OBSIDIAN DENSITY, CONNATE WATER AND HYDRATION DATING

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ABSTRACT

The search by many authors for the chemical components most influential in determining hydration rates, for obsidian dating purposes, has had mixed results. Recently it has been demonstrated that hydration dating is more reliable when individual artifacts are assayed for their compositional or connate water content, rather than relying on a single source specific chemical compositional determination which may overlook the formational water variations between different parts of an obsidian flow. Water measurement may be difficult to achieve for every dateable artifact using the currently preferred system of infrared spectroscopy; small sample size and lack of transparency can significantly reduce the quality of the measurement. The relationship between obsidian connate water and density is presented to show that simple density measurement can in many cases be an alternative to infrared spectroscopy. Results from the analysis of 31 obsidians ranging from North America to the southwest Pacific show that useful estimations of obsidian connate water can be achieved by density measurement. An important finding is the marked difference between the potential hydration rates of 'dry' higher density obsidians of the southwest Pacific compared with 'wet' lower density specimens from North America.

KEYWORDS: Obsidian, hydration, dating, connate water, infrared spectroscopy

INTRODUCTION

Obsidian hydration rate dating requires an accurate assessment of the basic hydration rate constants. For this reason many authors have sought to isolate the key chemical components that have the most influence on hydration velocity (Ambrose 1976; Ericson *et al.* 1976; Ericson 1981, 1988; Friedman and Long 1976; Kimberlin 1976; Stevenson and Scheetz 1989; Suzuki 1973). The identification of chemical elements that enhance or restrict hydration has resulted in proposals for compositional indices that are seen to account for more or less of the variability in hydration velocity. For example the Chemical Index of Friedman and Long (1976), the S-value silicon oxygen ratio and Zeta chemical structural factor of Ericson *et al.* (1976), and the K_2O/Al_2O_3 ratio of Suzuki (1973, 302), but chemical composition is not the only possible source of variation in hydration velocity. Obsidian, as a volcanic aluminosilicate glass related to rhyolite, has a relatively narrow possible range in its major element chemistry but a wider range of physical characteristics affected by its transitional history from magma to glass. These factors include refractive index, density, hardness, transparency, colour, and non-glassy inclusions. The latter may occur as gas vesicles or microcrystalline minerals that can affect the other physical properties while producing a gradient from vesicular pumice through obsidian to stony rhyolite. Hydration is part of a normal weathering process in volcanic glass; its relative durability being a product of its chemical and physical characteristics as well as the weathering environment in which it lies (Ambrose 1994). This paper explores the relationship between major element chemistry, water content and density for 31 obsidians from sources in North America, New Zealand and Papua New Guinea.

OBSIDIAN HYDRATION DEPENDENCE ON CONNATE WATER

Although none of the chemical indices has been adopted as a predictive system for determining hydration rates, a more generally accepted indicative component is the connate water as part of the obsidian's original chemical composition. Friedman *et al.* (1966, 326), following Haller (1963, 218), suggested that the hydration rate increased with increasing original water concentration, and that the abrupt inflection in the microscopically observed hydration front was a concentration dependent property of hydration in obsidian; Lee *et al.* (1974, 46) noted a correlation between the original water content and the saturation level of water in the hydrated layer; Kimberlin (1976, 80) used weight loss at 975°C to measure water content and thought that obsidians with an original water content less than 0.2% may not hydrate but that values above this have little or no effect on the hydration rate. Ericson (1981, 67) refers to a "suggestive" relationship between intrinsic water content and the hydration rate, although his data do not show a strong correlation, and Suzuki (1973, 291) also mentions that obsidian water content was thought to affect the hydration rate without further developing his comment. These early reports pointing to a correlation between water content and hydration rate have been superseded by the demonstration of Mazer *et al.* (1992) and Stevenson *et al.* (1993) that compositional or connate water has a crucial role in controlling the diffusion rate of "water" into the obsidian. This correlation between the connate water and the hydration rate will have a significant effect on the progress of obsidian hydration dating.

MEASUREMENT OF CONNATE WATER CONTENT IN OBSIDIAN

Ross and Smith (1955) investigated connate water and other volatiles in obsidians by measuring weight loss at >600°C and produced tables showing a strong relationship between refractive index and obsidian water content, therefore indicating it would be practicable to measure refractive index in order to determine the original water content. They also showed a change in the RI to water relationship at about 0.3% H_2O. Long and Friedman (1968) confirmed this correlation and suggested a change in the RI to water relationship at around 0.4% H_2O. Friedman and Smith (1958) used a more precise standard volumetric method in separating water as hydrogen in their study of the deuterium content of volcanic glass. A similar system has been used by Newman *et al.* (1986) but with greater accuracy in making measurements of the water content of rhyolitic glasses. By using the volumetrically measured water in a range of obsidians outgassed at up to ~1200°C, they were able to set up precise reference standards for measuring the forms of water by infrared spectroscopy on a larger set of specimens with a greater precision than previously. Water as a component in the formation of obsidian occurs in the form of molecular H_2O and hydroxyl group (OH) appearing in the IR absorbance bands most usefully at 5200 cm^{-1} and 4500 cm^{-1}, and these can be integrated to calculate total water content. The analytical error associated with the infrared analysis is +/-3.6% for the H_2O peak at 5200 cm^{-1} and +/-1.1% for the OH band at 4500 cm^{-1} (Newman *et al.* 1986).

Mazer *et al.* (1992) and Stevenson *et al.* (1993) have used only the hydroxyl measurement from the IR analysis (OHir), to indicate the "water" content of their obsidians rather than the procedure used by Newman *et al.* (1986) where both the 5200 and 4500 cm^{-1} wave bands are employed. They supported this
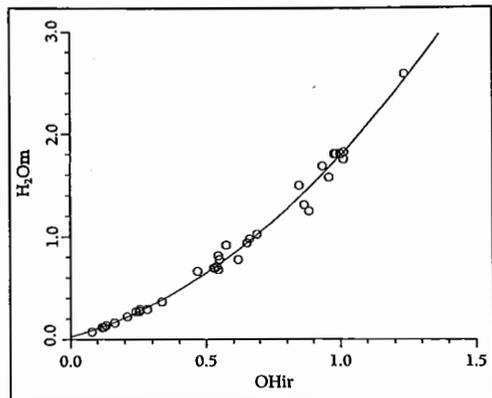

Fig. 1: The relationship of the hydroxyl content of obsidians determined by infra-red spectroscopy in the 4500cm^{-1} waveband and the total water content determined by manometry; data from Newman *et al.* (1986). The curve indicates that hydroxyl contributes most of the connate water up to around 0.4% when H2O gradually increases in dominance. The predicted curve is a 2nd order polynomial.

procedure on the basis that the water band at 5200 cm^{-1} is not detectable at low concentration, and that hydroxyl is the main determinant of hydration velocity by modifying the obsidian silicate structure to make it more amenable to hydration. At the same time it is clear that there is not a simple constant ratio between the water precisely measured by manometry (H_2Om), and the hydroxyl group measured by infrared spectroscopy (OHir). The relationship of H_2Om to OHir can be found by examining the data presented by Newman *et al.* (1986) for natural obsidian, and Silver *et al.* (1990) for artificially treated obsidians. This is shown in Figure 1 from the data of Newman *et al.* (1986) with total H_2Om plotted against OHir making it clear that the two are not simply correlated, with a break in the water/hydroxyl ratio of the obsidians at around 0.4%. For obsidians below 0.4% where OH is the fraction exclusively measured, it would be possible to estimate total water content with the single 4500 m^{-1} band by using the

regression of H_2Om over $OHir$ from the Newman et al. data. Both H_2Oir and $OHir$ contribute to the total water content in obsidians above 0.4% but with an increasing proportion of H_2Oir. Figure 2 presents the data transformed to give a linear correlation between H_2Om and $OHir$ that allows an estimate of total water from the measurement of hydroxyl represented by the 4500 cm^{-1} wavelength. A linear least squares regression of the data in Figure 2 gives:- $H_2Om = .00844 + 1.725 \cdot OHir^{1.62}$ with a correlation (r^2), of 0.98.

ALTERNATIVE STRATEGIES

The diverse volcanic origin of obsidian-bearing lavas having different thermal histories can produce wide variations in physical properties within a single flow or from one flow to another with an otherwise similar chemical composition (Friedman and Long 1984, Ericson 1989,14). In their study of hydration rates calculated from short term exposure at 160°C of compositionally diverse obsidians, Mazer et al. (1992) and Stevenson et al. (1993), demonstrated a correlation between the intrinsic water content, measured as hydroxyl by IR spectroscopy, and the hydration rate. From this it was possible by extrapolation to calculate the hydration constants for obsidians at normal terrestrial temperatures. As Stevenson et al. (1993), have shown this differential water content will affect the hydration rate at a small scale so that ideally each obsidian artifact should be assayed for its water content before its individual hydration rate is determined.

Archaeological collections of obsidian artifacts often include examples that are dark coloured or contain microscopic inclusions that produce poor transparency and renders them unsuitable for IR spectrographic analysis. The high IR absorption of low transparency glasses may result in measurements that erroneously inflate the water values. As well, the need to produce polished sections up to 1mm thick to present to the IR beam can eliminate many small obsidian artifacts from the analysis, despite the reduction of the beam diameter. In some instances it would be necessary to destroy a small artifact in order to provide a thick section for IR analysis. With these constraints on the systematic use of IR spectroscopy for each artifact an alternative system for determining water content for archaeological applications of obsidian hydration dating would be advantageous.

The presence of water in vitreous silica has long been known to effect several glass properties including density, refractive index, and viscosity (Heatherington and Jack 1962), while Haller (1963, 218) states that "the well-known relation between viscosity and diffusivity, suggests that the diffusion coefficient for water [in glass] increases with increasing water concentration". Viscosity measurement is not feasible but both refractive index and density are relatively simple determinations. Their correlation with water content can provide an alternative means for independently calculating hydration rates in obsidian. The large technical glass literature has many studies examining the relationship of glass chemistry to its many physical properties including refractive index and density. Of interest are the work of Kuan-Han Sun et al. (1940) and Huggins and Kuan-Han Sun (1943), who attempted to predict glass density and refractive index from its chemical composition, but as Ericson et al. (1975) show, the Huggins method failed when applied to density determinations on 28 obsidian sources from western United States. The failure was attributed to the variables that are not included among the Huggins chemical components, namely crystal inclusions and gaseous vesicles, but particularly water as the dominant volatile. Although crystal inclusions and voids could be quantified and be used to

correct for density errors, the water content was not so easily accounted for as an indicator of hydration rates. In the present study we show that measurement of density can give a useful correlation with connate water and can be useful in determining the hydration rates of individual obsidian specimens.
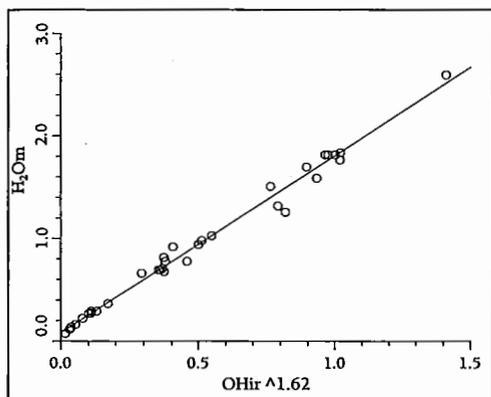

Fig. 2: The relationship of the same data on hydroxyl content measured in the 4500cm^{-1} waveband as presented in Figure 1 (from Newman et al. 1986) but transformed as OH$ir^{1.62}$, against total water content from manometry. A least squares regression gives the predicted relationship as Y = .00844 + 1.725 • X$^{1.62}$, with a correlation (r^2) of 0.98.

DENSITY MEASUREMENT

The relative density of an object can be found by using the Archimedes principle of measuring the difference in weight between an object weighed in air compared with its weight fully immersed in a liquid of known density. Density is expressed as kg/m^{-3} but by convention relative density is density divided by the maximum density of water. In this paper we report density in this sense. It is more convenient to express density in terms of weight to volume in g/ml so that at its maximum density water has a value of 1.00. Water is often used for density measurements but better immersion fluids are those that are heavier that water, and maximise the difference between the weight of an object in air and its weight in liquid. Density can be calculated from the following: -

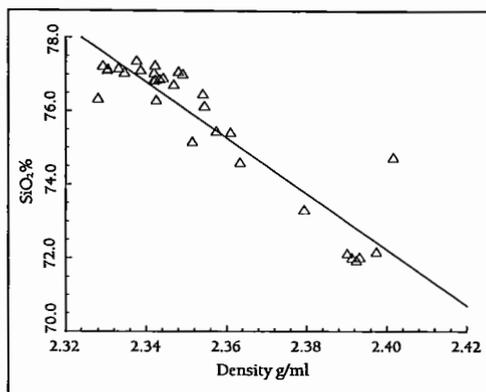$$d = \frac{m_a - d_{liq}}{m_a - m_{liq}} \qquad (1)$$

Fig. 3: The figure shows the negative correlation between density in g/ml against percentage SiO$_2$. The outlier is from the New Zealand Mayor Island source. A least squares regression gives the predicted slope as Y = 254.6+(-76.0) × X, with a correlation of (r^2) = -0.84

where d is density, m_a is weight of the object in air, d_{liq} is the density of the immersion liquid, and $m$liq is weight of the object in liquid.

In a survey of liquids suitable for density measurements by the liquid displacement method, Hughes and Oddy (1970) concluded that perfluoro-1-methyl-decalin (PFMD) had several advantages over water or other liquids. At 20°C PFMD has a density of 1.967 g/ml, giving a good separation between the weight of on object in air compared with its weight in liquid. The surface tension of PFMD is about one fifth that of water, giving it better wettability and reducing the problem of air entrapment and artificial buoyancy in the submerged object. With a high boiling point of around 160°C, PFMD produces negligible evaporative cooling at a steady room temperature to give a stable liquid temperature with minimum convective turbulence. PFMD

also has low flammability, is inert and said by Hughes and Oddy to be non-toxic. Nevertheless due care should be exercised in using this material and any manufacturer's precautions should be observed. The coefficient of thermal expansion of PFMD at around .0021 per degree Celsius is about ten times greater than water at 20°C so that a precise measurement of liquid temperature is necessary for consistent density measurements on obsidian. As the weighing operations in this study were done in laboratory conditions at 20°C ±2° no additional correction for the thermal expansion differential of obsidian flakes was necessary.

In order to calibrate the density of our batch of PFMD to temperature, its density at 10°C, 20°C and 30°C was measured using a 50ml volumetric flask. At each of the three temperatures the stoppered flask was suspended for one hour in a temperature controlled water bath held at ± 02°C of the target temperature, while the PFMD liquid level was adjusted to the 50ml calibration line of the flask. The flask with PFMD was then removed, dried and weighed to the nearest 0.1mg to find the density of the liquid at each temperature in g/ml. The capacity correction for the flask at 10°C and 30°C was made using the known values for the volumetric change of laboratory glassware at those temperatures, namely -.012 and +.012. From the three density and temperature values intermediate values can be calculated using the regression slope -480.88 and intercept 965.99 with a correlation (r^2) of 1.000. During weighing operations for determining artifact density the temperature of the PFMD is continuously measured by thermocouple and the value (T) is used to calculate the final artifact density by introducing the relevant figures to substitute for dliq as follows: -

$$d = \frac{m_a \times (T\text{-}965.99 / (\text{-}480.88))}{m_a \times m_{liq}} \quad (2)$$

A Mettler® electronic balance with a density kit was used for all the weighing operations. Repeated density measurements on a quartz crystal standard gave a precision at 1 sigma of ±.06%. The estimated error for each density measurement is +/-0.005g/ml.

OBSIDIAN COMPOSITION

The samples of obsidian were cut with a Lastec® diamond wire saw to produce wafers up to 1mm thick to be polished for the IR determinations. Small fragments up to 2mm wide were cut from these wafers for mounting as polished sections for the chemical analysis. Major chemical components were analysed by scanning electron microscope fitted with a Link Analytical® PCXA energy dispersive spectrometer, and employed the ISIS software package. The major elements calculated as oxides were SiO_2, Al_2O_3, Na_2O, K_2O, FeO, CaO, TiO_2, Cl, MgO and MnO, but MgO and MnO were close to minimum detection levels for many specimens. An estimated error of +/-%5 is associated with each of the determinations.

These analyses aimed to examine any correlation between the chemistry, density and water content of the 31 obsidians. The results of the chemical analyses are presented in Table 1. A least squares regression of the major element oxides against obsidian density yields high to low correlations (r^2) in the following sequence: - SiO_2 -0.84, TiO_2 0.76, FeO 0.75, Cl 0.73, Na_2O 0.64, CaO 0.39, K_2O -0.29, Al_2O_3 0.11. Apart from silica, which correlates inversely with density (Figure 3), the other major elements with significant correlations are additive in increasing obsidian density. Aluminium, although the second most prevalent element, and potassium that is an important glass modifying element are not correlated with density but iron, despite its relatively low concentration, is correlated with density (Figure 4).
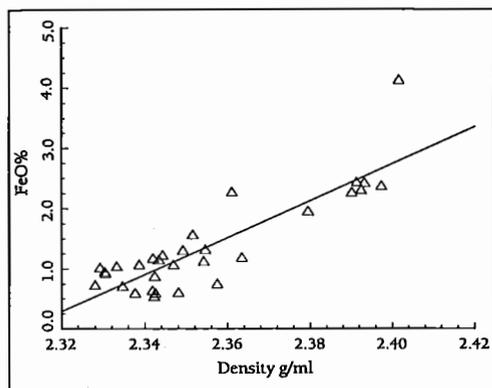
Fig. 4: A positive correlation between iron content and density contrasts with that of Figure 3. Predicted values between iron and density are given by
$Y = -70.8 + 30.6 \times X$ with a correlation (r^2) of 0.75.

The relationship of water content with silica and iron provides an interesting contrast. A two-phase correlation exists between SiO_2 and water with a major change around 76% (Figure 5), while FeO shows the same effect in reverse at around 1.5% (Figure 6). This indicates that while density has a
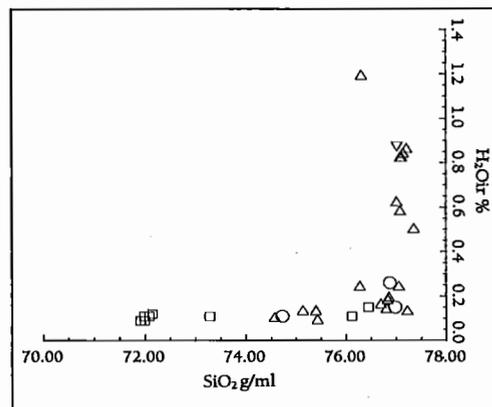

Fig. 5: The figure shows an abrupt change in the increased accommodation of connate water above about 0.2% occurring at around 77% SiO_2. Triangles are obsidians from America, squares indicate those from Papua New Guinea, circles those from New Zealand, and the inverted triangle indicates obsidian from Turkey.

generally linear relationship with the elements silica and iron the relationship between these and water is more complex. In their major influence on density these elements also influence the connate water accommodation in obsidians. The additive effect of Ca, Na, and Ti reinforces the density figure but overall silica maintains its strong correlation with the final density value by virtue of its dominance. From this it appears that a more open structure of the obsidian aluminosilicate glass can accommodate an increasing volume of water with an increasing silicate concentration above 76% SiO_2.

DENSITY AND WATER CONTENT

The relationship between water content and density is presented in Figure 7. The total water content is approximated from the relationship of infrared hydroxyl content to total water content from the figures of Newman *et al.* (1986), and given in Figure 2. Figure 7 shows a two-component curve with an inflection at a density of about 2.35 and a water content of around 0.15%. The "dry" obsidians denser than 2.35 have a very low water to density ratio, while those less dense than 2.35 have a high water to density ratio and can be typified as "wet". The "wet" obsidians show a sharp decrease in water accompanying a small increase in density to about 2.35. Conversely the H_2O-density trend line for the "dry" high-density obsidians above 2.35 indicates that a relatively small decrease in water accompanies a large increase in density.

The most significant feature of Figure 7 is its demonstration of a two-component curve for the water/density relationship where a marked decrease in water content is accompanied by a small increase in density to the inflection point. This implies that water is being accommodated by a relatively open structured aluminosilicate glass with only a minor affect on the volume compared with the
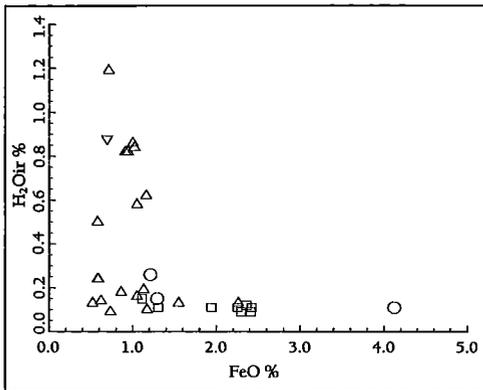
Fig. 6: The inverse of Figure 5 is shown by the strong negative association of iron to connate water where there is an abrupt decrease in connate water at around 0.2% with the increase in FeO above about 1.5%. Triangles indicate obsidian from America, squares from Papua New Guinea, circles from New Zealand and the inverted triangle an obsidian from Turkey.

significant density change associated with a constrained water concentration below around .15%. The correlation between water content and density above about 2.35 is poor and clearly indicates a quite different water /density relationship with a very limited range for water content accompanying density values higher than this. The relationship between water content and density appears in other reports where it is generally seen as an accommodation of the silicate structure to the depolymerising effect of hydroxyl in silicate glasses (Heatherington and Jack 1962, 131). It might be possible to account for this inflection by reference to a change from hydroxyl to water except that the figures given by other authors suggest that this water species change occurs at a higher hydroxyl concentration between 0.3% and 0.4% as seen in the precise water measurements of Newman and others (1986) as presented in Figure 1.

From the analysis of density and water content in the 31 obsidians in this study a working approximation for water content as

H_2O or OH can be found from the density value according to the following equation:

$$Y = A + Bd + (d-D) \bullet C \bullet SGN (d - D) \qquad (3)$$

Where	$Y =$	H_2O	OH
	$A =$	61.56	35.21
	$B =$	-26.19	-14.95
	$C =$	25.59	14.59
	$D =$	2.346	2.348
		(density inflection point)	
	$d. =$	density	
	r^2	.90	.88

The obsidians used in this study are not flawless glasses although none have major mineral or gaseous inclusions. Small sections of obsidians that showed visible signs of a non-glassy phase such as flow banding were removed. Nevertheless, despite the reasonably good correlation between water and density, caution should be exercised in using this equation; this follows from the nature of obsidian as a natural glass where density errors can be caused by the effects of mineral inclusions and gaseous vesicles. No attempt has been made here to derive an effective undiluted glass phase density value by allowing for density differences arising from these two factors, but the residuals deviation from the regression line analysis of the two components in the curve of Figure 7 are likely to have some contribution from both these variables. To some extent the presence of vesicles and mineral inclusions will have opposite affects on density, except that vesicles, having zero density will be far more influential than the likely mineral inclusions, where for example feldspars may range from 2.5 to 2.8 compared with the obsidians ranging in this collection from 2.3 to 2.4. The limits of useful application for density measurements, as an indicator of obsidian's connate water, could be extended if the relative contribution of the diluting microscopic inclusions in the final density determination were precisely measured.

As Mazer *et al.* (1992) and Stevenson *et al.* (1993) have shown there is a close association between obsidian hydration rate and water content. In practical hydration dating terms this means that the wide range of connate water within the "wet" obsidian is accompanied by large differences in hydration velocity with very small differences in glass density whereas conversely the "dry" higher density glasses will have little change in connate water, and hydration velocity, with larger differences in density. For the range of "wet" obsidians from North America with densities less than 2.35, and a relatively wide range of connate water values it will be important to have a precise measurement of water content, whether by density correlation or IR spectroscopy. In this context extra attention to factors, which might affect the density/water correlation, could have some advantage. On the other hand, for the "drier" southwest Pacific obsidians with densities greater than 2.35 and with a much narrower range of water content and hydration velocities, a simple density measurement could provide a useful and acceptable alternative, provided again that any significant density dilution from vesicles and inclusions is taken into account. The equation derived from the analysis of obsidians from widely spaced sources in North America, Papua New Guinea and New Zealand can be a useful way for estimating connate water as a primary variable in hydration dating, or as an alternative test when IR measurement is not possible.

Application to obsidian dating

A recent demonstration of the utility of measuring density as a factor in determining obsidian hydration rates, and using these for dating purposes, comes from its application to archaeological sites in New Zealand (Stevenson *et al.* 1996). The obsidian hydration dating of six sites ranging in age from around 1250AD to early 19th Century correlate well with the radiocarbon dates from the same site context.
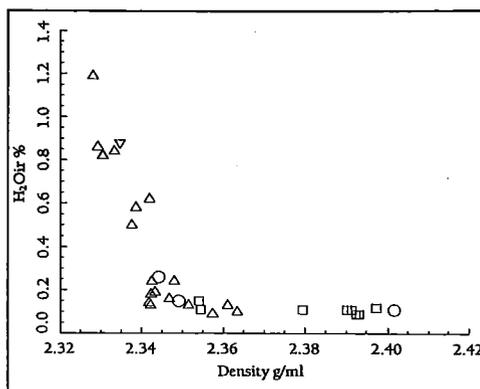

Fig. 7: The clear break in the relationship of connate water to density is shown in this two phase curve. Triangles represent obsidians from America, squares indicate obsidians from Papua New Guinea, circles New Zealand and the inverted triangle obsidian from Turkey. It will be particularly important in obsidian hydration dating for careful measurement of the high connate water in the low density obsidians with their large range of values as shown in the data. On the other hand the southwest Pacific obsidians with density above 3.5 have a very narrow range of low water content that can be well estimated on the basis of density.

CONCLUSIONS

The data for total water and hydroxyl content from 39 obsidians analysed by manometry and infrared spectroscopy, listed by Newman *et al.* (1986:1535), for the relationship between the 5200 cm^{-1} wave band water, and the 4500 cm-1 hydroxyl shows an abrupt increase in the water/hydroxyl ratio at around 0.4% H_2O (Figure 1). The measurement of hydroxyl from the infrared 4500 cm-1 band, as used by Mazer *et al.* (1992) and Stevenson et al. (1993), does not give a direct measure of "water", as H_2O. A closer linear approximation for total water content as a ratio to the hydroxyl content can be found by using the transformation presented in Figure 2 and its associated regression equation. Although water is a minor component in obsidian it nevertheless is

reflected by a high correlation with the density values, and as Mazer *et al.* (1992) and Stevenson *et al.* (1993) have shown, it is closely involved in determining obsidian hydration rates. It appears that silica and iron content are both influential in controlling the accommodation of connate water and in determining the density of obsidians. Measuring water content in obsidian by infrared spectroscopy requires special sample preparation and equipment; on the other hand the measurement of density is relatively simple, requires no special preparation and uses basic laboratory equipment. The equation (3) derived from the relationship of connate water to density presented in Figure 7 provides a simple means for approximating water values either as total water or hydroxyl when these are employed to calculate the hydration rate constants of obsidians. Provided that care is taken to avoid obsidians with heavy concentrations of mineral inclusions or gaseous vesicles, or allowance is made for these, density measurement can provide a simple means for estimating water content for calculation of obsidian hydration rates.

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Location	No	Na₂O	MgO	Al₂O₃	SiO₂	Cl	K₂O	CaO	TiO₂	FeO	Dens	H₂O ir	H₂O d
North America													
A-5 Coso	4937	4.52	-	12.75	76.83	0.12	4.53	0.39	0.04	0.86	2.3423	0.18	0.30
C1	4938	4.38	-	12.69	76.90	0.11	4.67	0.45	-	0.91	2.3386	0.58	0.49
D5	4939	4.41	-	12.47	77.14	0.11	4.54	0.35	0.01	1.02	2.3332	0.84	0.77
D6	4940	4.40	-	12.69	77.11	0.08	4.50	0.36	-	0.91	2.3305	0.82	0.91
F2	4941	4.40	-	12.61	76.69	0.05	4.72	0.37	0.13	1.05	2.3468	0.16	0.13
G2	4942	4.35	-	12.49	76.85	0.06	4.69	0.42	0.10	1.13	2.3433	0.19	0.25
Superior	4952	4.41	-	13.38	76.27	0.05	4.58	0.55	0.08	0.58	2.3425	0.24	0.29
Mullimica	5014	4.02	0.07	12.95	77.05	0.11	4.26	0.73	0.20	0.59	2.3480	0.24	0.13
Coso 4-1	5015	4.11	-	12.56	77.08	0.13	4.70	0.48	0.11	0.94	2.3303	0.82	0.92
Red Hill	5016	4.19	-	13.36	76.31	0.08	4.65	0.64	0.01	0.71	2.3280	1.19	1.04
Red Hill	4947	4.26	-	12.77	77.22	0.05	4.78	0.39	0.06	0.52	2.3422	0.13	0.31
Red Hill	4949	4.23	0.03	12.68	76.80	0.07	4.85	0.49	0.12	0.62	2.3418	0.14	0.33
Gwynn	5	4.01	-	12.68	75.13	0.13	4.90	0.34	0.12	1.55	2.3515	0.13	0.13
Pachuca	6	5.28	-	11.27	75.39	0.19	4.43	-	0.10	2.26	2.3610	0.13	0.12
El Chayal	7	4.28	-	13.60	75.42	-	3.90	0.84	0.13	0.73	2.3574	0.09	0.13
Ixtepeque	8	4.04	-	13.53	74.57	0.13	4.11	0.96	0.21	1.17	2.3634	0.10	0.12
Greco	5017	3.73	0.07	12.73	77.35	0.05	4.85	0.60	0.05	0.58	2.3376	0.50	0.32
DL-93-28	4996	4.51	-	12.34	77.01	0.14	4.57	0.22	0.02	1.16	2.3419	0.62	0.15
DL-93-26	4997	4.41	-	12.19	77.21	0.17	4.70	0.23	0.08	1.00	2.3292	0.86	0.75
Papua New Guinea													
Wekwok	2000	4.90	0.20	13.77	73.28	0.31	4.16	1.10	0.31	1.94	2.3794	0.10	0.10
Rei	280	5.31	0.20	14.15	72.09	0.33	4.12	1.09	0.35	2.25	2.3901	0.10	0.09
Rei	281	5.26	0.30	14.10	71.99	0.32	4.08	1.19	0.31	2.41	2.3932	0.08	0.09
Rei	1858	5.36	0.28	14.09	71.91	0.37	3.94	1.25	0.43	2.29	2.3924	0.07	0.08
Mine 4	1131	5.21	0.22	14.06	72.14	0.37	4.12	1.19	0.34	2.36	2.3973	0.12	0.08
Mine 19	3885	5.27	0.22	14.23	71.98	0.34	4.02	1.24	0.31	2.42	2.3913	0.11	0.09
Mt Bao	287	3.97	0.17	12.78	76.44	0.17	3.93	1.13	0.26	1.11	2.3541	1.15	0.13
Garala	2367	4.22	0.10	12.66	76.11	0.16	4.11	0.96	0.25	1.30	2.3545	0.11	0.13
New Zealand													
Kinloch	177	4.03	0.14	12.53	76.98	0.15	3.56	1.08	0.21	1.29	2.3491	0.15	0.14
Whitipirorua	4920	4.20	-	12.51	76.87	0.23	4.23	0.08	0.08	1.21	2.3442	0.26	0.14
Mayor Is	4921	5.59	-	10.35	74.72	0.23	4.53	0.12	0.25	4.12	2.4016	0.11	0.08
Turkey	4922	4.47	-	12.83	77.02	0.08	4.49	0.39	0.02	0.69	2.3346	0.88	0.47

Table 1. Chemical composition (% by weight) of obsidians used in this study by SEM EDAX Analysis. H₂Oir is determined by infra-red spectroscopy using the procedure of Newman et al. (1986) for OH and recalculated as H₂O using the data and equation from Figure 2. H₂Od is water determined from Figure 7 and equation 3.