kinetics of the transport of water through silicate glasses at ambient temperature. *Physics and Chemistry of Glasses*, vol. 1, No 2, 46-51.
- Hepburn, R.W. and Tomozawa, M. (2001) Diffusion of water in silica glasses containing different amounts of chlorine. *Journal of Non-Crystalline Solids*, vol. 281, 162-170.
- Jones, Martin (2002) *A brief prehistory of time*. Unpublished PhD Thesis, University of Auckland, Auckland.
- Liritzis, I. & Diakostamatiou, M. (2002). Towards a new method of obsidian hydration dating with secondary ion mass spectrometry via a surface saturation layer approach. *Mediterranean Archaeology and Archaeometry* 2, 1-20.
- Liritzis, I., Diakostamatiou, M., Stevenson, C. M., Novak, S.W. and Abdelrehim, F. (2004) Dating of hydrated obsidian surfaces by SIMS-SS. *J. Radioanalytical & Nucl. chem.*, vol. 261, No. 1, 51-60.
- Mcgrail, B. P., Icenhower, J. P., Shuh, D. K., Liu, P., Darab, J. G., Baer, D. R., Thevuhasen, S., Shutthanandan, V., Engelhard, M. H., Booth, C. H., and Nachimuthu, P. (2001) The structure of  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$  glass: impact on sodium ion exchange in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ . *Journal of Non-Crystalline Solids*, vol. 296, 10-26.

- McGrail, B. P., Icenhower, J. P. and Rodriguez, E. A. (2002) Origins of discrepancies between kinetic rate theory and experiments in the  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$  system. *Material Research Society Symposium Proceedings*, vol. 713, No 13.1.1-10.
- Michels, J.W., Tsong, I.S.T. and Smith, G.A. (1983) Experimentally derived hydration rates in obsidian dating. *Archaeometry*, vol. 25, 107-117.
- Poggemann, J. F., Goß, A., Heide, G., Rädlein, E. and Frischat, G. H. (2001) Direct view of the structure of a silica glass fracture surface. *Journal of Non-Crystalline Solids*, vol. 281, 221-226.
- Riciputi, L.R., Elam, J. M., Anovitz, L. M., and Cole, D.R. (2002) Obsidian diffusion dating by Secondary Ion Mass Spectrometry: A test using results from Mound 65, Chalco, Mexico. *Journal of Archaeological Science*, vol. 29, 1055-1075.
- Stevenson, C. M., Abdelrehim, I. & Novak, S. W. (2000) Infrared photoacoustic measurement of obsidian hydration rims. *Journal of Archaeological Science*, vol. 28, 109-115.
- Stevenson, C. M., Friedman, I. and Miles, J. (1993) The importance of soil temperature and relative humidity in obsidian dating, with case examples from Easter Island, In Fischer S.R., (ed) *Easter Island Studies, Contributions to the History of Rapanui in Memory of William T. Malloy*. Monograph 32, Oxbow Books, Oxford, vol. 96-102.
- Tooley, F.V. and Parmelee, C.W. (1940) Powder method for measurement of chemical durability of glass. *Journal of the American Ceramic Society*, vol. 23, No 10, 304-314.
- Torrence, R. and Summerhayes, G. (1997) Sociality and the short distance trader: Intra-regional obsidian exchange in the Willaumez region, Papua New Guinea. *Archaeology in Oceania*, vol. 32, 74-84.
- White, W.B., (1988) Glass hydration mechanisms with application to obsidian hydration dating. *Materials Research Society Symposium Proceedings*, vol. 123, 225-235.