



INVESTIGATIONS TOWARDS THE HYDRATION DATING OF AEGEAN OBSIDIAN

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ABSTRACT

Obsidian from the Melos source area (the sources of Adamas and Demenegaki) is one of the most widely distributed natural glasses in the Aegean region and potentially a powerful chronological tool for the study of regional archaeological sequences. However, the usefulness of the Melos obsidian and lesser sources for hydration dating has never been explored. In this paper, we have conducted a series of analyses to assess the weathering characteristics of three obsidian sources (Melos, Yiali, Antiparos). Infrared spectroscopy and heavy-liquid density measurements have demonstrated that Melos and Antiparos obsidians contain little structural water (0.11- 0.13%) while the Yiali source shows a large range (0.09-0.59%). Consequently, hydration rates will be highly variable for some non-Melos glasses. In microscope thin-section, the hydrated surfaces on Melos obsidian tend to be optically weak and poorly defined therefore making precise measurements difficult. However, the measurement of hydrated surface by secondary ion mass spectrometry

(SIMS) and infrared photoacoustic spectroscopy (IR-PAS) has the potential to produce precise thickness determinations that can be used in the dating process.

KEYWORDS: obsidian, Aegean, hydration, Melos, Yiali, dating

INTRODUCTION

Obsidian exchange systems within the Mediterranean, Europe and Anatolia consisted of large regional networks in which obsidian was procured and transported beginning in the Neolithic Period (6000-3000 BC). The regional networks that used the Central Europe (e.g., Vinicky), Eastern Mediterranean (e.g., Mt. Archi, Lipari, Palmarola, Pantelleria) and Aegean (e.g., Melos, Yiali) obsidian sources were closed exchange systems

with little inter-regional overlap (Fig. 1a) (Tykot 1998). In the Aegean region, the Melos obsidian source was extensively exploited by numerous persons who had direct and unimpeded access to the source for thousands of years (Torrence 1984). As a result, Melos obsidian is frequently found in many archaeological contexts thought the Late Bronze Age (Fig. 1b, c).

Obsidian sources within the eastern and western Mediterranean regions have been extensively characterized for their

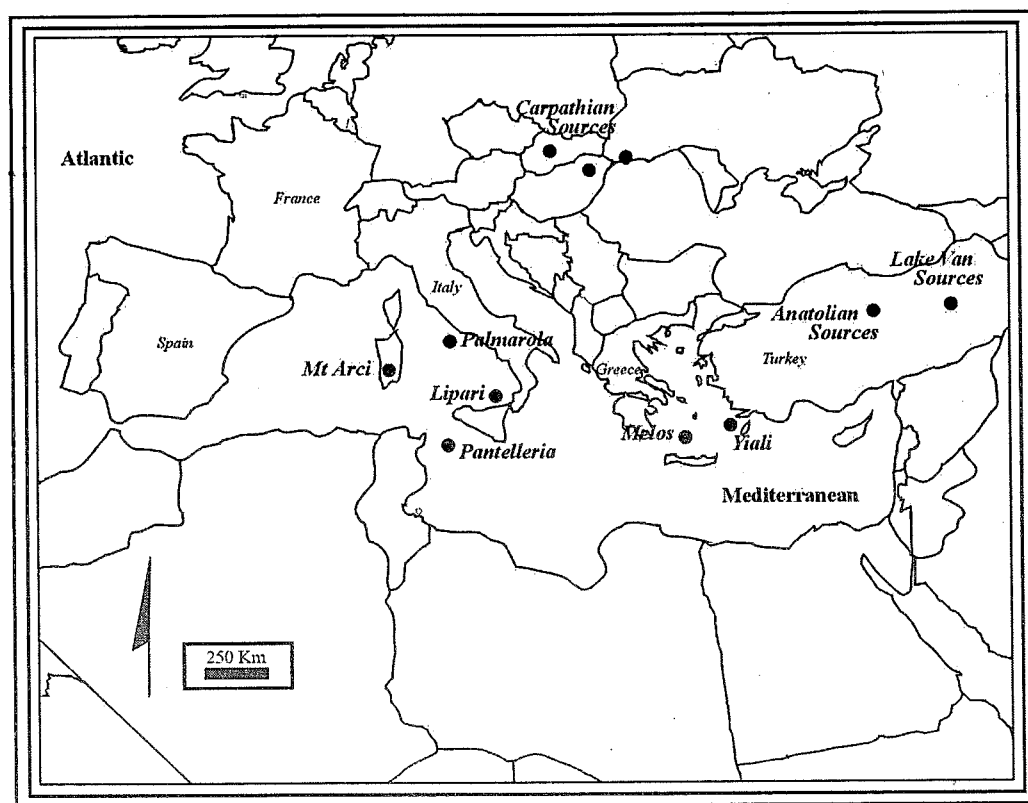


Figure 1a. Map of the Mediterranean region showing the location of obsidian sources.

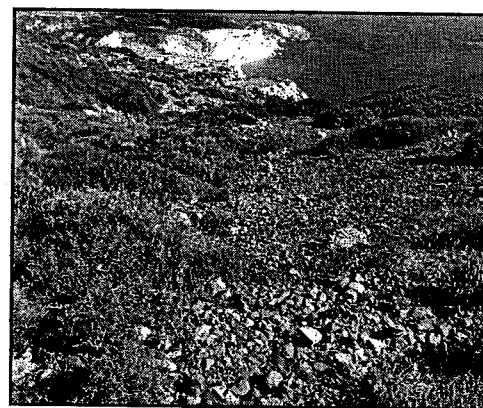


Figure 1b. Obsidian scrap lying today on the ground of Demenegaki source area.



Figure 1c. A close up of four pieces of obsidians at Adamas source area.

trace element chemistry and artifacts may be provenienced to their geological source areas with high levels of confidence (Gratuze 1999; Tykot 1995, 1998; Williams-Thorpe 1995). In the Aegean region, the chemical signature for the Melos obsidian source has been well developed and has shown that glass originated from two flows within the Melos source; that of the Adamas (Sta Nychia) and Demenegaki. Other less utilized deposits occur on Yiali Island and from the Soros Valley on Antiparos Island.

Obsidian hydration dating has received only limited use in the Mediterranean region (Dyson *et al.* 1990; Michels 1982, 1987; Michels *et al.* 1984; Stevenson and Ellis 1998; Stevenson *et al.* 2002). However, the nearly ubiquitous presence and chemical uniformity of the Melos source area make this glass a potentially useful material to date the numerous archaeological contexts within the Aegean. In this paper, we investigate the potential of the Melos obsidian and two secondary sources (Yiali, Antiparos) for use as an absolute dating tool. Geological and archaeological samples are used to: 1) establish archaeological hydration rate

constants for the obsidian sources, 2) to assess the suitability of hydration layers for optical and infrared measurement techniques, and 3) to determine if aggressive archaeological contexts are interrupting the natural hydration process. Based upon preliminary research results in these three areas, problems are identified and guidelines for the application of obsidian hydration dating in the Aegean are proposed.

SCIENTIFIC BACKGROUND

Obsidian hydration dating (OHD) relies upon measuring the depth to which water has diffused into a rhyolitic glass surface and converting the thickness to an age using experimentally derived diffusion coefficients (Fig. 2). This diffusion coefficient in amorphous silicates is strongly correlated with the concentration of water within the surface hydration layer (Drury *et al.* 1962; Lanford 1977; Nogami and Tomozawa 1984) and is referred to as concentration-dependent diffusion. The anhydrous component of the glass has little influence on the mobility of water within a narrow compositional range (Behrens and Nowak 1997). As molecular water

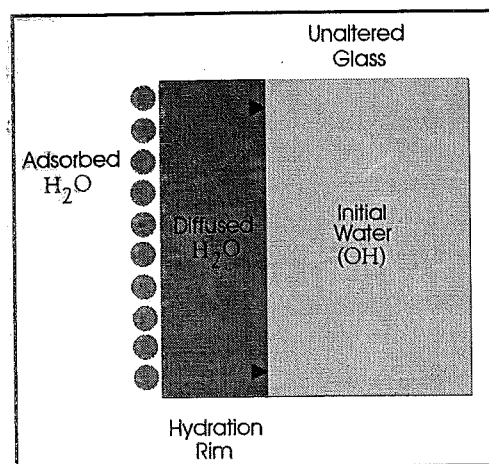


Figure 2. A model of water diffusion in obsidian.

enters the glass, the structure of the glass matrix is altered and allows the diffusion coefficient to increase. This results in the formation of an S-shaped concentration-depth profile (Tsong *et al.* 1980; Lee *et al.* 1974; Anovitz *et al.* 1999) (Fig. 3). However, Lanford *et al.* (1979) has shown

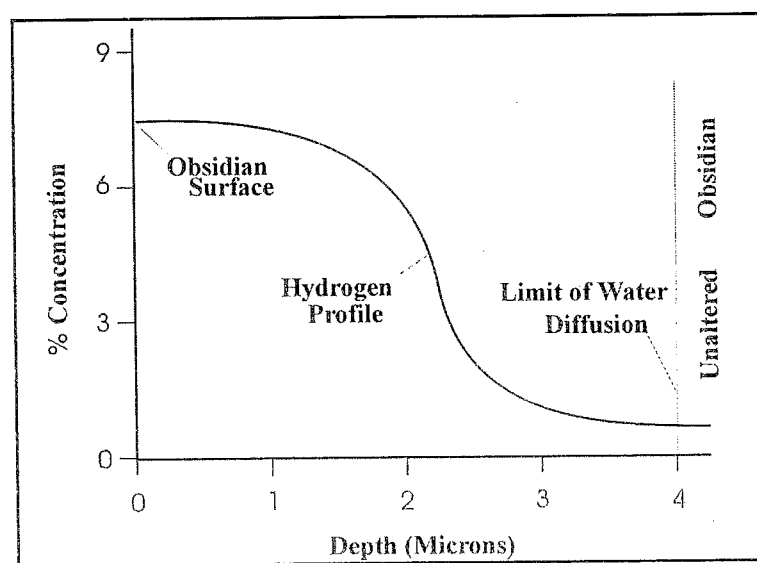


Figure 3. Secondary ion mass spectrometry hydrogen profile of an obsidian hydration rim.

that the hydration front in concentration-dependent diffusion advances with the square root of time in soda lime glass and it is this model that we currently use for water diffusion in obsidian. Liritzis and Diakostamatiou (2002, this issue) propose that the water concentration-dependence of the diffusion coefficient has an exponential form, $e^{f(x)}$, $f(x)$ is a polynomial, which in turn provides to the Ficks 2nd law a specific solution, that contains the diffusion time considered equal to the sample age.

SAMPLE SELECTION

Geological obsidian samples and archaeological obsidian of known provenience were obtained for study (Table 1). On Antiparos Island obsidian nodules are found at multiple locations within the Soros Valley and four samples were selected from surface contexts (2000-128, 141/143). This occurrence is minor in comparison to the vast obsidian distribution

on the island of Melos at the flows of Adamas (Sta Nychia) and Demenegaki where obsidian manufacturing by-products cover approximately a square kilometer in each area (Torrence 1981, 1984). Eight samples from the Adamas flow (2000-129/136) and four fragments from the Demenegaki flow (2000-137/140) were obtained. From the obsidian source of Yiali (also known as Giali, Fig. 1), sixteen

TABLE 1: Provenience Locations for Geological and Archaeological Study Specimens.

Lab No.	Provenience
2000-128	One fragment from the Soros Valley on Antiparos Island that is a spherulite found within volcanic tephra
2000-129/130	Melos Island, Adamas Source: obsidian outcrop, Site 1
2000-131/132	Melos Island, Adamas Source: bedrock exposure, Site 1
2000-133/134	Melos Island, Adamas Source: bedrock exposure, Site 2
2000-135/136	Melos Island, Adamas Source: surface sample from Nychia Valley
2000-137/140	Melos Island, Demenegaki Source: surface sample
2000-141/143	Three specimens from the Soros Valley on Antiparos Island
2000-144/146	Melos Island, Philakopi Site, Early Bronze Age: three blades from the excavated area
2000-147	Melos Island, Philakopi Site, Early Bronze Age: fragment from a tomb at Kapari
2000-148/150	Mykonos, Ftelia Site: three blades from excavated trenches
2000-151	Stavraki Site (Kea)
2000-152	Cyclops Cave, Yioura: Section XX, Layer 14, Sq. 11-14, AA412
2000-153	Cyclops Cave, Yioura: Section X West, Layer 4, AA45
2000-154	Cyclops Cave, Yioura: Section X, Layer 7, AA259
2000-155/160	Mykonos, A5, t. 2, 4, 5, 7, 8
2000-161	Sarakino Cave: Section X, Layer 1
2000-162	Sarakino Cave: Section A, t.8
2000-163	Yiali: Section 2
2000-164	Kythnos Island: Mesolithic layer
2000-165	Yiali: Section A
2000-166	Yiali: Section Z
2000-176/181	Yiali: Geological
2000-182	Melos: Philakopi Site, blade
2000-183	Melos: Demenegaki Source, blade

geological samples (2000-176/181 and 2001-1/10) and three artifact samples (2000-163, 165/166) were acquired from the immediate source or nearby archaeological sites. In addition, archaeological samples were recovered from excavated collections obtained from Philakopi (Melos), Ftelia (Mykonos), Stravraki Site (Kea), Cyclops Cave (Youra, Alonisos), Sarakino Cave (Kopais), and Kynthos Island. All of these artifacts have been assigned to the Melos obsidian source

based upon their macroscopic attributes.

ANALYTICAL PROCEDURES

Hydration Rate Determination

The development of obsidian hydration rates has been a fundamental issue for users of the method. To be a useful dating method, and it must be demonstrated that molecular water diffuses into obsidian at a predictable rate as a function of temperature and relative humidity. Low

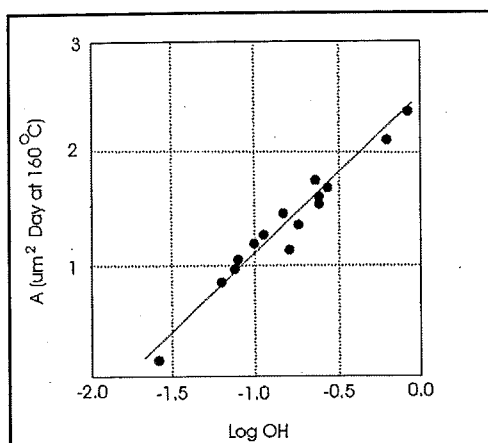


Figure 4. The relationship between the pre-exponential (A) at 160°C and the log of the structural water concentration (OH).

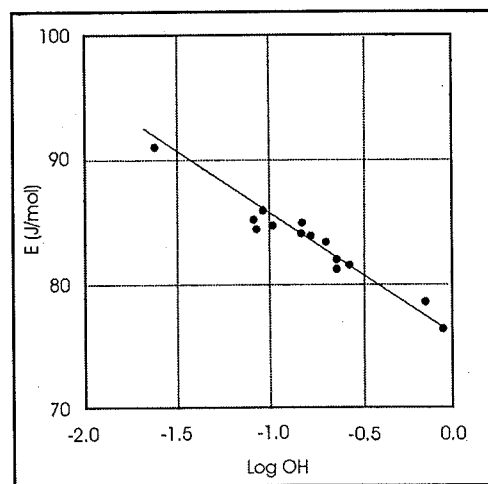


Figure 5. The relationship between the activation energy (E) and the log of the structural water concentration (OH).

temperature (<180°C) hydration on geological samples is currently the preferred approach to establish hydration rates on an empirical basis. This approach has been extensively investigated using a variety of reaction media and temperature settings (Ambrose 1976; Ericson 1981;

Friedman and Long 1976; Michels *et al.* 1983; Stevenson and McCurry 1990; Stevenson and Scheetz 1989; Stevenson *et al.* 1989). In these experimental designs, fresh obsidian surfaces were exposed to either a liquid or vapor atmosphere within an open or sealed reaction vessel maintained at temperatures between 90°C and 250°C. The experimental data have repeatedly documented that hydration proceeds with the square root of time and this supports the traditional age equation given by $x^2 = Kt$, where x is the hydration depth or hydrated rim, K is the diffusion rate ($\mu\text{m}^2/1000$ yrs) and t is time. However, the diffusion rate controlling parameters are still poorly understood and impact our understanding of obsidian hydration (Anovitz *et al.* 1999).

The hydration rims formed at elevated temperature were measured and used to calculate the pre-exponential (A) and the activation energy (E). These constants were used to estimate archaeological hydration rates at ambient conditions with the Arrhenius equation:

$$K = Ae^{-E/RT} \quad (1)$$

where: K = archaeological hydration rate

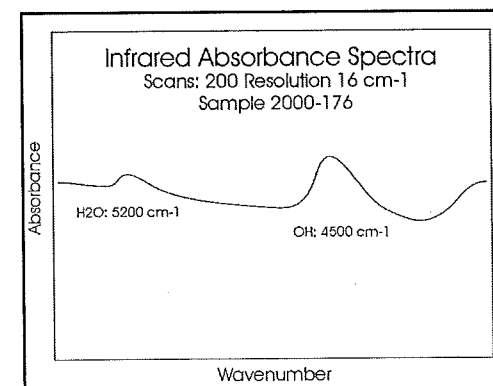


Figure 6. Infrared absorbance spectra of sample 2000-176 showing the H₂O and OH peaks.

A = source specific rate constant
E = activation energy
R = universal gas constant
T = temperature

The dependence of hydration rate on obsidian chemical composition has been addressed through theoretical considerations (Ericson 1981) and by correlation of high temperature hydration rates with glass chemical constituents (Friedman and Long 1976). Recent work by Mazer *et al.* (1991), Stevenson *et al.* (1993), and Stevenson *et al.* (1998) has shown a strong dependence between the structural water content (OH) of the glass with the 100% relative humidity pre-exponential at elevated temperature (A) and the activation energy (E), (Fig. 4, Fig. 5). With this calibration established, it was now possible to estimate archaeological hydration rates for individual artifacts from the concentration of OH contained within the glass.

Bulk density and structural water of Aegean obsidians

In order to develop an OH-based hydration rate calibration, the structural water content was precisely determined on transparent obsidian sections using the infrared spectroscopy protocol (FTIR) of Newman *et al.* (1986) (Fig. 6). The application of the calibration to archaeological obsidians was significantly hindered by the lack of infrared transparency in many obsidians. A approximate method to avoid this limitation was proposed by Ambrose and Stevenson (1994) who developed an additional calibration demonstrating a mathematical relationship between total water content and glass density. High-density obsidians will have low quantities of structural water and hydrate slowly while low-density glasses will have higher water concentrations and faster hydration rates. With this relation-

ship precisely established, water values, and thus hydration rates, for virtually all archaeological obsidians can be non-destructively estimated.

Structural water values were estimated from bulk density values using the Archimedes methods with heavy liquids (Ambrose and Stevenson 1994; Stevenson *et al.* 1996). The results (Table 2) show that each of the four sample locations have overlapping ranges for their structural OH contents. Soros Valley obsidian ranges between 0.11 to 0.13%, Adamas between 0.11 and 0.12%, Demenegaki between 0.11 and 0.12%, and Yiali between 0.12 and 0.85%. The Yiali source is highly variable and an infrared water analysis was conducted to confirm this range.

To our knowledge, the structural water content has not been determined for obsidian sources and flows within the Aegean region. In this study, infrared (FTIR) water determinations were performed on two high-water samples from the Yiali source that were transparent to light when cut into 1-2 mm thick, parallel sided, sections. Glass from the Melos and Antiparos sources is opaque even when polished to a thickness of less than 1 mm. The infrared spectrum revealed that each specimen from Yiali was high in structural water concentration and included contributions by molecular water (H₂O) as well as hydroxyl (OH). Specimen 2000-176 had an OH concentration of 0.59% and an H₂O value of 0.19% (Table 2, Fig. 6). Similarly, sample 2000-181 contained 0.43% OH and 0.15% H₂O. These high concentration values confirm the elevated structural water levels for the Yiali source, but they are not in agreement with the OH concentrations estimated from density values. We believe that the non-convergence is due to inclusions or air bubbles in

TABLE 2: Water Contents of Obsidian Sources at Antiparos Island (Soros Valley) Melos Island (Adamas, Demenegaki) and Yiali. Values in brackets represent infrared (FTIR) water analyses. All other water values are estimated from obsidian density; N/A= Not applicable.

Lab No.	Provenience	Density	%OH-
<i>Antiparos Island</i>			
2000-128	Soros Valley	2.3466	0.13
2000-141	Soros Valley	2.3467	0.13
2000-142	Soros Valley	2.3548	0.12
2000-143	Soros Valley	2.3661	0.11
<i>Melos Island</i>			
2000-129	Adamas	2.3615	0.12
2000-130	Adamas	2.3582	0.12
2000-131	Adamas	2.3639	0.11
2000-132	Adamas	2.3588	0.12
2000-133	Adamas	2.3623	0.12
2000-134	Adamas	2.3556	0.12
2000-135	Adamas	2.3569	0.12
2000-136	Adamas	2.3605	0.12
2000-137	Demenegaki	2.3737	0.11
2000-138	Demenegaki	2.3485	0.12
2000-139	Demenegaki	2.3704	0.11
2000-140	Demenegaki	2.3806	0.11
<i>Yiali</i>			
2000-176	Yiali ¹	2.3275	0.85 (0.59)
2000-177	Yiali ²	2.3320	0.59
2000-179	Yiali ¹	2.3589	0.12
2000-180	Yiali ²	2.3422	0.13
2000-181	Yiali ²	2.3391	0.17 (0.43)
2001-1	Yiali (Elos) ³	N/A	(0.10)
2001-2	Yiali (Elos) ³	N/A	(0.09)
2001-3	Yiali (Elos) ³	N/A	(0.09)
2001-4	Yiali (Elos) ³	N/A	(0.10)
2001-5	Yiali (tephra)	N/A	(0.09)
2001-6	Yiali (tephra)	N/A	(0.10)
2001-7	Yiali (tephra)	N/A	(0.09)
2001-8	Yiali (tephra)	N/A	(0.10)
2001-9	Yiali (tephra)	N/A	(0.10)
2001-10	Yiali (tephra)	N/A	(0.10)

¹ from within the pumice

² from Elos source

³ spotty sample ref: YLEL / 2-5

the Yiali obsidian, which would reduce the overall density and inflate the water content. This appears to be the case for sample 2000-176 (note that structural water can consist of both OH and H₂O. They can coexist together. In the case of the Melos sources only OH is present and in very low concentration. However, in the water rich Yali samples both forms of water are present as structural water).

For the moment, we do not have an explanation as to why the density determined OH value (0.17%) for sample 2000-181 resulted in such a low concentration value. A first explanation is that it may be due to the high dispersion in water versus density especially at the inflection point in the exponential like curve of $d=2.34$ and at higher density values (see e.g., Fig. 2 in Stevenson *et al.* 2000). The occurrence of non-consistent results on the Yiali obsidian indicates that density measurements of OH concentration should not be conducted for Yiali obsidians. The inhomogeneity in the Yali glass can severely effect the densities, and thus the water estimation derived from them, resulting in inaccurate determinations. Therefore, the results from IR absorbance can be very different. In cases of difference, we trust the IR absorbance measurements.

In light of this situation of variable water content, four additional geologi-

cal samples (2001-1/4) from the Elos source, with characteristic white spotty inclusions, and six samples (2001-5/10) from the tephra deposits (no inclusions) were analysed by infrared transmission procedures (Table 2) to more fully characterize the source. The closeness of the results amongst the Yiali obsidians for the two sources based on the data from samples 2001-1/10, show them to be identical in water content. There is no significant variation within or between the sources. The difference between the Yiali samples with low water (0.09 to 0.1%) and the higher water Yiali samples (0.12 to 0.59%), appears to be the result of variation in water within the source. We are using very small numbers of samples from each source and the source may be variable. Samples 2000-176 and 2000-179 are derived from within the tephra deposits (non-spotty) and are of pyroclastic origin. Samples 2000-180, 181 are spotty from Elos. Volcanic ejecta are sometimes higher in water because of their rapid cooling history. This reduces the time for water and gases to be given off.

The low structural water concentrations for the Melos, Antiparos and a portion of the Yiali glasses indicates that the hydration rates will be slow and highly similar. Pre-exponential (A) values are estimated to range between 1.14 and 1.28 um^2/day at 160°C and activation energy values vary from 85321 and 84889 Joles/mol. As a result, hydration rims will form slowly even at higher ambient temperatures. In contrast, the Yiali obsidian with high structural water will hydrate faster as OH concentration increases from 0.12 to 0.59%. Infrared spectroscopic analysis on a larger number of samples will be required to establish the water concentration range, and the rate range, for this source.

Optical Hydration Rim Measurement

The measurement of hydration rim thickness with an optical microscope and micrometer has been standard practice for approximately 40 years. However, obsidians that are opaque and contain high numbers of microlite inclusions are frequently problematic because the image is interrupted or weakly defined. This problem is enhanced when the hydration of the glass is slow and the hydration bands thin.

A set of 25 archaeological samples were investigated. Twenty-two were visually determined to be from the Melos source and three samples were from Yiali. Six geological samples from Yiali with old surfaces were also included (Table 3). Standard petrographic thin sections were prepared and examined at a magnification of 800X. Observable exterior hydration bands were observed on 16 of the Melos specimens and ranged in thickness from 1.43 um to 4.35 um with the most frequently occurring widths between 3-4 um (Table 3). These rims were weakly birefringent and the diffusion front boundary was frequently difficult to identify. In seven cases, or 32% of the samples, there was no observable hydration. The surface of the sample did not appear to be newly created nor was there evidence of abrasion. It was hypothesized that hydration was present but was not optically visible. In contrast, the Yiali geological and archaeological samples had clear and well-defined hydration rims that ranged between 4.84 um and 28.91 um .

In some regions of the world, high ground temperatures, high rainfall and alkaline soils can result in environments that attack the surface of the obsidian and remove the hydration layer. Abrasion by wind-blown deposits can also remove the developing layer and result in erroneous

dates. To check for alteration, we compared the surface hydration layers with protected rims found within impact fissures that penetrate the glass structure (Ambrose 1996). Within the fissure, moisture vapour may enter but transport of silica away from the glass is hindered by the very narrow, sub-micron width, of the fissure.

Impact fissures were identified on three samples (Table 3). In two cases (2000-144, 2000-180), the surface hydration layer is slightly less in width than the fissure band width by about 0.3-1.0 μm . Because the difference exceeds the error limits of the optical microscope (± 0.2 μm) it is inferred that a small portion of the surface has been removed by abrasion or dissolution. However, on the third sample (2000-181) the surface and fissure widths are within measurement error and demonstrate that the obsidian surface has not been altered. A larger sample of specimens must be examined but these preliminary results suggest that archaeological contexts should be evaluated on a case by case basis each time the dating method is applied.

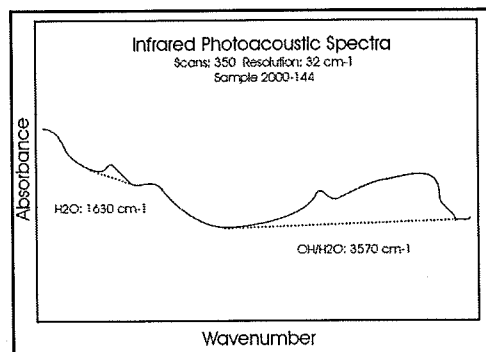


Figure 7. Infrared photoacoustic spectra of an obsidian hydration rim showing the H₂O and OH/H₂O water bands.

TABLE 3: Optically Measured Obsidian Hydration Rims NH= No hydration visible; ---- = insufficient sample.

Lab No.	Provenience	Rim
<i>Archaeological Samples</i>		
2000-144	Phil-1 (Ext.)	4.33
	(Fissure)	4.99
2000-145	Phil-2	3.78
2000-146	Phil-3	NH
2000-147	Phil-3; Tomb	3.1
2000-148	Myconos #1	NH
2000-149	Myconos #2	3.59
2000-150	Myconos #3	NH
2000-151	KEA	NH
2000-152	YR-1	1.43
2000-153	YR-2	3.37
2000-154	YR-3	3.21
2000-155	MYC-1	3.27
2000-156	MYC-2	2.82
2000-157	MYC-3	NH
2000-158	MYC-4	4.35
2000-159	MYC-5	3.27
2000-160	MYC-6	NH
2000-161	SAR-1	3.92
2000-162	SAR-2	NH
2000-163	YAL-1 (Yiali)	6.43
2000-164	KYT-1	3.06
2000-165	YAL-2 (Yiali)	6.41
2000-166	YAL-3 (Yiali)	5.43
2000-182	Melos	4.35
2000-183	Melos	3.86
<i>Geological Samples</i>		
2000-176	Yiali	28.91
2000-177	Yiali	25.10
2000-178	Yiali	-----
2000-179	Yiali	4.84
2000-180	Yiali (Ext.)	9.60
	(Fissure)	10.62
2000-181	Yiali (Ext.)	10.31
	(Fissure)	10.23

Non-optical Hydration Rim Measurement

A variety of high precision, non-optical, depth profiling techniques exist for measuring the width of the hydration rim (Lee *et al.* 1974; Tsong *et al.* 1978; Duerden *et al.* 1982). In this study, we have selected secondary ion mass spectrometry (SIMS) and infrared photoacoustic spectroscopy (IR-PAS) to measure the depth of hydration based upon the concentration of the H₂O water species in the hydrated layer (Fig. 3, Fig. 7). In the latter method, an obsidian sample less than 10 mm in diameter is placed in a helium filled chamber equipped with a high sensitivity microphone. The infrared beam is trained on the sample surface. The specimen absorbs the infrared radiation and undergoes an oscillatory heating and becomes a source of thermal waves. The waves within the bulk sample propagate to the surface and into the helium atmosphere. The photoacoustic signal is generated at the surface and is caused by the thermal expansion of the gas (McClelland *et al.* 1993). The magnitude of the signal varies in proportion to the concentration of the water species. The depth of water penetration has been calibrated through the correlation of SIMS depth values with absorbance intensity values (Stevenson *et al.* 2001). Precision is estimated to be ± 0.1 μm .

Six samples were first analyzed by IR-PAS and included optically measured specimens with and without visible hydration rims (Table 4). Each sample was run at a

resolution of 32 wavenumbers for 350 scans. Carbon black, supplied by the manufacturer, was used to establish the background conditions for the instrument. The absorbance values were calculated from peak heights and converted to micron values. Each absorbance value represents an averaged measure for the entire surface of the sample exposed to the 5 mm diameter infrared beam. The water band at 1630 cm⁻¹ (H₂O) was monitored (Fig. 7).

The optical and IR-PAS measurements on Table 4 reveal two interesting observations. First, obsidian hydration layers were verified by IR-PAS to be on samples without observable hydration at high optical magnification. This confirmed the hypothesis that water diffusion had occurred but was not birefringent in nature. Second, the IR-PAS hydration layers did not correlate well with the optical measurements with significant under or over estimation occurring. This was surprising because a previous comparison between these types of data revealed them to be highly inter-correlated (Stevenson *et al.* 2000). To further investigate these results SIMS analyses was undertaken.

Hydrogen (H) profiles were acquired by secondary ion mass spectrometry (SIMS). The analyses are to be performed

TABLE 4: A Comparison of Optical, IR-PAS and SIMS Hydration Rim Measurements.

Lab No.	Optical (μm)	IR-PAS (μm)	SIMS	Profile
2000-144	4.33/4.99	3.14	4.05	Step
2000-145	3.78	3.90	4.10	Step
2000-146	-----	4.24	4.38	Sloping
2000-147	3.10	4.38	3.90	Step
2000-148	-----	4.51	4.07	Sloping
2000-149	3.59	3.01	5.31	Sloping
2000-150	-----	1.2	1.50	ERFC

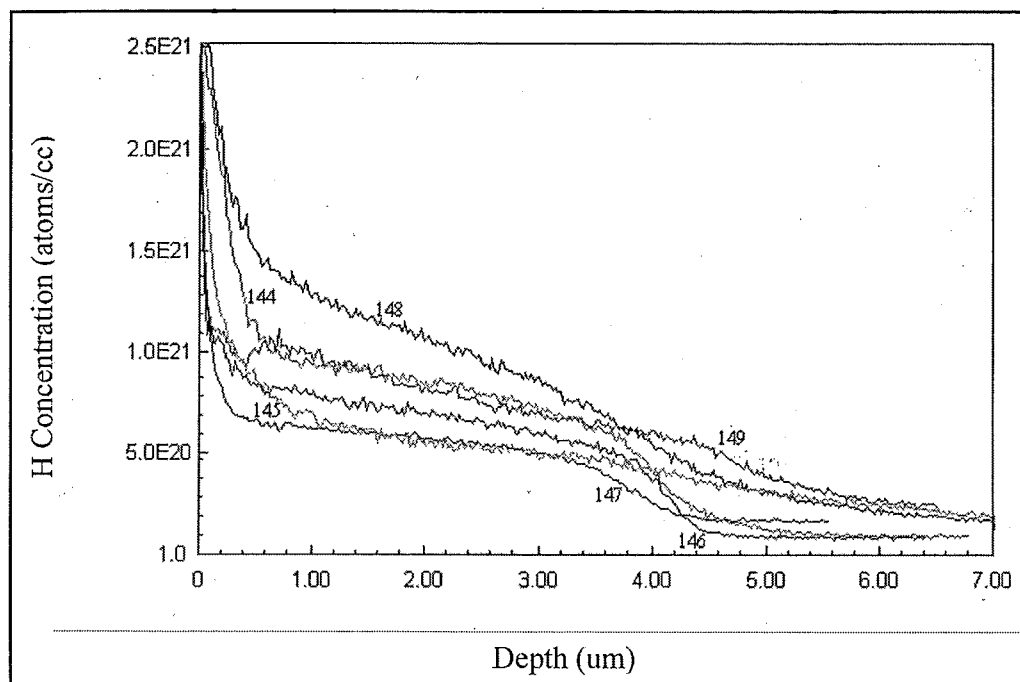


Figure 8. SIMS hydrogen profiles for samples 2000-144 to 2000-149.

using a PHI Model 6300 quadrupole-based secondary ion mass spectrometer. A 5.0 KeV Cs⁺ primary ion beam with an impact angle of 60° with respect to surface normal was used and negative secondary ions were detected. Charge build-up during profiling was compensated for by use of an electron beam. The measurements were performed using a 300 x 300 micron ion beam raster, which resulted in very little visual disruption to the sample surface. Quantification of H was accomplished using the relative sensitivity factor (RSF) obtained by analysing a deuterium implanted standard. The sputter rate (A/s) for the profiles was determined by measuring the time required to sputter to the 1.6 um D peak depth. The thickness of the hydrated layer was calculated at the point where the H curve reaches full width-half maximum (FWHM).

Generally, the SIMS depth scale accuracy is within 5-10% although repeat measurements performed during other similar studies show a 3-5% error (Note: the optical measurement does not locate the point where the water reaches background levels. It is not sensitive enough. The glass structure must be altered by diffused water in order to bend the light differently. This we think occurs near the FWHM point on the hydrogen profile. That is why the FWHM point is used in the comparison).

The SIMS analysis verified the presence of hydrated surfaces on all of the artifacts (Table 4), thus verifying the IR-PAS results. Unexpectedly, sample 2000-150 exhibited a very narrow hydrogen layer with an error function type profile. A reinspection of sample 2000-150 revealed that the artifact was a chert. This

sample was eliminated from further consideration. For the remaining samples, the SIMS thickness values differed significantly from the optical measurements with deviations of up to 1.7 um. The IR-PAS measurement convergence was only slightly better with four of the 6 specimens being within half a micron of the SIMS value. This lack of correspondence between any of the three techniques was disturbing and required an explanation.

The form of the hydrogen profile offered a possible answer. Characteristic sigmoid (S-shaped) profiles were present on three samples (2000-144/145, 2000-147) and sloping profiles without the characteristic step were present on the remaining three samples (2000-146, 2000-148/149 (Fig. 8). The profile full-width half-maximum (FWHM) point is the approximate location of the optically visible hydration layer. At a point along this gradient the stress in the glass from diffused water increases to the point where birefringence is created. The hydration layer becomes optically visible although the exact point along the front of the profile can exhibit variation (Anovitz *et al.* 2000). With a sloping profile this problem is amplified. The lack of a steep rise in concentration would hinder the formation of a birefringent layer and this is what we see in samples 2000-146 and 148 where no optical hydration layer is present. Sample 2000-148 also has a sloping profile and it is the sample with the widest divergence between the optical width and SIMS thickness measurement (1.7 um).

In addition, the amount of diffused water in the Hydration layer, as reflected by the shape of the hydrogen profile, will affect the final thickness measurement IR-PAS. The SIMS profiles of all the samples approach the same background concentration of hydrogen and indicate that

the samples are the same glass with low structural water (e.g. Melos). However, the concentration of hydrogen in the near surface regions is highly variable. This variation in surface hydrogen concentration may reflect different amounts of available moisture present during the hydration history of the artifact and impact the shape of the curve in the near surface region and the overall amount of diffused water. Obsidian with a low concentration (e.g. 2000-147) may have been subjected to a low environmental relative humidity. As a result, two samples with identical diffusion front depth locations but different profile concentration levels will produce variable IR-PAS depth values. This is because the IR-PAS approach measures all the diffused water under the curve to arrive at a depth value. In contrast, depth estimates from the SIMS hydrogen use the location of the diffusion front to estimate depth without reference to the near-surface concentration.

DISCUSSION

Our preliminary examination of the hydration properties of the Melos, Yiali and Antiparos obsidians has revealed the dating potential as well as problematic areas in the application of the method. The Melos obsidian appears to be highly uniform in structural water content even between the two flows of Adamas and Demengaki. This suggests that one set of average hydration rate constants (A, E) may be applicable to all Melos obsidian that is distributed throughout the Aegean once a statistically reliable number of samples have been evaluated. In contrast, the Yiali obsidian can be highly variable in structural water concentration from sample to sample. The OH content will need to be determined in conjunction with each dated sample using infrared absorbance

spectroscopy. Because of inhomogeneity in the Yali glass, the use of density-based estimates of OH cannot be used with confidence at this time.

The identification and measurement of hydration rims also has both positive and negative aspects. The Melos hydration layers are weakly defined and frequently not optically identifiable even though they are present. In contrast, the hydration rims on Yali obsidian are clearly visible and large. Yali obsidian is not as widely dispersed as Melos obsidian and is thus more geographically limited as a dating tool. IR-PAS measurement can be used on both types of glasses and has the ability to provide measurements irrespective of the optical qualities of the glass.

The hydration measurement data of external surfaces and protected internal fissures has shown that hydration is proceeding in a natural and uninterrupted manner in some cases. The surface of the glass is not being dissolved, pitted or removed by highly alkaline soils. As a result, the measured thickness may be converted to estimated ages once the temperature and relative humidity regimes of

the soil have been documented (digital temperature and humidity sensors are already placed in sites and results will become available later this year). In other contexts, the surface of the obsidian appears to be slightly eroded by 0.3-1.0 μm , an amount that could seriously effect the final age determination of an artifact, based solely on the depth of the hydrated rim. The researcher must evaluate the context of each investigated site to determine the extent of surface deterioration and the suitability of the obsidian for dating.

Another problematic aspect is the lack of convergence between optical, IR-PAS and SIMS techniques. It is our current opinion that this variation is a function of artifact context and the temperature/moisture conditions that are experienced during hydration history. Careful sampling of artifacts from contexts with equivalent moisture regimes make alleviate part of the problem. However, further studies will be required to determine why the hydrogen profile diverges from its characteristic S-shaped profile.

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