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Recent Developments in Obsidian Hydration Dating

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ABSTRACT. This paper presents recent experimental results from the obsidian hydration dating research programme conducted at the Centre for Archaeological Research (CAR), Auckland University. Two elements of the essential hydration rate component are examined. First, the influence of potentially significant environmental variables other than ambient temperature is explored. Our results demonstrate that environmental variables other than temperature may have a significant influence on hydration rate, though for many archaeological situations their influence is insignificant. Second, an alternative approach to estimating the exponential mean temperatures necessary for dating is presented. It is based on modelling the soil surface energy balance. A comparison with other prediction methods shows it to be a preferable approach. Finally, the results of a blind dating applications are presented. These show that the dating method can produce results which are both sensible and useful.

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Obsidian hydration dating (OHD) involves converting a measured hydration rim thickness into a “date” based upon an estimated hydration rate. As the rate at which obsidian hydrates depends on the ambient temperature and glass chemistry (Ambrose, 1976; Friedman & Smith, 1960), accurate temperature control and an understanding of the glass reaction are fundamental to producing accurate obsidian hydration dates. This applies equally whether the OHD is produced using an independently calibrated hydration rate (a hydration rate calibrated via a primary dating technique such as a dated historic context or ^{14}C) or an intrinsic hydration rate (a hydration rate calculated on the basis of glass chemistry) (Jones *et al.*, 1997).

The purpose of this paper is to present recent results clarifying hydration rate estimation, by evaluating the influence of the hydration environment and modelling the ambient temperature regime.

Hydration rates

Hydration rates are influenced by the conditions under which the chemical conversion of obsidian into perlite takes place. Thus the rates are influenced by the environment within which the artefact is stored, and the chemical composition of the obsidian itself. Research to date has suggested that the two most important controls on hydration velocity are the storage temperature and glass chemistry (Ambrose, 1976; Friedman & Long, 1976; Michels *et al.*, 1983; Stevenson *et al.*, 1989). To verify these results a series of induced hydration experiments were conducted during 1996. One of the main questions examined in these induction experiments was “What influence do environmental variables other than temperature have on hydration rates?”. This is of considerable importance to the application of obsidian hydration dating as there are

a wide number of potential reactions between obsidian and the environment that may not be taken into account in standard high temperature experimental induction programmes. While various research programmes have demonstrated the thermal dependence of hydration, the influence of other environmental variables have largely been ignored and it is possible that these factors will have a significant influence on archaeological hydration rates. In part, this is prompted by results from nuclear waste glass research that have demonstrated different rates of glass corrosion in different environments (e.g., Christensen *et al.*, 1984; Doremus, 1994; Lokken & Strachan, 1984; Shade *et al.*, 1984). Additionally archaeological research has demonstrated that surface corrosion is significant in some archaeological environments (e.g., Ambrose, 1994).

Based on this previous research it was established that the factors of pH, solute cation concentration and soil composition were likely to have an influence on archaeological hydration rates. To explore the influence these factors may have on net hydration rates an experimental induction was conducted comparing the effects of different induction media (pH, solute cation concentration and soil composition). In total nine induction media were compared, with the pH controls ranging between 3.5 and 11 (pH 3.5, 6.8, 8.0 and 10.5 using standard TRIS buffers) and the cation solute controls consisting of a brine solution ranging from 0.1 M to 2.0 M (0.1, 0.5, 2.0 M—laboratory grade NaCl solution in distilled water). As an additional experiment, the media of distilled water, silica saturated water, water vapour, soil (organic/clay mix) and silica sand were compared as induction environments. Four source samples of obsidian were used in the experiment (Table 1). They were chosen to be chemically representative of New Zealand obsidian in general and allowed any potential variation in hydration response due to glass chemistry to be outlined.

The inductions were conducted in pressure chambers

maintained at a constant temperature in an incubator. Temperature measurements conducted during the hydration experiments have confirmed that the temperature within the incubator was maintained to an accuracy of $\pm 0.1^\circ\text{C}$. Vapour inductions were conducted by suspending freshly flaked obsidian in a pressure chamber maintained at 100% rH. The non-vapour media were contained in Pyrex beakers which had been autoclaved for four weeks at 120°C prior to the experimental run to ensure that any potentially confounding leaching reaction of the Pyrex was minimised. This experimental was conducted at 112.5°C for 8.5 days. The experimental hydration rim thicknesses were measured following the pixel intensity integration approach developed by Ambrose (1993).

The induction results (Table 2) show that there are no differences in the results obtained among inductions in distilled water, silica saturated water, water vapour, soil, silica sand, brine, or pH above 6.8. This pattern is consistent for the four obsidian sources used in the experiment, and suggests that induction experiments conducted in water vapour provide suitable data for estimating hydration rates in these media at 112.5°C .

While none of the results are statistically significant the pH experiments suggested that there was an effect generated by this environmental variable. The low pH rims were larger, as expected from similar experiments in glass science (Doremus, 1994), whereas the high and neutral pH rims gave identical results to the inductions conducted in water vapour.

Brine concentration may also have had the anticipated effect of suppressing the hydration rate, though the results are not at all significant in this study. The conclusion from these results is that solute cation concentration ($< 2\text{ M}$) will not have a significant effect on apparent hydration rates for hydration rim thicknesses less than $1\ \mu\text{m}$. This result may also be applicable to larger hydration rims, although our study has focussed on rims $< 1\ \mu\text{m}$ thick.

Table 1. Major elemental composition (Molar %) of obsidian used in the induced hydration experiments.

	Ben Lomond	Huruiki	Taumou Beach	Waiere
Si	71.01	69.85	67.09	67.24
Al	13.04	13.66	10.37	10.30
Fe	1.95	1.88	6.51	6.25
Mn	0.07	0.04	0.15	0.12
Mg	0.22	0.09	0.02	0.02
Ca	1.59	1.09	0.27	0.19
Na	6.08	6.69	8.18	8.49
K	5.68	6.40	6.94	6.70
Ti	0.22	0.11	0.26	0.17
P	0.02	0.01	0.01	0.01

Table 2. Combined percentage deviation from average thickness results for the induction media.

medium	average deviation %	standard deviation
vapour	- 2.4	4.4576
distilled water	- 2.2	4.6115
silica saturated water	- 2.2	4.3157
pH 3.5	+ 7.7	4.4361
pH 6.8	- 2.1	4.5641
pH 8	- 2.2	4.5762
pH 10.5	- 2.3	4.6829
NaCl 0.1 M	- 3.7	4.5093
NaCl 0.5 M	- 2.6	4.4404
NaCl 2 M	- 2.7	6.3323
silica sand	- 2.1	4.8820
soil	- 2.3	4.6155

The inference from this set of experiments is that obsidian that has not been exposed to pH extremes or high levels of brine will hydrate at a rate described by the hydration behaviour of glass in a saturated vapour environment (112.5°C). Fortunately the set of conditions under which hydration proceeds normally, prevail within archaeological sites in New Zealand. Though there will be problems in some tropical regions where pH extremes may exist (e.g., Sheppard & Pavlish, 1992).

Temperature

Temperature is an important governing variable in the hydration of obsidian (Ambrose, 1980, 1984; Friedman, 1976; Friedman & Smith, 1960; Jones *et al.*, 1997). As the hydration rate is exponentially related to the ambient temperature, arithmetic mean temperatures are unsuitable as estimates for the effective storage temperature (EHT) of an artefact. Many methods have been developed to provide estimates of EHT's, but they all have limitations (e.g., Jones *et al.*, 1997; Ridings, 1996).

A useful estimation model should have the following attributes:

1. *Model long term climatic trends.* Some modelling methods make use of short term data and make the assumption that this is representative of the storage history of an artefact. This will rarely be the case.
2. *Hydration model independence.* The model should be able to provide an estimate for any hydration mechanism. This is important if future research revises the current temperature dependence of the hydration reaction, and ensures *forward compatibility* of EHT estimates. Similarly the estimate should not be *analogue dependent*. Some estimations are made by measuring the mean reaction rate of an analogous system

(Ambrose, 1980; Trembour *et al.*, 1988). As the exponential temperature response of these systems will be different from that of obsidian the analogue rate cannot be used in its raw form.

3. *Model small scale temperature variation.* It has been shown that significant variations in archaeological soil temperature regimes can occur over small spatial scales (< 10m), and that this variation is driven by variables governing the surface energy balance of the soil (Jones *et al.*, 1997). A useful estimate should model these small scale variations.

None of the current estimation procedures meet all of these requirements. The procedure that most closely meets them is the use of zeolite temperature cells (Ambrose, 1980, 1984). Surveys with these devices can be designed to model small scale temperature variation, and methods have been developed to correct the estimate for the reaction rate of the analogous system (Ambrose, 1984; Chappell & Ambrose, undated). The limitation of these devices is in modelling long term temperature trends. Long term information cannot be practically incorporated into an estimate from a cell survey alone.

In response a new method based on estimating soil surface energy balances has been developed. In this model the soil surface is treated as an energy interface between the soil body and the atmosphere. The energy balance of this interface is set equal to the net external energy flux. Thus when there is more energy arriving at the soil surface than is being lost, on a hot sunny day for instance, the soil surface energy balance is positive. On the other side of this energy interface is the soil heat flux which is modelled as being driven by the soil surface energy balance. Thus when the soil surface energy balance is positive energy flows into, and is distributed throughout, the soil body. Whereas energy flows from the soil body when the surface energy balance is negative.

The temperature at any point in the soil body can be described as a function of the soil heat flux and the thermal capacity of the immediate matrix. Thus by modelling the net external energy flux we can estimate the soil heat flux through time and develop a temperature time series for any point in the soil body. This time series can be represented as a time dependent function by techniques such as harmonic decomposition and then an exponential mean temperature can be modelled for any proposed reaction mechanism.

Thus to produce an estimate we:

1. *Model the net external energy flux.* This can be a model of any degree of complexity (e.g., Ayra, 1988; Campbell, 1985; Mahrer & Avissar, 1985; Monteith & Unsworth, 1990; Oke, 1987; Stathers & Bailey, 1986; Stoutjesdijk & Barkman, 1991) incorporating all known information about long term climatic trends and responding to small scale variation.
2. *Model the soil heat flux.* This flux is dependent upon the driving external flux, and again a variety of techniques can be used to model heat flow through the

soil matrix (Campbell, 1985; Chudnovskii, 1962; Clothier *et al.*, 1986; Hanks & Ashcroft, 1980; Mahrer & Avissar, 1985; Persaud & Chang, 1984; Richter, 1987). These techniques can make allowance for variations in thermal properties of the soil matrix through different strata.

3. *Develop a temperature time series for the location.*
Produce a temperature time series for the soil location.
4. *Produce an EHT.* The soil temperature time series is reduced to a time dependent equation which is integrated through time with any proposed hydration model to produce a model specific EHT.

In an evaluation of this model 10 zeolite temperature cells were placed in a meteorological station and the weight gain of these cells over a six month period was predicted on the basis of a surface energy balance integration model. The results of this prediction were then compared to the performance of other mainstream EHT estimation procedures.

Cells were placed every 10 cm from the surface to a depth of 40 cm, with two cells at each depth. The governing meteorological variables for the location were predicted via a simple ARIMA model and the soil heat flux was calculated via a numerical capacitor analogue after Campbell (1985). The resulting temperature series was reduced to a time dependent function via a 10 element harmonic decomposition and integrated via the following equation to produce a predicted cell weight gain over the survey period.

$$\Delta W = \int e^{\frac{A}{f(t)+273.16} + B} dt$$

A and B are cell hydration constants; $f(t)$ is a time dependent temperature function in degrees celsius.

The predicted and actual cell weight gains have been converted to an EHT for comparison with the prediction of other estimation methods, and these results are presented in Figure 1. As can be seen, the performance of this approach to producing estimates of the recorded cell temperatures is better than the alternatives presented.

The conclusion from these results is that the energy balance integration approach is an accurate method for estimating EHT's that fulfils the requirements of a useful estimation method. The approach is not restricted to any single hydration model and can incorporate any level of complexity in the modelling of soil climate.

Case study

As a final component of this paper we present the results of a blind dating trial of obsidian from the proto-historic site of Papahinu, New Zealand (Table 3; Foster & Sewell, 1996). In this trial 39 samples of obsidian were submitted for dating where the operator was not aware of the site, association or age of the artefacts. The dates were produced by measuring the hydration rims after Ambrose (1993), and using estimated hydration rates based on the results of

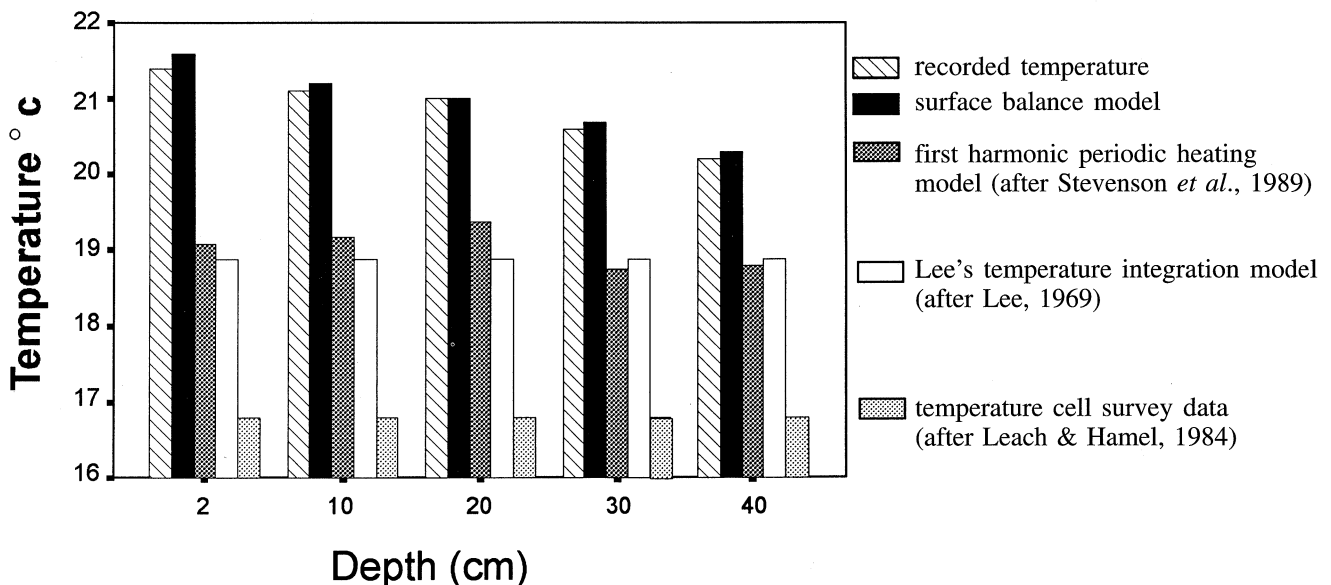


Figure 1. Recorded and predicted cell temperatures at different depths: Kumeu Meteorological Station 12 November 1995 to 14 March 1996.

Table 3. Blind dating results for archaeological obsidian from Papahinu.

lab number	description	rim (μm)	age (B.P.)	date (A.D.)	error (years)
AKU-95-74	f162	0.6	102	1848	39
AKU-95-75	nil	0.7875	176	1774	55
AKU-95-76	pit_next_to_house	0.7125	118	1832	42
AKU-95-77	house_drain	0.6	101	1849	38
AKU-95-78	f738	0.75	112	1838	38
AKU-95-79	eastern_terrace	0.825	193	1757	59
AKU-95-101	House_8_floor	0.7	106	1844	36
AKU-95-102	House_8_floor	0.6	102	1848	39
AKU-95-103	fill_firescoop	0.9	88	1862	25
AKU-95-105	fill_pit_15	0.675	129	1821	45
AKU-95-107	midden_top	0.6	102	1848	38
AKU-95-108	fill_posthole	0.75	160	1790	52
AKU-95-110	posthole_fill(early)	0.75	160	1790	52
AKU-95-112	feature_292	0.75	154	1796	50
AKU-95-113	feature_292	0.75	156	1794	51
AKU-95-114	feature_292	0.75	158	1792	52
AKU-95-115	feature_292	0.798	182	1768	57
AKU-95-117	spoil_heap	0.6	103	1847	39
AKU-95-119	spoil_heap(late)	0.675	130	1820	45
AKU-95-121	nil	0.675	130	1820	45
AKU-95-122	nil	0.5625	90	1860	36
AKU-95-123	nil	0.7875	171	1779	55
AKU-95-124	nil	0.675	129	1821	45
AKU-95-125	nil	0.675	129	1821	45
AKU-95-126	nil(early)	0.6	102	1848	39
AKU-95-127	nil	0.5625	88	1862	35
AKU-95-128	nil	0.6	96	1854	36
AKU-95-129	nil	0.525	79	1871	32
AKU-95-130	nil(early)	0.9	231	1719	67
AKU-95-131	nil	0.525	78	1872	32
AKU-95-132	nil	0.675	124	1826	43

a series of high temperature induction experiments (Jones *et al.*, undated). In total only 31 dates were produced, as eight of the samples had surface damage and were rejected. Temperature control was by the use of data generated in a regional soil temperature survey (Jones *et al.*, 1997) and the estimated EHT was 17°C. The expected date range of material from this site is from the late eighteenth century through to the mid nineteenth century on the basis of historical records and the artefacts present (Foster & Sewell, 1996; Sewell, pers. comm.). As can be seen the obsidian hydration dates for the material recovered from this site cluster tightly within the expected date range. Further more, in two cases multiple samples were submitted from single features and the date cluster from these features was very tight. In one case we have two dates within four years and in the other we have four dates

within 27 years. This case study demonstrates the degree of precision and accuracy now possible with OHD in New Zealand.

Conclusion

The results presented here have demonstrated that we can describe the age of an artefact as a function of hydration rim thickness and that it is possible to control for environmental influence of the hydration rate. Further we have demonstrated that obsidian hydration dating can provide consistent dates that conform well to independently dated material. Thus we are confident that the base has been established for obsidian hydration dating to function as a useful tool for archaeology in New Zealand.

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