OBSIDIAN AS A TIME KEEPER:
AN INVESTIGATION IN ABSOLUTE AND RELATIVE DATING

by

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ABSTRACT

Purpose of the Study:

Over the last 30 years, obsidian has served archaeologists by providing a means to estimate age in one capacity or another. An ultimate objective of this thesis was to reexamine both absolute and relative dating approaches.

Procedure:

Two lines of action were pursued in this endeavor. First, an extensive review of studies on glass surface reactions was undertaken, with the intent to synthesize the information gathered, and assess both its pertinence to the obsidian hydration process and its implications regarding dating issues. Secondly, accelerated hydration experiments were conducted, reacting California North Coast Ranges obsidians, with the intent to evaluate the application of the experimental method for both absolute and relative dating purposes.

Findings:

From the review of studies on glass surface reactions, it was found that glass scientists have made considerable advances recently in their understanding of glass weathering kinetics. Many factors, working synergetically, have been shown to affect both mechanisms and rates of reaction, reflecting the complexity of glass weathering processes. As the literature search indicates, such factors as solution pH, solution composition, glass surface area-to-solution volume (SA/V), relative humidity, and temperature, all affect experimentally determined rates of reaction. The extent of their significance to naturally hydrating obsidian, in archaeological site contexts, needs to be assessed to fully evaluate implications to obsidian dating in its absolute chronometric capacity.

From accelerated hydration experiments, designed primarily to investigate the replicability of test results, it was found that some variability between results occurred. This variability was attributed to small differences in condition such as non-standardized flake sizes (affecting SA/V ratios), and differences in solution composition (deionized water vs. silica saturated solutions). Although it was determined that test results appear to be reproducible if all factors are held constant, the appropriateness of applying condition-specific rate constants (derived from these high-temperature essentially closed-system experiments) to field conditions was questioned.

Conclusions:

I conclude, based on the review of glass surface reaction studies and accelerated hydration experiments, that the **absolute** dating of obsidian remains less than secure. From a more practical standpoint, until problematic issues are resolved, perhaps a **relative** dating approach has more merit. An investigation was conducted exploring the potential of accelerated hydration experiments to enhance this approach. A proposed application is suggested to obtain relative calibrations of hydration measurements between sources, allowing temporal ordering and providing a means to make cross-source comparisons of obsidians exposed to similar temperature histories and conditions.

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Chapter 1

OBSIDIAN DATING

Introduction

The origins of obsidian dating began with two studies. First, while investigating the water content of volcanic glasses, Ross and Smith (1955) noted that obsidian contained approximately 0.1% water. Perlite, hypothesized to be formed by the hydration of obsidian (a process of diffusion or gradual adsorption of water into glass), was found to contain 2-5% water. Comparing the physical properties of these two glass phases (obsidian and perlite) with increasing water content, Ross and Smith observed a corresponding increase in indices of refraction. This and an optical effect called strained birefringence (caused by a theorized increase in surface density), allowed distinction between hydrated and non-hydrated portions of obsidian under microscopic examination using polarized light. Secondly, Friedman and Smith (1958) presented evidence suggesting that hydration was a post-magmatic process slowly occurring at atmospheric temperature and pressure.

In 1960, Friedman and Smith investigated whether glass hydration develops at a fixed rate. Results of hydration analyses on obsidian from archaeological strata indicated a correlation between the depth of water penetration into glass and the passage of time, suggesting the possibility for establishing a rate of hydration. On the basis of these findings, Friedman and Smith proposed using obsidian as a dating method; the basic premise being that if the rate of hydration is known, then the thickness of the hydrated layer on a specimen could be used to determine the time elapsed since exposure to its surface began. This method is described as having potential to date "any event that causes a fresh surface-be it the purposeful flaking of a tool by ancient craftsmen or the casual chipping and abrading of an obsidian pebble in transport by a glacier or river" (Friedman and Trembour 1978:46). They acknowledged in 1960 that the validity of utilizing hydration measurements as a basis for dating depended on the constancy of the hydration rate, and additionally, that many problems geochemical and archaeological in nature needed solving. Soil temperature and glass chemical composition were identified as the principal factors affecting the rate of hydration.

Based on plots of dated archaeological specimens and their hydration rim measurements, Friedman and Smith suggested that "the rate of increase of the hydrated layer is inversely proportional to the thickness of the layer" (1960:486) as defined by the equation:

$$x = kt^{0.5} \tag{1}$$

where x = depth of water penetration in microns, k = rate constant at a fixed temperature, and t = lapsed time in years. Other investigators have debated the given time exponent of 0.5 on the basis of archaeological evidence, finding values ranging from 0.33 to 1.0 (e.g., De Atley and Findlow 1980; D.L. Clark 1961, 1964; Ericson 1975, 1977; Findlow 1977, Findlow et al. 1975; Friedman and Smith 1960; Friedman and Trembour 1983; Hurtado de Mendoza 1981; Kimberlin 1976; Leach and Naylor 1981; Minor 1977). To date, there remains a lack of consensus (see Ericson 1988; Meighan 1983), although the disagreement seems to have narrowed between a diffusion model ($t^{0.5}$) and a linear model (t). Ericson (1977:68) suggests that "the variety of descriptive models in the literature may be the result of inadequate control of temporal association, source specification, or hydration (thermal) environment." Findings by glass scientists regarding time dependency are presented in Chapter 2.

Trends in Use*

Two different approaches to the application of obsidian dating have developed: absolute and relative. In the **absolute** approach, archaeologists have attempted to calibrate hydration measurements with calendar years. Calibration is achieved through the determination of source- and temperature-specific hydration rates. Two types of data have been used in determining rates; archaeological and experimental.

Archaeologically derived rates are generally sought through the correlation of hydration measurements with an independent chronometric scale such as associated radiocarbon assays or dendrochronology (e.g., Ericson 1975; Findlow et al. 1975, 1982; Hurtado de Mendoza 1981; Minor 1977). Correlation sets of hydration thickness and time must represent obsidian originating from the same geochemical source and having experienced similar temperature histories. The temperature parameter for a rate derived in this manner is treated implicity (see Equation 1).

Experimentally derived rates are sought through the monitoring of accelerated hydration development induced by elevated temperature conditions, a method pioneered by Friedman et al. (1966). The relationship between the diffusion rate constant k, and the absolute temperature T (^{o}K), stemming from Fick's law on diffusion, is given as:

$$k = Ae\ [-E/RT] \tag{2}$$

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* For a thorough review, see Michels and Tsong (1980)

where A = a constant, E = activation energy in kcal/mol, and R = gas constant. According to this technique, rate constants are derived from experimental data by calculating a source-specific activation energy and pre-exponential constant which are then entered into Equation 2 (see Michels et al. 1983). This rate constant must then be extrapolated to those ambient temperature conditions at which the obsidian has been exposed. This requires the estimation of an effective or integrated soil temperature representing, as accurately as possible, the obsidian's temperature environment.

Relative dating developed early on "to avoid the problems connected with determining hydration rates of specific archeological areas" (Michels 1967). Michels points out several major difficulties which discouraged early absolute dating applications: (1) separate rates of hydration have to be established for each microenvironment given temperature dependence; and (2) different rates of hydration have to be established for each obsidian source given glass compositional dependence (Michels 1967). The first major relative dating application was conducted by Michels (1965) in his dissertation <u>Lithic Serial Chronology through Obsidian Hydration Dating</u>.

Although much progress has been made towards identifying sources of obsidian and characterizing their chemical compositions, difficulties still persist in securing reliable hydration rates (e.g., R. Jackson 1984a:103-105, 1984b:184; T. Jackson 1984; Jenkins and Warren 1984:54). Therefore, relative dating continues to be employed by some. In a relative dating approach, obsidian artifacts are ordered according to successive increments of hydration measurement in order to place them in relative chronological context. To operationalize this approach, the obsidian's chemical composition and temperature history must be held constant for a given population of artifacts.

Present Status

How is obsidian dating regarded by archaeologists today? A survey of nationally and some internationally distributed literature published over the past 10 years, indicates that few researchers analyzing obsidian are conducting hydration studies (e.g., Baugh and Nelson 1987; Boksenbaum et al. 1987; Ferriz 1985; Healan et al. 1983; Hughes 1982, 1986; Hughes and True 1985; Rice 1984; Thorpe et al. 1984). However, less-circulated materials and CRM reports were not examined. Meighan (1983:600) notes "there has been a surprising growth in the application of obsidian dating to chronological problems, particularly in environmental impact reports in California."

Obsidian dating has been received by the archaeological community with varying degrees of acceptance. Leach and Naylor (1981:33) observe that "measurements of hydration depths of prehistoric obsidian artefacts by thin section techniques have yielded dates of mixed accuracy in different parts of the world, but have been notably unsuccessful in New Zealand." They assert, after examining hydration with resonant nuclear reactions that the relationship between the theoretical and actual character of the diffusion (hydration) front is more complex than is widely assumed. They conclude that after 18 years of trying in New Zealand, they still do not have a reliable method of obsidian dating, either relative or absolute, and highlight areas which they consider in need of further work.

Some researchers, although questioning the reliability and accuracy of dating obsidian absolutely, have used it as a foundation for asserting relative chronometry with good success (Bramlette 1988; Fredrickson 1984; R. Jackson 1984b; T. Jackson 1986; Origer 1987; Origer and Wickstrom 1982; Raymond 1984; Wickstrom 1986; G. White et al. 1982). Although not yielding absolute dates, this approach has been found useful for: (1) establishing "Units of contemporaneity" (Fredrickson 1984); (2) allowing temporal ordering of archaeological assemblages (Origer and Wickstrom 1982); (3) evaluating stratigraphic integrity of a site; (4) identifying horizontal stratigraphy, and evaluating relative intensity of obsidian use at a site over time (Michels 1967); (5) identifying discrete occupational periods (Raymond 1984); and (6) distinguishing diachronic shifts in procurement patterns.

For those with expectations of dating absolutely, the relative dating approach has been dissatisfying. There are some who accept but do not place complete confidence in the extant capabilities of the absolute dating approach, recognizing room for improvements in understanding and refinements in technique (Ericson 1988; Meighan 1983; Trembour and Friedman 1984). Meighan (1983:601) reiterates commonly acknowledged problems for archaeologically derived hydration rates. Data to determine such rates require input from three distinct laboratory procedures (dating, sourcing, and hydration measurement), from which mistakes, uncertainties, or error factors may arise. And, given that archaeologically derived rates are commonly calculated based on samples reflecting a narrow range of hydration measurements and short time span, the data can fit a wide variety of formulae, therefore limiting our confidence in any derived specific hydration model.

Findlow et al. (1982:39) point out another potential problem with archaeologically derived rates of hydration. Ideally, sets of associated data (hydration thickness and time) are selected with the temperature parameter held constant. However, in those situations where data sets are selected which reflect variable temperature, significant errors may occur.

Thus, in practice, dating has been realized through qualifying statements of rate "estimations" and "tentative" or "working" rate determinations (e.g., Bell 1977; Hurtado de Mendoza 1981), while "revised" rates have been proposed with the availability of additional data (Findlow 1977; Findlow et al. 1982). In terms of "established" rates, Meighan (1981) suggests that "there is probably no hydration rate that is so clearly known that it cannot be subject to some revisions." He finds that while "investigators cannot have total confidence in the exact answer they get from obsidian chronology...they can have a reasonable degree of confidence that their dating is in the ball park and that they can reliably discriminate the time periods of sites and collections" (Meighan 1983:808).

In contrast, with the use of **experimentally** derived rate constants, Michels et al. (1983:116), suggest that obsidian dating has "reached a stage in development in which it is a thoroughly operational chronometric technique." This conclusion is reached based on the following studies.

First, experiments conducted on Cerro de las Navajas obsidian samples from the Valley of Mexico were completed in which hydration rates from data produced for reaction at 90° C and 200° C were calculated. The rate calculated at 90° C was then extrapolated to 200° C and compared with the experimentally determined rate at 200° C. Because these rate solutions were in close agreement, differing by only 2.4%, they conclude that "hydration induced at temperatures not exceeding 250° C can be used in the determination of hydration rate and safely extrapolated to ambient temperature conditions" (Michels et al. 1983:113).

Secondly, when comparing archaeologically and experimentally determined hydration rates for four different obsidian sources, Michels et al. (1983:115) find "convergence between expected dates based on archaeological evidence and dates generated by means of laboratory-induced hydration rates has been sufficient to produce over-lapping error ranges of one sigma standard deviation or less." These findings are used to suggest that laboratory conditions simulate hydration processes that occur in the natural environment.

Few have whole-heartedly accepted the assertion that the dating technique has attained an absolute dating capability. Ericson (1977), experimenting with the induced hydration approach, observed a great deal of variability in source-specific activation energies and diffusion coefficients. Because of this, he declined to compare experimentally and archaeologically derived rates. Ericson concludes that the experimental method was useful for establishing the "rank-order" of source-specific hydration rates in relation to other obsidians.

Recently, Ericson (1988) suggests that there remains a problem of closure on hydration rate determinations. He reiterates the lack of consensus among researchers as to which of the proposed rate models best describes the relationship between time and rate of hydration for source-specific obsidians. He points out, as others have, that paleotemperature changes should be incorporated into the effective hydration temperature estimation for specific locales. He encourages standardization of hydration measurement among laboratories. The possibility that intrasource chemical variability may potentially influence hydration rates is re-acknowledged (see also Hughes 1988). Further, potentially effective environmental variables not previously considered by archaeologists are identified (i.e., percent soil saturation, cation exchange capacity of the soil, ionic composition of soil moisture, iron speciation and concentration in the soil, and pH).

Statement of Purpose

In 1966, Eitel described **glass science** as "explosive". With the advent of totally new types of hydrothermal bombs, a tremendous extension of possible pressure-temperature conditions became accessible for experimentation. Doremus (1973:4) terms the 1960s the "golden age" of glass science as the understanding of glass structure and composition increased sharply. In retrospect, progress made during this "golden age" is surpassed by advancements made in the 1980s, as illustrated in Chapter 2. Many articles have been published on glass surface reaction studies. The existence of this large and valuable body of knowledge has gone largely unheeded by the archaeological community.

Recognizing the need for examination of these glass studies, it became partly my objective to: (1) review the extant and pertinent literature on the physical-chemistry of glass; and (2) synthesize and integrate this knowledge into the foundation that provides the basis for obsidian dating. This task was considered essential to a further objective, (3) to knowledgably assess the use of accelerated obsidian hydration experiments for absolute dating purposes. A final objective of this thesis was (4) to explore the use of accelerated obsidian hydration experiments for relative dating purposes.

In the course of this thesis an overview of glass surface reaction studies is presented. Implications for obsidian dating are discussed. A research design is outlined with specific objectives regarding accelerated hydration experiments and their applications in both absolute and relative dating. Methods for achieving these objectives are outlined. Experimental results are discussed and conclusions drawn.

Chapter 2

OVERVIEW OF GLASS SURFACE REACTION STUDIES

Background

Studies on the weathering of glasses have been conducted for a variety of reasons. Aspiring to date the age of obsidian artifacts, archaeologists' primary motivation for conducting accelerated glass reaction experiments has been to obtain rates of hydration. In contrast, recent interest in using glass repositories for containment of nuclear high-level radioactive waste has stimulated studies on glass durability in order to project future glass-life expectancy. The nuclear waste management industry (involving countries such as the United States, Canada, Japan, Belgium, Switzerland, Sweden, France, the Federal Republic of Germany, Italy, and the United Kingdom) has engaged in a huge international effort to study glass reactions. Grambow et al. (1988: 531) state that "there has rarely been a need to extrapolate the properties of a material over such long periods of time...and there has never been a more important need to make accurate and verifiable 'predictions' of long-term performance."

Glass science has also gained increasing importance in steelmaking, ceramic fabrication, and glass making as high technology industries including the medical, dental, chemical, communications, aerospace, and nuclear fields demand more durable products (D. E. Clark and Yen-Bower 1980). In addition to these more commercial incentives, Winchell (1969) points out that diffusion in silicates is important when studying the histories of planets, meteorites, tektites, and fallout particles. The above examples are intended to illustrate the diverse motivations for the study of glass corrosion processes.

In this chapter, I have attempted to synthesize the findings of scientists regarding factors affecting glass weathering rates, present a variety of proposed weathering models, and discuss possible implications for the dating of obsidian. Achieving this objective has meant familiarizing myself with terms, concepts, and procedures of applied physical-chemistry in order to understand and extract information from the many articles and books reviewed.

The majority of studies to date can be classified as **parametric**, that is, designed to examine the effect specific parameters such as glass composition, temperature, solution pH, and glass surface area-to-solution volume (SA/V) have on glass reactions. In these studies, conditions are **static** with other parameters held constant. Very recent studies can be classified as **analogue**, geared towards simulating **dynamic** field conditions (e.g., reaction to different groundwater compositions and flow rates, and interactions with specific geologic matrices) in order to model a total or open system.

Until recently, testing procedures and conditions of exposure for glass surface reaction studies have varied considerably producing differing results and prompting a variety of explanations. With the formation of the Materials Characterization Organization, established by the US Department of Energy in 1980, guidelines for standardized tests have been developed for the nuclear waste management industry to follow in an effort to make results comparable.

Over the years, testing procedures have been conducted for temperatures ranging from 1-350 ^{o}C. They have been conducted in aqueous solutions of varying pH as well as exposed to vapor phases of varying relative humidity. Ratios of glass surface area-to-solution volume have varied to extremes, having reacted both glass bulk samples and powdered samples. Two basic types of analyses have been conducted: (1) analyses of ionic concentrations in solution after reaction with glass; and (2) glass surface analyses after reaction with liquid or vapor. Analyses of ionic concentration have been commonly conducted according to colorimetry, atomic absorption, and optical emission spectroscopy. Glass surface analyses have been conducted according to a wide variety of techniques (e.g., optical microscopy, scanning electron microscopy plus energy dispersive x-ray analysis, wide-angle x-ray diffraction, electron microprobe analysis, infrared reflectance spectroscopy, auger electron spectroscopy, secondary ion mass spectroscopy, rutherford backscattering spectrometry, elastic recoil detection, and HF leach profiling). To place these studies in context and make evaluations, it was necessary for me to categorize them according to conditions of exposure and types of analyses conducted as illustrated in Table 1.

Glass Weathering Reactions

Simplistically, the weathering of glass can be characterized by four geochemical reactions:

(1) Leaching or release of alkali ions (Na, Al, Mg, Ca, and K) from the glass into either solution or atmosphere;

(2) Adsorption or diffusion of "water", referring to hydrogen bearing groups such as hydrogen and/or hydronium ions, from either solution or atmosphere into glass. Note: Multicomponent interdiffusion kinetics, or the exchange between water and alkali ions (reactions 1 and 2), leads to the formation of a hydrated silica-rich (alkali-depleted) layer on the glass surface. This exchange is commonly

Table 1. Example of Classified Glass Surface Reaction Studies

Date	Author(s)	Sample form	Phase	Temp (oC)	Reaction Time	Soltn pH	% rh	SA/V (cm-1)	Analyses	Constituents Analyzed
1983	Olbert & Doremus	2 glasses powder & bulk	liquid	85	4-22 h	dist H2O Initial 5			Surface	OH, H2O
1983	Wassick et al.	2 glasses bulk	liquid	88	to 800 h	buffered 5.3			Surface & Solution	Si, Na, Ca, O, H Na, Ca
1983	White	3 glassy rock types; grains	liquid	25	to 3 mos	1-6.2 pH stat system			Surface & Solution	Na, K, Al Si, Na, K, Al
1984	White	perlite, obs, tuff, ash grains	liquid	25	2h-2mos	1-7 pH stat system			Surface & Solution	Na, K, Al Si, Na
1985	Smets & Tholen	bulk	liquid	70	to 16 h	buffered 4.5-13			Surface	Na, K, H
1986	Shade & Strachan	glass powder	liquid	90	to 1 y	di H2O, in 5.5 Si soltn, in 9		6.7, 17.8, >17.8	Solution	Si, B, Fe, Zn, U, & pH
1988	Barkatt et al.	glass powder	liquid	90	to 7 d	di H2O groundwater seawater		0.1 and 27	Surface & Solution	Si, Fe, Na, B, Al, Ca... Si, Fe, Na, B, Al, Ca...
1988	Bates et al.	glass & obs bulk	vapor & liquid	187,200, 240	14 d 375 d		60-100	1	Surface	Si, Na, Ca, Hydration
1988	McGrail et al.	bulk & granules	liquid	90	28 d	demineralized H2O		0.01 - 200	Surface & Solution	Na pH, & elements (?)
1988	Zoitos & Clark	bulk glass	liquid? * water flow rate 0.27 ml/h	90	to 2 y	groundwater		1	Surface & Solution	Si, B, Li pH
in press	Stevenson & Scheetz	obs bulk	liquid	130-190	to 18 d	di H2O w/ Si sat.			Surface	Hydration

associated with a **parabolic** rate of reaction ($t^{0.5}$);

(3) Surface dissolution of glass silica, referring to the breakdown of the silica network which provides structure to the glass. This reaction is commonly associated with a **linear** rate of reaction (t^{1}); and

(4) Precipitation of reaction products on the glass surface.

Factors Affecting Glass Reactions

It is clear that many factors affect the reactions involved in the weathering of glass. D. E. Clark et al. (1979) provide one of the most comprehensive list of conditions affecting glass weathering in Table 2. They identify such factors as glass composition, temperature, exposure time, relative humidity, glass surface area-to-solution volume (SA/V),

Table 2. Factors Affecting Glass Durability*

I. Environmental Factors
1. temperature
2. exposure time (continuous or cycled)
3. relative humidity
4. solution pH
5. presence of inhibitors in the corrosion solution
6. external stresses upon specimen
7. radiation
8. solution composition

II. Physical Factors
1. weathering vs aqueous corrosion
2. dynamic vs static corrosion
3. exposed surface area-to-solution volume ratio (SA/V)
4. corrosion behavior of bulk glass vs powdered glass

III. Specimen State
1. bulk glass composition
2. thermal history
    a. degree of annealing for stress and density
    b. phase separation (glass in glass)
    c. % crystallization, if any
3. prior corrosion exposure history
4. surface features
    a. surface roughness
    b. surface composition
5. homogeneity of glass
6. surface treatments

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* out of Clark et al. (1976:6)

solution pH, and solution composition. These factors are synergetic, that is, they are dependent upon each other, so in order to understand their effects, they must be placed in context. For example, in a **static** situation, temperature and SA/V ratios affect solution pH and solution concentration. In a **dynamic** situation, depending upon the groundwater flow rate and SA/V, solution composition can become under-saturated, near-saturated, or super-saturated with specific element concentrations. The discussions following will focus on solution pH, solution composition, SA/V, relative humidity, and temperature. The effects of glass composition on weathering rates is beyond the scope of this thesis.

Solution pH

During the interaction of glass with standing water (static aqueous corrosion conditions), solution pH increases with time, reflecting the diffusion of hydrogen or hydronium ions into glass. Recognizing this process, Lasaga (1984:4012) reports that without buffering (controlling) pH, effects of merely changing pH from those due to complexing cannot be separated out. Earlier, El-Shamy and Douglas (1972) pointed out that without controlling the pH of the attacking solution during an experiment, significant rate equations for extraction of glass constituents cannot be obtained. Responding to this problem, some researchers have been utilizing buffering agents to maintain pH levels during experiments.

El-Shamy et al. (1972), reacting glass in buffered solutions ranging from pH 1-13, characterized effects on alkali and silica extraction (i.e., leaching or release from glass). Experiments ran at temperatures of 35 and 80^{o} C for 4 hours. They found that for solutions **less** than pH 9, the rate of alkali extraction remained constant and independent of pH. Silica extraction for pH less than 9 remained constant at so low a value that it was not much different from the blank solution. For solutions **greater** than pH 9, alkali extraction rates decreased; silica extraction increased. These early findings and subsequent findings supported the generalization that for short reaction times in **acid** and **neutral** solutions the ion-exchange reactions are enhanced and network dissolution suppressed (cf. D. E. Clark et al. 1979; Bunker et al. 1983). In **basic** solutions greater than pH 9, silica dissolution increases and alkali diffusion decreases.

More recent findings indicate that silica dissolution can be significantly increased for very high or very low pH values (Wicks et al. 1982; A. White 1984). However, interpretations and explanations appear to be conflicting for these and other findings regarding both mechanisms and rates of reaction as a function of pH. Therefore, the following findings are simply presented. I make no attempt to reconcile these discrepancies.

Based on findings produced at 90^{o} C after 1 month during reaction in non-buffered solutions, Wicks et al. (1982:423) suggest that for reactions at pH less than 5, both selective leaching of alkali ions and network dissolution occur. Between pH 6 and pH 8.5, reactions are primarily diffusion controlled ($t^{0.5}$). Above pH 8.5, network dissolution is dominant (t kinetics).

The control pH has on the form of the rate expression is discussed by A. White and Claassen (1979:464-465). In contrast, they found just the opposite effect for reactions of plagioclase at 25^{o} C. Reactions at low pH (3-4) followed a parabolic ($t^{0.5}$) rate. Those at pH 5 and 6 followed a linear rate. And at high pH (7-8) a parabolic rate was again followed. They conclude that pH not only controls the **form** of the rate expression, but the **magnitude**. In a further publication, they note that increased aqueous pH decreases rate constants of diffusing (alkali) species proportional to their valence states, and define a generally linear relationship between the log of the apparent (Na) diffusion coefficient and pH (A. White and Claassen 1980:106-107).

Bunker et al. (1983:299) observe during experiments of fixed pH solutions ranging from 1-12, and reactions at 25^{o} C for 400 minutes, that alkali leaching occurs under **all** conditions, and that silica dissolution is **negligible** compared with alkali leaching even when the leaching kinetics are linear with time (high pH?).

Smets and Tholen (1985) conclude on the basis of data generated during reaction of glass at 70^{o} C for 16 hours in buffered solutions, that in the pH range 4.5-9.0 the aqueous attack on glass can be described as concurrent dissolution of Si and diffusion-controlled leaching of alkali ions. For this pH range, as found by others, alkali release rates are independent of solution pH. At a pH of 13, alkali leach rates are retarded.

A clear understanding of the effect solution pH has on glass reactions has not yet been achieved. Despite this fact, I have searched for findings that might shed light on the effects of groundwater pH on the weathering rates of obsidian. For a particular artificial glass, Bunker et al. (1983:314) find, during their experiments, that a "leached layer grows three times faster in pH 1 solutions than in pH 12." Although the effects of pH will be different for other glass compositions, it might at least be suggested that the differences between weathering rates reacted at pH 5 versus pH 7 would not be as great.

Several studies on the weathering of buried glass are currently being conducted. The Experimental Earthworks Committee of the British Association for the Advancement of Science (Newton 1981), buried samples of nine different types of glass in both alkaline (pH 9.55-9.75) and acidic soils (pH 4.5-5.0). So far, samples have been recovered and semi-quantitatively analyzed after 1, 2, and 8 years for degree of deterioration. Recovery of additional samples after 16, 32, 64, 128, 256, and 512 years is planned. Schedule for completion is October of the year 2,482. It is assumed that an alkaline environment will produce a faster rate of surface deterioration. Extant results indicate no visible deterioration to glasses exposed to acidic soils after 8 years. Only one of the nine glasses show signs of severe surface deterioration in alkaline soils. However, it is noted (Fletcher 1972:151) that one year of burial in alkaline soils yields more surface deterioration on glass samples than 5.25 years in acidic soils, clearly demonstrating the effect of increased alkalinity.

Other in-situ tests include reactions of glass in repositories of sandy soil, granite, clay, salt, and tuff (e.g., Tait et al. 1986; D. E. Clark et al. 1984; Van Iseghem et al. 1986; Wicks and Molecke 1986; Bibler et al. 1985). The majority of these burials are at great depths (350-650 m below surface), where effects of interaction with the geologic matrix, ground water composition and flow rates are being studied.

What pH values can be expected for groundwaters? Lasaga (1984:4012) notes that "natural solutions have widely ranging pH values." A. White (1984) identifies a pH range of 4.5-8.0 as representative of long-term natural weathering. Antweiler (1983), measuring pH of percolating waters through a late Tertiary volcanic ash during a 150-day period, found solution pH ranged from 4.3-6.5. He attributes changes in pH to biological mechanisms, asserting that "organic material provides the major control on the chemistry of near-surface waters in ash by complexation of Al and Fe, and by lowering pH" (Antweiler 1983:628).

Lasaga (1984:4014), commenting on the formation of acidic solutions, states that "the dominant acid in natural weathering solutions is carbonic acid." Carbon dioxide in the atmosphere or in soil air, arising from the oxidative decomposition of organic matter, will dissolve in aqueous solutions. To act as an acid, the dissolved carbon dioxide must be converted to carbonic acid. This conversion to acid is a slow process which "may actually control the overall rate of water-rock interaction under some circumstances" (Lasaga 1984:4014). He reports that "the experimental work carried out thus far indicates that the variations in the dissolution (and precipitation) rate of minerals can be significant under fluctuating pH conditions" (Lasaga 1984:4012).

Solution Composition

A. White and Claassen (1979:470) assert that "the **composition** of the aqueous media can **also** exert a strong control on the rate constant" [emphasis added]. As an example, Hermansson et al. (1983:145) find when experimenting with a specific glass at 90°C for 28 days, that reactions were more aggressive in leachants (solutions) containing Na and simulated ground silicate water than distilled water. However, the modeling of weathering rates can be considerably complicated. As A. White (1984:242-243) notes, "when natural glasses are present in geochemical systems, such as in sequences of volcanic rocks, their relatively rapid weathering tends to strongly influence associated water chemistries by releasing high concentrations of Si and Na."

From the literature, it can be concluded that **contact time** (the extent to which aqueous leachant is in contact with glass) is a function of groundwater flow rates. Ground water flow rates determine the degree of species concentration in solution (the degree of **saturation**), which in turn determines the mechanisms and rates of glass surface reaction. Spinosa and Means (1986) point out that dissolution takes place only when the solution is under-saturated with respect to the glass. Precipitation occurs when the solution is super-saturated with respect to the precipitate.

Hench (1988:195) asserts that:

> the extent of matrix dissolution and onset of surface precipitation (advanced stages of leaching) will depend on the time required to reach saturation in solution. Saturation of species is a function of the initial solution pH, amount of alkali in the glass and rate of alkali release, temperature, initial concentration of species in the solution, SA/V which influences solution concentration, or flow rate which also affects solution concentration.

Under static and **low groundwater flow** rate conditions, concentrations are allowed to rise exponentially to **solubility** limits (Strachan 1984). Barkatt et al. (1984) note that a decreased flow rate also results in a solution pH increase. As documented by others, D. E. Clark et al. (1984:27) find that "in static and low-flow tests, a stagnant solution layer [precipitate] forms adjacent to the glass surface during leaching." At the lowest flow rates, W. B. White

(1986:436) reports that **saturation** effects determine the main mechanism controlling glass surface dissolution. According to Barkatt et al. (1985:230), at slow flow rates, the release of glass components is markedly **incongruent**, with B, Na, and Li having the highest concentrations in the leachate (indicating primarily alkali diffusion reactions). Most of the silica (80%) stays behind (indicating limited Si dissolution).

Adiga et al. (1985:48) find leach rates increase nearly proportionally with flow rates up to approximately 1 ml/h. For flow rates greater than 10 ml/h, leach rates are almost independent. W. B. White (1986:436) finds that "at **high flow** rates, the glass is simply corroded by highly **under-saturated** solutions with all elements dissolving at about the same rates. The leach rates become maximum and constant [steady-state]" [emphasis added]. Barkatt et al. (1984:647) observe for a glass reacted at 90°C up to 2 years in high flow rates (greater that 1 m/y) nearly **congruent** corrosion (leaching linear with time) occurred.

The above findings demonstrate the strong affect solution composition has on glass surface reactions. Relating these findings to obsidian hydration dating, I infer that rates of hydration are dependent upon groundwater composition. Before significance of its effects can be assessed, near-surface soils need to be characterized. The following is provided as an example. D. E. Clark and Maurer (1982) conducted a shallow burial experiment in the vicinity of an archaeological site near Gainesville, Florida. Ten types of glass and ceramics were buried at 0.5 and 1 meter depths in soil described below.

At 0.5 m, soil is characterized as sand, experiencing cyclic wet and semi-dry conditions depending upon the frequency of rainfall. These conditions are correlated with **flow leaching**. In contrast, at 1 m depth, soil is characterized as a sandy clay mixture (50% smectite, 30% kaolinite, and 20% quartz), situated below the water table and experiencing continuous aqueous contact. These conditions are correlated with **static leaching** (assume no flow?). Soil pH ranged from 3.5-4.0. Temperature ranged from 11-30 ^{o}C. Rainfall during the burial period (16.5 months) totaled 63 inches. On preliminary examination of these reacted glasses, D. E. Clark and Maurer (1982:79) conclude that "surface films form during burial and the protectiveness of these films depend on soil composition."

Glass Surface Area-to-Solution Volume (SA/V)

Researchers have conducted experiments with both powdered glass and bulk glass for SA/V ratios ranging from 0.01 - 15,000 cm^{-1} at temperatures ranging from 25-100 ^{o}C. What do their findings indicate regarding the effect of SA/V ratios on glass surface reactions? SA/V ratios, closely related to flow rates, influence the time required for solutions to reach saturation. Chandler et al. (1986:456) observe under static conditions that saturation of the glass constituents in solution occurs faster at the higher SA/V ratios.

The effect of high surface area to volume ratios on waste glass is investigated by Shade and Strachan (1986) as a potential means to quickly achieve advanced stages of leaching useful for predicting long term waste form alteration trends. They assert that "**low** SA/V static tests using monolithic test specimens, do not readily provide saturation values for all elements over reasonable test durations and are probably better suited for studying dissolution kinetics and mechanisms that occur prior to saturation (earlier stages of leaching)" [emphasis added]. However, long term tests (e.g., longer than 6 months) using monolithic specimens may yield results approaching saturation. D. E. Clark et al. (1979:37) reacted glass at 100 ^{o}C, for up to 10 days with an initial 6.5 pH solution (non-buffered). They found that SA/V ratios affect the rate controlling mechanism for glass weathering. Specifically, they found at a SA/V of 0.07 cm^{-1} that the primary mode of corrosion was selective Na leaching. For a greater SA/V of 0.77 cm^{-1}, the major corrosion mechanism was total glass dissolution.

Contradictory findings are made by Machiels and Pescatore (1983:215). For high SA/V ratios, leach rates are observed to decrease. Specifically, for a SA/V of 100 m^{-1} (during static reaction at 90 ^{o}C, in deionized water), Na releases are higher than those of Si, indicating a selective leaching process assumed to be diffusion. For low SA/V ratios, leach rates are independent of time and SA/V. Specifically, for a SA/V of 1 m^{-1}, the amounts of Si and Na released practically coincide, indicative of network dissolution control.

These findings are supported by Pederson et al. (1983:47,49).

> Dissolution rates per unit exposed surface area [for a specific glass composition] are unaffected by changes in SA/V ratio for relativly low SA/V values. For larger SA/V values, dissolution rates per unit surface area fall sharply with increasing SA/V, an effect attributed largely to silicon solubility considerations.

Taking stock, it appears that the rate controlling mechanism for glass weathering is dependent upon SA/V ratios; however, the manner by which this occurs is not agreed upon. Implications for obsidian dating are difficult to assess. Buckwalter et al. (1982) find that the thickness of the leached layer decreased with increased SA/V. Between the highest SA/V (160 cm^{-1}) and the lowest (0.01 cm^{-1}), more than an order of magnitude difference in leached layer thickness was evident.

Determining the expected range of SA/V ratios representative of obsidian in archaeological sites would help in evaluating the significance of SA/V effects. Lasaga (1984:4016) suggests ways to estimate SA/V from field data. Claassen and White (1979:791-2) present a technique for determining effective aquifer surface area in contact with unit volume of composite saturated-unsaturated groundwater systems. These techniques could prove useful to archaeologists for approximating SA/V ratios.

Ethridge et al. (1979:40) note that "for bulk glasses, a plot of the time to reach a particular extent of corrosion against SA/V yields straight lines with predictable slopes." They propose that this type of representation offers a means of predicting glass corrosion at different SA/V ratios. If their findings have merit, perhaps they can be used to assess effects on the hydration of obsidian.

Relative Humidity (rh)

The majority of experiments reported have reacted glass submerged in aqueous solutions. Although glass exposure conditions often reflect reaction with water vapor contained in the atmosphere, comparatively few researchers have conducted experiments reacting glass with vapor. Of those vapor-phase experiments conducted, very few investigate effects of varying rh on glass surface reactions.

An early study by Stockdale and Tooley (1950:16) reports on five glasses in bulk form, which were reacted at 90°C for up to 1296 hours, for relative humidities of 57, 73, and 95%. They find to reach a comparable state of weathering as that for glass exposed 24 hours at 95% rh, it took 15 times as long at 73% rh, and 54 times as long at 57% rh.

Sanders and Hench (1973) conduct experiments ranging from 85-100% rh, at room temperature up to 600°C, for as much as 239 hours. They find that "the corrosion of [a specific glass composition] at an rh of 85% proceeds much more slowly than the 100% rh exposures." They conclude that "the amount of water present determines the kinetics of the corrosion process and extent of alkali release from the silica gel layer formed."

Bartholomew et al. (1980) react glass for relative humidities ranging from 56-100%, at temperatures ranging from 225-350°C, for up to 24 hours. Water penetration rates into two artificial glasses decreased with decreasing rh [note: they refer to rh as %saturation, where P%=P(T)/Ps x 100. (P(T)= actual pressure, Ps= saturation vapor pressure of water at T)]. These findings agree with Stockdale and Tooley (1950) and Sanders and Hench (1973).

Walters and Adams (1975) reacted 26 glasses at 50°C for up to 16 weeks with relative humidities of 30, 50, 75, 90, and 98%. Their observations differ somewhat: (1) weathering effects have been measured down to 30% rh (some glasses weathered as much at 30% as at 90%); (2) weathering is visually evident in the absence of significant alkali leaching; and (3) although for the majority of glasses weathering increased with increasing rh, the opposite also occurred...weathering decreased with increasing rh for some glasses. To explain this last phenomenon, they suggest that dilution effects (i.e., large amounts of adsorbed water into glass) changes the alkalinity of reacted glass surfaces so as to depress the weathering rate.

What do these studies regarding relative humidity imply for the dating of obsidian? Obsidian is reacting to both liquid and vapor in the soil. The rh of soil air in archaeological sites may potentially affect the rate that obsidian hydrates. If the range of expected rh representative of soil air at archaeological sites can be determined, perhaps its significance to dating obsidian can be evaluated. Trembour et al. (1988) provide a means to accomplish this, having developed diffusion cells which measure both temperature and rh of soils.

Temperature

Temperature has long been recognized as affecting glass surface reaction rates. Although researchers have conducted experiments ranging from 0-600 °C under varying conditions, little attention is given to temperature dependence in the recent literature. It has been commonly understood and accepted that glass surface reaction rates increase exponentially with increasing temperature, behaving according to an Arrhenius type equation given as:

$$K = Ae^{[-E/RT]} \qquad (3)$$

where K = reaction rate; A = preexponential constant (g cm^{-2} d^{-n}); E = activation energy (J/mole); R = gas constant (8.3146 J/mole K); T = absolute temperature.

Evidence challenging this understanding is presented by Van Iseghem et at. (1982). They react six glasses at temperatures between 40 °C and 200 °C for up to 80 days in distilled water (SA/V = 1 cm^{-1}). For one glass composition, an Arrhenius type behavior was found between 40 and

200 °C, yielding an activation energy of 34.8 kJ/mol^{-1}. However, the other five glasses behaved differently. Between 40 and 90 °C, activation energy values of 53 and 35 kJ mol^{-1} were obtained. Above 90 °C, values between 35 and 13 kJ mol^{-1} were obtained. They conclude that "in general, no simple Arrhenius-type temperature dependence for the corrosion behavior [of glass] is found for the interval between 40 and 200 °C" (Van Iseghem et al. 1982:219).

Vernaz et al. (1988:555), concerned with effects of temperature on glass reactions under near-saturated conditions, report that high temperature experiments (generally performed with low SA/V values) tend to neglect saturation phenomena, and thus largely overestimate long-term alteration of glass. They ask two fundamental questions: (1) if the temperature dependence of normalized mass loss (of glass constituents) follows an Arrhenius type law; and (2) whether corrosion is simply enhanced at high temperature or the mechanisms are completely different. To address these questions, static experiments were conducted between 100 °C and 300 °C in deionized water for up to 28 days. Results indicate that the influence of temperature is not a simple phenomenon.

They find that the temperature effect is not the same for all the elements released from glass. For B, Na, Li, and Mo, concentrations in solution at 250 °C were 27 to 43 times higher relative to those at 100 °C. For Si, U, and Ce, concentrations were 12 times higher. For Al, Ca, Sr, Zn, Fe, and Zr, concentrations were only slightly affected. Total mass loss was 22 times higher. Average activation energies for Si and B were 24 kJ/mole. Normalized mass loss for Si followed an Arrhenius law regardless of duration up to 250 °C.

Between 250°C and 300°C, solution concentration was observed to increase 10 to 20 times. The alteration profile thickness increased 100 times. The activation energy increased to 150 kJ/mole. These observations indicate that a drastic change in the alteration mechanism occurs when temperature exceeds 250°C. "At 300°C the phenomenon may no longer be glass corrosion but rather a transformation of the glass under the combined effects of water, temperature, and pressure" (Vernaz et al. 1988:563).

Vernaz et al. (1988:563) conclude that although

> high temperature experiments may be useful to accelerate some processes very difficult to measure at low temperatures...a direct extrapolation of the overall corrosion behavior to low temperatures does not seem possible. Each mechanism (diffusion, dissolution, hydration, and phase formation) has to be identified and its temperature dependence understood.

The above findings place some doubt on the appropriateness of extrapolating reaction rate constants derived from high-temperature experiments to field temperatures. In contrast, Bates and Steindler (1983:89) assert that "the Arrhenius behavior that has been observed for the hydration of defense waste glass allows the hydration process to be cautiously extrapolated to various time/temperature conditions, provided that saturation at noncondensing conditions [during vapor-phase experiments] exists and that the hydration follows the kinetics noted in the initial hydration curve ($t^{0.5}$)."

High-temperature hydrothermal experiments (> 225°), used to produce hydration rate constants, have been observed to cause substantial silica dissolution (Stevenson et al. 1989). Because dissolution causes retreat of the glass surface, concern has been voiced that the actual depth of hydration is being underestimated (Bates et al. 1988:243).

Further, at temperatures greater than 180°C, hydration diffusion fronts have, under microscopic examination, been observed to loose definition, inhibiting the ability to reliably discern and measure depths of water penetration (see Ericson 1977; Friedman and Long 1976; Stevenson et al. 1989; Tremaine and Fredrickson 1988). Stevenson et al. (1989) propose revisions in methodology be made either by (1) lowering reaction temperature and saturating solution with powdered silica, or (2) reacting in vapor rather than hydrothermal-phase.

Besides implications of temperature studies to accelerated obsidian hydration experiments, what can be determined regarding the significance of **field** temperatures to rates of hydration and age estimates? For instance, how significant are the effects of temperature variation within the geographic range which source-specific obsidians are distributed? How significant are the effects of temperature variation within a smaller regional domain, where in practice similar temperature histories are often assumed? How significant are the effects of soil temperature differences with depth, where obsidian artifacts are distributed stratigraphically within a site from surface to several meters below surface? And, how significant are effects of paleotemperature fluctuations to age estimates of obsidian, where in practice, rates of hydration are temperature-specific and are assumed constant over time of exposure?

To answer these question, an estimate of the significance small temperature changes have on rates of hydration would be helpful. Based on accelerated hydration rate determinations of high temperature extrapolated to ambient temperature, Trembour and Friedman (1984) find for a specific obsidian and given hydration depth, that a 2°C difference in effective temperature gives a 500 year difference in age. Leach and Hamel (1984:406) suggest on the basis of archaeologically dated sites and mean exponential soil temperature that "an error of 1°C introduces a dating error of up to about 150 years over the last millenium" for a specific obsidian source. This suggests that small temperature differences can significantly affect rates of hydration.

For the geographic range delimiting the distribution of source-specific obsidians, temperatures may range widely (e.g., Coso obsidian, originating in the desert of southern California, can be found in sites along the Pacific Coast where temperatures are drastically different). Given this fact, it seems reasonable to conclude that for analysis of source-specific obsidians on such a large spatial scale, temperature should be considered to have a significant effect.

How significant are the effects of soil temperature variation within a smaller regional domain, where in practice similar temperature histories are often assumed? Carson (1963:2229) states that "soil is a complex medium (mineral and organic solids, air and water) in which several heat-transfer mechanisms are operating simultaneously: molecular conduction, movement of water and air, vapor distillation, and radiation." A review of literature on soil temperature studies indicates that temperatures are affected by soil diffusivity, depth, geothermal activity, latitude, elevation, slope, aspect, microtopography, and vegetation (e.g., Lettau 1971; Bocock et al. 1982; Olmsted et al. 1981; Vann and Cline 1975; Smith et al. 1964; Shreve 1924; and Qashu and Zinke 1964). It is possible that these factors may cause significant regional soil temperature variation.

Leach and Hamel (1984) report in a soil temperature study of archaeological sites in New Zealand and surveys of soil studies in Papua New Guinea, that site aspect and soil depth are significant factors affecting thermal environment. Based on these findings, they suggest that one cannot assume that two nearby archaeological sites will necessarily have the same mean exponential temperature. They conclude that "it will not be feasible eventually to draw up a chart of likely temperatures for archeological sites organised by location, and abandon further thermal monitoring. Each precise provenance must be carefully monitored if dating obsidian is envisaged" (Leach and Hamel 1984:407). Are such stringent practices required? The determination of soil temperatures ranges within other regions will help to evaluate how significant effects of temperature are on a regional scale.

How significant are the effects of soil temperature differences with depth, where obsidian artifacts are distributed stratigraphically within a site from surface to several meters below surface? Because the accumulation of archaeological sediments reflects a complex history of both cultural and natural processes, Leach and Hamel (1984:409) point out that the temperature affecting obsidian within a site may not be uniform. And therefore, in some cases, younger artifacts near the surface of a site may have greater hydration than those older artifacts which are more deeply buried. Layton (1973:131) recognizes problems of this nature with surface-collected obsidian from the Nevada desert. Friedman and Obradovich (1981:4) estimate for obsidian found at an archaeological site in West Yellowstone, Montana, that given differences in effective temperature, surface samples "exposed to the sun can expect to hydrate at a rate five times as fast as samples buried to a depth of 2 m."

Soil temperature studies by depth show that for depths down to 10 feet below surface, the average annual temperature is nearly constant (Fluker 1958; Penrod 1960). However, amplitude of fluctuation is greater at shallower depths. Mean exponential soil temperature, reflecting the amplitude of temperature fluctuation, is not constant with depth. Bocock et al. (1982) find that the exponential mean temperature decreases significantly with soil depth ($P<0.0001$). The rate of this decrease varied significantly between different areas tested ($0.001<P<0.01$). For two locations, mean exponential temperature differences between surface and 50 cm were 1.5 and 5°C respectively, At one particular location, findings indicate "the logarithm of exponential mean temperature, as an index of amplitude, decreased very highly significantly and linearly with soil depth ($P<0.001$))" (Bocock et al 1982:59).

Friedman and Norton (1981) find mean exponential soil temperatures in and near Yellowstone National Park to vary with depth. Mean exponential soil temperature differences for depths between 0.5 and 2 meters at 45 locations, ranged from -1.6 to 2.9°C. These differences reflect both positive and negative gradients (directions of heat flow upward and downward). Negative gradients are common for geothermal areas.

As reported by Leach and Hamel (1984), Ambrose (1975:8-9) observed a 4°C difference in mean exponential soil temperature beween 18 and 90 cm depth for an open beach location in Papua New Guinea. He adds that a 4°C difference in temperature might produce a dating error of about 1000 years for an obsidian artifact aged 2000 years.

Zeier and Elston (1984) collected mean exponential temperatures in the southern Great Basin desert/geothermal region of California, near the Sugarloaf obsidian quarry of the Coso volcanic fields. Five stations recorded temperature with depth. In one case, between surface and two meters, temperature **decreased** by 10.5°C. In another case, temperature **increased** by 11°C, reflecting geothermal activity. Three other cases found differences between surface and one meter to average 10.4°C ± 3°C.

Given these findings, which record significant differences in mean exponential soil temperature with depth for a variety of climatic regimes, it can be unfortunately concluded that in extreme environments obsidian artifacts found at different depths within an archaeological deposit may be significantly affected by differences in temperature. In contrast, Friedman and Trembour (1983) suggest that "the temperature effect on the hydration rate is of minimum importance in assigning a **relative** age for a series of artifacts buried at one site, where all the samples have experienced the same microclimate" [emphasis added]. Collection of soil temperature data may help in evaluating how significant temperature with depth is for particular locations.

Beyond temperature variation within a **spatial** dimension, temperature fluctuation within a **temporal** dimension requires consideration. In dealing with obsidian in the subarctic of Alaska, D. W. Clark (1984:104) discusses the problem of "variable previous contexts":

> Initially, nearly all [obsidian] specimens occupied a surface context regardless of their provenience at the time of recovery. In locations where soils are formed and subsequently removed or where solifluction and frost action occur, an artifact, unless well sealed in a stratified site, may have occupied various contexts over a span of many millenium. It thus may have been subjected to exposure, to fires, and to differing depths of burial and types of vegetational cover with changes in the effective hydration temperature of its context.

Paleotemperatures reflecting the history of glass exposure are rarely considered. Just how significant are effects of paleotemperature fluctuations to age estimates of obsidian, where in practice, rates of hydration are temperature-specific and are assumed constant over time of exposure? This complication may affect age estimates significantly. Suzuki (1974) presents cumulative effects of paleotemperature fluctuation on the formation of hydration-rims for obsidian artifacts in Japan. More recently, **integrated** rates of hydration, reflecting changes in temperature over time, have been attempted by Friedman and Obradovich (1981) in dating volcanic events. Assessing the importance of temperature for dating obsidian in New Zealand, Leach and Hamel (1984) give, in years, **thermal errors** which are potentially introduced by temperature varying by ±1 °C.

Glass Weathering Models

How are the four basic surface reactions (i.e., outward leaching of alkali ions, inward diffusion of water, silica dissolution, and precipitation), and the variables just discussed, reconciled into a model for glass weathering? A variety of models have evolved recently to account for different behaviors observed. The most common and simpler classic model based on mass transfer concepts, accounts for interdiffusion and matrix dissolution reactions, describing a two-stage process.

Bunker and Arnold (1983:151) characterize this model.

> In the first stage, alkali leaching proceeds as a function of t0.5...This stage is [most commonly] attributed to a simple ion exchange process in which H+ or H30+ from the leachate diffuse into the glass, and alkali cations diffuse out. The rate of interdiffusion is often equated with the self-diffusion coefficient of the slowest moving

> cation in bulk glass. The common explanation for the second stage of leaching, where alkali leaching is linear with time, is that the leached layer eventually becomes so thick that it serves as an alkali diffusion barrier. Alkali release becomes as slow as the dissolution rate of the silicate network, resulting in uniform glass dissolution, and a leached layer which reaches a constant steady state thickness as a function of time.

A similar description is given by A. White (1983:812), where "alkali diffusion and silica dissolution reach a steady state condition where the rate of increase in the diffusion path length approaches the rate of retreat of the solution-solid interface [due to Si dissolution], after which all constituents [alkali ions and Si] will be controlled by linear release rates."

These findings suggest that, as acknowledged earlier, dissolution is competing with interdiffusion processes. However, Bunker et al. (1983) observe that silica dissolution is negligible when compared to alkali leaching even when the leaching kinetics are linear with time. They propose that deviation from $t^{0.5}$ kinetics is not the result of "uniform dissolution", but reaction to a changing interface. Rather than reacting to a "dry" glass, solution is reacting with a hydrated glass surface (hydrosilicate phase, or gel layer). They assert that "the kinetics of alkali leaching at long times are controlled by the extent and rate of reactions between water and the silicate network in both the low and high temperature regimes" (Bunker et al. 1983:318).

Bunker et al. (1983:315-316) explain that:

> At **higher** leaching temperatures, the hydrated glass surface is converted into a gel due to the hydrolysis crosslinks (Si-O-Si bonds) in the silicate network. The t0.5 leaching kinetics are observed only until enough water has diffused into the glass to produce this glass:gel transition. Diffusion in the gel is rapid relative to the rate at which water can hydrolyze dry glass at the glass:gel interface, resulting in linear leaching kinetics...

> On low leaching temperatures, deviation from $t^{0.5}$ kinetics are observed when the concentration gradients of H2O, H3O+, and alkali cations in the leached surface layer eventually create tensile stresses sufficient to crack the hydrated glass. Cracks continue to form and grow in the narrow transition zone between hydrated and unhydrated glass, which eventually moves into the glass at a constant rate. One possible explanation for deviations from t0.5 kinetics is that once the hydrated glass cracks water can penetrate this surface layer, and it no longer functions as a diffusion barrier [emphasis added].

Many glass scientists have observed a transition from parabolic to linear kinetics. Transition times have been found to be dependent on a variety of factors. Rana and Douglas (1961:187) find "the time of the change from the first to the second mechanism depends upon the temperature and composition of the glass." D. E. Clark et al. (1979:33) find that temperature dictates the rate controlling mechanism of corrosion. They observe that "at 121 °C, corrosion is controlled by total dissolution (t kinetics) after one hour, while at 37 °C selective leaching is rate controlling." Barkatt et al. (1988:130) assert that the cross-over time occurs at earlier times with increasing temperatures. Findings of A. White and Claassen (1979) "clearly indicate a shift between linear and parabolic rates as a function of pH." Wicks et al. (1982:426) suggest "a diffusion-controlled process ($t^{0.5}$ kinetics) between pH 6 and pH 8.5, and primarily network dissolution (t kinetics) above pH 8.5." Ethridge et al. (1979), as well as Wicks et al. (1982) document dependence of rate expression on glass surface area to solution volume (SA/V). Both Wicks and Ethridge find shorter transition times with increased SA/V ratios.

Summarizing, transition times have been found to be dependent upon glass composition, solution pH, temperature, and SA/V. Table 3 gives transition times for specified conditions. For low temperature

Table 3. Transition Times from t1/2 to t Kinetics

Date	Author(s)	Temp (C)	Soltn pH	SA/V (cm-1)	Tt
1961	Rana & Douglas	50	?	100-720	9 m
		60			4000 m
		84			1600 m
1972	El-Shamy & Douglas	30-90	in 4.5/fin 11	5000-15000	occurs w/i 6 h
1972	El-Shamy et al.	35-80	buff 1-13	grains	not reached after 4 h
1972	Luce et al.	25	non-buff	grains	occurs w/i 6-100 h
1976	Clark et al.	100	in 6.5/fin10.8	binary comp, bulk	occurs w/i 1 h
				ternary comp, bulk	occurs w/i 2 d
1978	Laursen & Lanford	90	dist H20	bulk	not reached after 348 h
1979	Clark et al.	100	in 6.5/fin 7	0.077	not reached after 10 d
			in 6.5/fin 8.6	0.77	occurs w/i 10 d
			in 6.5/fin 10	7.7	occurs w/i 10 d
		121	in 6.8/fin 7.7		1 h
		37	neutral		1 h
1979	Ethridge et al.	50		0.77	16 h
				0.034	7 d
1979	Lanford et al.	90	dist H20	bulk glass	400 h
1979	White & Claassen	25	1	375-3000	3 weeks
			6.2		not reached after 3 mos
1980	Das	1-67	1.4-10.9	grains & rods	occurs w/i 3.5 d
1980	Houser et al.	25-40	buff 4.9	bulk glass	not reached after 1 h
1982	Smets & Lommen	70	di H20	bulk glass	not reached after 1 h
1982	Wicks et al.	90	in 5/fin 9-11	10	occurs w/i 1 mos
				0.1	occurs w/i 1 mos
1983	Bates & Steindler	162-240	non-buff?	bulk	occurs w/i 2.5 and 3.6 d
		120	vapor	bulk	not reached after 37 d
1983	Bunker et al.	25-80	buff	0.02	occurs w/i 400 m
1983	Michels et al.	200	non-buff	bulk	not reached after 6 d
1983	Olbert & Doremus	85	5, no buff	powder & bulk	not reached after 22 h
1985	Smets & Tholen	70	4.5-13	bulk	occurs w/i 2 h and 2 mos

Tt= transition time; in= initial pH; fin= final pH; buff= buffered

* Note: These data represent reactions of varying glass composition.

experiments (1-90 ^{o}C), many of which were conducted with high SA/V ratios, transition times range from 9 hours to 3 months. The few cases listed in Table 3 not reaching transition can be characterized as either bulk glass samples (usually indicating low SA/V conditions), or reactions of short duration. Transition times may be lengthened for reactions of lower SA/V, although no quantitative studies have been conducted addressing this issue.

What does all this mean in terms of obsidian dating? Archaeologists, as mentioned in the introduction, have debated over the best rate expression to describe hydration, usually presenting cases for $t^{0.5}$ or t based upon archaeological evidence. From the classic model and findings presented above, it might be suggested that a combined parabolic to linear rate is indicated. However, as A. White and Claassen (1979:470) point out, "although simple rate expressions can be utilized to explain short-term lab-controlled dissolution of many silicate phases, their application to model natural weathering processes is much more difficult."

Barkatt et al. (1988:130) suggest that for predicting long-term durability of nuclear waste glass, the second kinetic stage (linear dependence) is expected to prevail, and is therefore of primary concern. However, there are recent conflicting observations regarding time dependency (t^{n}).

Westik and Peters (1981) have investigated time and temperature dependence of glass weathering. Static tests were conducted, reacting glass samples in deionized water for temperatures ranging from 25-250 ^{o}C, and periods of up to 341 days. They find a time exponent of 0.43 at 25 ^{o}C (reaction period less than 32 days?). Between 50 and

150 ^{o}C, values of n ranged from 0.58-0.75. At 250 ^{o}C, the time exponent was 0.20. Based on these findings, they consider the possibility that the time exponent decreases with time, acknowledging however that leaching experiments need to be extended to resolve the question of long-term rate tendencies.

Altenhein and Lutze (1983) also discuss time dependence. They suggest that values of n between 0.5 and 1.0 may result if there is a change in mechanism from matrix dissolution to control by diffusion through a surface layer. Values of n less than 0.5 are explained by back-reactions, precipitation, or surface sorption. They conclude that based on natural systems, it is reasonable to assume that n will decrease with time due to the mechanisms referred to above (i.e., back-reactions, precipitation and surface sorption). Their findings reflect the controversy which has recently developed over the role solubility effects and precipitation play on long-term weathering. Both factors are reported to have reaction-limiting effects.

Kuhn and Peters (1983) present two models: one which results in the accumulation of a protective layer of insoluble reaction products; the other which results in the adsorption of reaction products on the surface. In either case, they predict a change from linear to parabolic rate laws (a complete reversal from the classic model!). They suggest that incongruent release ($t^{n<1}$) is attributed primarily to solubility effects (see also Ishiguro et al. 1983; Lutze et al. 1983).

A similar proposal is made by Wallace and Wicks (1983). They explain that "initially the slope will be equal to one when the rate of reaction of water with silica is controlling, and later change to one half as the surface layer becomes thicker and diffusion through it becomes controlling" (Wallace and Wicks 1983:26). Their explanation apparently rests on near-saturation or solubility effects.

In contrast, Conradt et al. (1985) explain kinetics less than $t^{0.5}$ according to transport-limiting processes due to a protective precipitated layer (a thin film of resistivity or phase formation). Haaker et al. (1985:121), investigating the effect of phase formation, find that the kinetics (after static hydrothermal reaction of glass at 200^{o} C for up to 1000 days), "gave no evidence for pure root time law or for pure corrosion which should result in a linear time law. Moreover, fits using a combination of these two processes gave unsatisfactory results." They too attribute deviations in glass behavior from the classic model to the formation of protective precipitates. Analcime is identified as the dominant reaction product. They are careful, however, not to rule out the effects of saturation.

These recent studies suggest a need to modify the classic glass weathering model. Hench (1988:191) proposes a general equation which describes the overall rate of glass surface reactions (R) having at least four terms:

$$R = k_1 t^{0.5} - k_2 t^{1.0} + k_3 t^{x} + k_4 t^{y} + k_n t^{z} \qquad (4)$$

Hench (1983:195) briefly describes this model:

> Although a short (several days) period of alkali-hydrogen ion exchange may occur [stage 1, t0.5], the dominant long term mechanism controlling corrosion is a combination of matrix dissolution [stage 2, t], followed by incongruent dissolution [stage 3, tx], and solution/precipitation reactions [stage 4, ty]. [Note: The exponential values for terms 3, and 4 have not been quantitatively established.]

As previously quoted, Hench explains that:

> The extent of matrix dissolution and onset of surface

> precipitation will depend on the time required for various species in the glass to reach saturation in solution. Saturation of species (i) is a function of the initial solution pH, amount of alkali in the glass and rate of alkali release, temperature, initial concentration of species (i) in the solution, surface area-to-volume which influences solution concentration, or flow rate which also affects solution concentration. Until saturation of some species in solution is reached, the glass dissolves congruently at a [linear] rate...

Implications for Obsidian Dating

As evident from the overview just presented, the field of glass science has been very active over the last few years. I have attempted to communicate as responsibly and comprehensively as possible the current status. It is clear that glass weathering is complex and that advancement in our understanding of this process has been made. It is probably also apparent that uncertainties still exist.

What does this overview of glass reaction studies imply for obsidian dating? Is there any concensus on the rate expression most appropriate to describe obsidian hydration? Glass scientists are still investigating this issue. My impression is that a long-term linear rate is favored. However, according to Grambow et al. (1988:531), it is still unclear whether the long-term rate is constant or decreases with time. This state of affairs suggests that dating obsidian in an absolute sense might be premature.

Nuclear waste managers are required by the Code of Federal Regulations, in its Titles 10 Part 60 (US Nuclear Regulatory Commision 1983), to provide "reasonable assurance" that their waste package system will perform according to specified criteria, in other words, demonstrate that glass used in the containment of high-level radioactive waste will endure into the far-future. Umeki et al. (1986)

point out that it is difficult to build deterministic models that predict in any definite manner the entire mechanism of leaching, as natural processes gradually change with time and space. To contend with this problem, researchers need to determine the **degree of confidence** they have in long-term extrapolations of leach rates.

Performance assessments or waste package reliability analyses are being conducted which evaluate the ability of conceptual weathering models (mathematical/computer models) to describe physical reality. There are many examples in the literature finding close agreement between calculated and experimentally determined data. Altenhein and Lutze (1983:270) conclude that "reasonable predictions can be made based on carefully measured, site-specific experimental data and the thoughtful use of analogous natural systems in selecting appropriate parameters for long-term extrapolations."

Weathering rates have been demonstrated to be condition-specific. Therefore, to extrapolate rates into the past, it seems important that conditions be identified. One of the most important conditions, in my opinion, appears to be the degree of saturation that solutions achieve, as they apparently influence the rate expression. Fillet et al. (1986) anticipate, based on very low flow rates, that geologic storage environments for the disposal of nuclear waste will attain saturation quickly, resulting in transport-limited corrosion. These same conditions are not necessarily achieved for near-surface soils in which archaeological deposits are located. Identifying the degree of saturation for near-surface soils may help in determining the primary mechanism controlling the weathering of obsidian.

Another consideration with important implications for obsidian dating, is the extent to which dissolution occurs, because in theory, dissolution causes the retreat of the glass interface as it competes with leaching reactions. Under circumstances expected at archaeological sites, does dissolution obliterate in part the hydrated glass layer? Are inaccurate age estimates being made as a result of dissolution processes? There are no definite answers to these questions. Zoitos and Clark (1988:175) contend that because the reacted glass layer is subject to dissolution, care must be taken when using reaction layer thickness as a measure of glass corrosion. To resolve the uncertainties regarding this issue, they are currently researching the degree to which dissolution occurs in a variety of environments through the use of inert, ion-implanted markers. The fact, however, that Bunker et al. (1983) found silica dissolution negligible when compared to alkali leaching even when the leaching kinetics were linear with time is encouraging.

In terms of hydrothermal experiments in non-buffered solutions greater than 200 °C, significant silica dissolution has been observed to occur. If, as Bates et al. (1988:243) conclude, dissolution of the glass matrix results in an underestimation of the actual thickness of reacted glass, hydration rate constants calculated from data generated in this manner should then reflect the net result of hydration and dissolution reactions, and may not provide reliable age estimates.

Steps to reduce dissolution reactions have been explored, such as lowering temperatures, saturating solution with amorphous silica (see Stevenson and Scheetz in press), and reacting in vapor rather than in hydrothermal phase (see Bates et al. 1988). Such revisions in method to accelerate reaction may provide data suitable for producing hydration rate constants. However, experimentally derived rate constants are condition-specific. Taking a cautious stance, it is not unreasonable to question the appropriateness of applying rate constants derived from high-temperature, essentially closed-system experiments, to field conditions. Most of the experiments reported on in this overview have accelerated reactions not by high temperature conditions but high SA/V ratios using glass in powdered form. Other experiments were not accelerated at all, but have relied on the use of sophisticated instrumentation and techniques to analyze concentrations of species in solution, at the glass surface, and at various depth (angstroms) within the glass.

As the literature search has shown, factors of solution pH, solution composition, SA/V, relative humidity, and temperature affect **experimentally** determined rates of hydration. The extent of their signicance to **naturally** hydrating obsidian in the context of near-surface soils needs to be assessed to fully evaluate implications to obsidian dating in its absolute chronometric capacity.

Chapter 3

RESEARCH DESIGN FOR ACCELERATED HYDRATION EXPERIMENTS

Background

Accelerated obsidian hydration experiments within the field of archaeology began with the pioneering work of Friedman, Smith, and Long (1966) who reacted obsidian for up to 4 years at 100° C in a furnace with dripping water, producing vapor-phase conditions. Since this time, a variety of experimental procedures have been employed, producing differing reaction conditions. It is important to note these differences in an attempt to understand inconsistent results.

Friedman and Long (1976) reacted samples of 12 obsidian sources in a vapor-phase at 95° C for up to 2 years; 150° C for up to 80 days; 195° C for up to 30 days; and 245° C for up to 8 days. Examining hydration development microscopically, they noted that "the hydration front tends to be more diffuse the higher the temperature (and water pressure)" (1976:347). In spite of the extrapolation that is necessary from high to low (ambient) temperatures, they concluded that calculating source-specific hydration rates according to this technique appeared satisfactory.

Ericson (1977) reacted samples of 40 obsidian sources and subsources in both a liquid-phase and a two-phase liquid/vapor system, using distilled water, at temperatures of 150, 163, 172, 193, and 200° C. Reaction times ranged from 3 to 45 days. Ericson noted "thermal discontinuities" (no microscopically observable hydration) for samples reacted at temperatures above 190° C. He also observed a great deal of variability in the source-specific activation energies and diffusion coefficients calculated, and a lack of concordance with results of Friedman and Long (1976). He cautioned that "we are not sure whether the accelerated hydration process activated at elevated temperatures and pressures is equivalent to the 'natural' hydration process observed in obsidian artifacts" (1977:84). Nevertheless, Ericson finds this technique "useful to establish the rank-order of the hydration rates of a series of obsidian sources" (1977:87).

Tsong et al. (1981) reacted obsidian in deionized water at 90 C for up to 72 hours, utilizing a large heated bath. Reactions were also conducted at 60, 70, 80, and 90^{o} C for 16-day periods. Hydration was not measured in the traditional way, since insufficient time had elapsed for development to be detectable microscopically. Tsong and his associates relied on hydrogen depth-profiling by secondary ion mass spectrometry and ^{19}F nuclear reaction techniques. They noted two potential problems with accelerated hydration experiments as related to solution pH and surface dissolution. Regarding solution pH, they asserted that "it is important that the volume ratio of water to obsidian be very large so that the pH of the water (due to dissolution of alkali from glass) would not change appreciably to cause a change in hydration rate of the glass" (Tsong et al. 1981:404). Further, results of experiments on La Ventilla obsidian indicated a linear rate of hydration in contrast to a parabolic rate, which Tsong et al. attributed to competing reaction between surface dissolution and hydrogen diffusion. They concluded that "it is important to resolve the problem of the surface dissolution in the hydration process before an absolute hydration equation can be established for a given type of obsidian" (Tsong et al. 1981:406).

Apparently having resolved this problem, Michels et al. (1983) set the stage for the commercial determination of obsidian hydration rates based upon experimentally produced data. Their experimental design specified reaction of nine obsidian samples in a 1-liter Parr pressure reaction vessel filled with 500 ml of deionized water. Reactions were conducted at temperatures of 150, 175, 200, 225, and 250°C for 4 days; and additionally at 200°C for 0.5, 1, 2, 4, and 6 days. This design has since been followed to produce over 80 obsidian hydration rate constants to date (see MOHLAB Technical Report Series, State College, Pennsylvania).

Stevenson and Scheetz (in press), following the experimental design set forth by Michels et al. (1983), have observed poorly defined to non-definable hydration rims under microscopic examination after reaction at temperatures greater than 180°C, which they attribute to surface dissolution of obsidian. They assert that observed hydration development at high temperatures represents the net result of hydration and dissolution processes, and not true hydration development (see also Stevenson et al. 1989).

To avoid the problems involved with reacting at high temperatures, Stevenson and Scheetz (in press) propose lowering reaction temperatures and inhibiting the rate of glass surface dissolution by saturating the solution with amorphous silica. They react eight obsidian samples with 500 ml of distilled deionized water saturated with one gram of amorphous silica, in a 2-liter Parr pressure reaction vessel, under the following conditions: temperatures of 130, 140, 160, 170, and 190°C for 12 day periods; and additionally at 160°C for 2, 6, and 18 days.

Stevenson and Scheetz have compared independently derived rates of hydration for the same obsidian source and find significant differences. To explain this variability, they point to: (1) slight differences in experimental condition; and (2) hydration measurement error due to differences in optical resolution and operator discretion. They suggest that "a thorough and critical review of current rate development methods from the standpoints of optical microscopy and the diffusion kinetics is clearly needed to establish which sets of techniques contributes the least amount of error and best replicates the natural hydration process" (Stevenson and Scheetz, in press).

Objectives

Given current developments regarding experimental design, an ultimate objective in conducting accelerated obsidian hydration experiments, as specified in Chapter 1, is to contribute towards an assessment of the use of accelerated experiments for application in absolute dating. A second objective is to explore the use of accelerated experiments for application in relative dating. To achieve these goals, research was conducted with these questions in mind. Are results obtained from accelerated experiments reproducible? If results are not reproduced, what factors account for variability? Are the problems noted by Friedman and Long (1976), Ericson (1977), Tsong et al. (1981), and Stevenson and Scheetz (in press), observed for samples reacted at the higher temperatures prescribed in Michels' experimental design? If so, how does saturating the solution with amorphous silica affect results? How does lowering the temperature of reaction affect results? The investigation of these issues is considered important to knowledgably assess the application of accelerated hydration experiments for dating purposes.

Methods

The initial task and intention of the present study was to replicate Michels' experimental design and compare results. However, some liberty was taken at the very outset, and several changes in design were implemented. Dissatisfied with the small number of samples prescribed per experiment, sample size was increased to provide a greater degree of confidence in our results. Further, in contrast to Michels' experimental design which reacted sample #1 for 0.5 day, sample #2 for 1 day, sample #3 for 2 days, etc., each sample was subjected to a cumulative reaction period of 6 days, with thin sections obtained for each sample after the first, second, fourth, and sixth days. Bates et al. (1986) identify such tests as **batch** versus **continuous** modes.

Michels' experiments react 9 source-specific samples, obtaining a total of 9 thin sections. Due to the changes initiated in the experiments conducted for this thesis, we reacted 25 source-specific obsidian samples during each experiment, and obtained a total of 65 thin sections (see Table 4). Lastly, as an additional modification, samples of more than one obsidian source were reacted simultaneously within the reaction chamber. Solution was replaced with fresh deionized water after each run. As a result of making these changes, we were forced to consider how variations in experimental procedure and condition may affect results.

Three sets of experiments were conducted using samples from four North Coast Ranges obsidian sources: Borax Lake (BL); Napa Valley (N); Mt. Konocti (K); and Annadel (A). Origins for these geochemical

Table 4. Initial Experimental Design

Temps oC	Days/ Run	Day # at which thin sections obtained	Sample/ Source	Thin Section/ Source
150	4	0,4	5	10
175	4	0,4	5	10
200	6	0,1,2,4,6	5	25
225	4	0,4	5	10
250	4	0,4	5	10
Total	22		25	65*

* With four sources reacted = 320 thin sections per experiment set

sources are located in Figure 1. Five freshly fractured flakes (averaging 2 cm in diameter) from each source* were placed in a 2-liter Parr pressure reaction vessel with 1 liter of deionized water and reacted at temperatures ranging from 150 to 250 °C, for periods ranging from 4 to 6 days. Thin sections of samples reacted at 200 °C were obtained at the first, second, fourth, and sixth day to observe hydration development over time (see Table 4). Thin sections of samples reacted respectively at 150, 175, 225, and 250 °C, were obtained after 4-day periods, to observe differences in hydration development due to changes in temperature. A fourth experiment set followed the above outline with the addition of amorphous silica to the solution. Beginning with the second set of experiments, initial and final pH of the solution was measured for each run.

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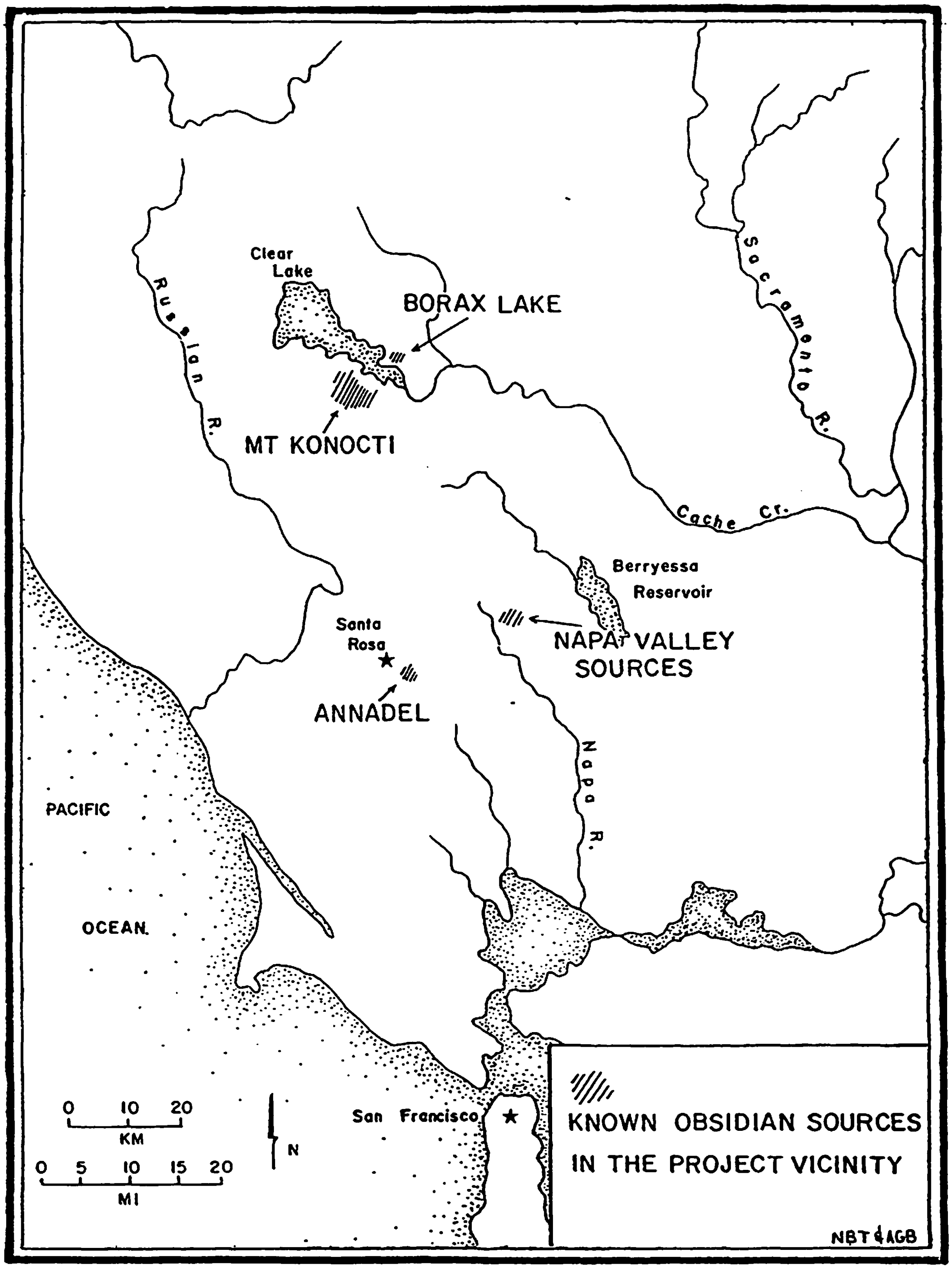
* Samples for all experiments were obtained from single parent specimens, thus eliminating the possibiliy for intrasource geochemical variation.

Figure 1. Map locating Borax Lake, Napa Valley, Mt. Konocti and Annadel Obsidian



Chapter 4

RESULTS

Findings of Accelerated Hydration Experiments

An initial set of experiments (Set 1) was conducted following the procedures outlined in the research design. Hydration measurements for this set are presented in Table 5. The expected trend of increasing hydration depth with passage of time and increasing temperature was observed. Hydration was measurable for samples reacted at temperatures of 150, 175, and 200 ^{o}C. However, after reaction at temperatures greater than 200 C, obsidian samples were covered with a gritty residue, attributed to surface dissolution. Upon microscopic examination, it was found that these samples exhibited increasingly reduced clarity at the hydrated/non-hydrated interface, inhibiting the ability to reliably discern and measure depths of water penetration.

Table 5. Average Hydration Measurements for Accelerated Experiment Set 1

A: 200 degrees C for 1 to 6 days

Day	$\overline{BL}$	n	s	$\overline{N}$	n	s	$\overline{K}$	n	s	$\overline{A}$	n	s
1	3.5	4	0.10	2.7	5	0.05	2.7	5	0.08	2.4	5	0.05
2	4.0	5	0.04	3.0	5	0.04	3.1	5	0.11	2.5	5	0.08
4	5.6	4	0.04	4.7	5	0.01	4.6	5	0.09	3.7	5	0.03
6	5.9	5	0.16	5.1	5	0.06	5.2	5	0.07	3.9	5	0.17

B: 4 day runs at varying temperatures

Temp	$\overline{BL}$	n	s	$\overline{N}$	n	s	$\overline{K}$	n	s	$\overline{A}$	n	s
150	2.1	5	0.03	1.6	4	0.07	1.6	4	0.07	1.3	5	0.04
175	3.5	5	0.05	2.9	3	0.10	2.9	5	0.04	2.3	5	0.04
225	dh			6.2	4	0.21	5.7	2	0.07	3.8	3	0.55
250	dh			dh			dh			dh		

Reacted in deionized water, measurements in microns, dh-diffuse hydration

For reactions at 225°C, 65% of the specimens (n=13) yielded diffuse hydration fronts. All of those samples reacted at 250°C (n=20) were found to produce diffuse hydration fronts. Similar observations have been made by Stevenson and Scheetz (in press), Ericson (1977), and Friedman and Long (1976). Michels, in contrast, does not report any problems with hydration rim resolution on`samples reacted at these temperatures.

Michels' (1982, 1986) hydration results for Napa and Annadel obsidians are presented in Table 6. Comparing these results to our initial experiment set (see Table 7), we observed only slight differences in hydration development for samples reacted at 150 and 175°C. However, for reactions at 200°C and greater, considerable differences were found (in one instance greater by a factor of two).

Table 6. Michels* Measurements Accelerated Hydration

A: 200oC for 1 to 6 days

Day	N	A
1	2.66	2.47
2	3.80	3.52
4	5.33	5.01
6	6.62	6.21

B: 4 day runs at varying temps

Temp (C)	N	A
150	1.51	1.38
175	2.86	2.65
225	8.76	9.25
250	14.37	14.25

* Michels (1982, 1986)
Reacted in deionized water.
Measurements in microns.

Table 7. Differences between Experiment Set 1 and Michels

A: 200oC for 1 to 6 days

Day	N	A
1	0.04	-0.07
2	-0.80	-1.02
4	-0.63	-1.31
6	-1.52	-2.31

B: 4 day runs at varying temps

Temp (C)	N	A
150	0.09	-0.08
175	0.04	-0.35
225	2.56	-5.45
250	-	-

Differences in microns.

On the whole (excluding results at 250°C for which we were unable to obtain measurable hydration), differences ranged from 0.04 to 5.45 microns, with the average difference being 1.2 microns ± 1.5 microns.

To account for these differences, we proposed several possible explanations: (1) differences in experimental procedure and conditions; (2) differences in hydration measurement technique; and (3) obsidian source chemical variability (probably minor). The most likely explanation in this case is the first, differences in experimental procedure and condition. Variables potentially affecting results were identified as: (1) differences in SA/V; (2) differences in initial and final pH of solution; (3) reacting single in contrast with multiple sources per run; and (4) differences caused by reusing vs. replacing solution during cumulative runs.

All these variables in some way potentially affect solution pH and saturation of glass constituents, which glass scientists agree affect surface reaction rates. If knowledge gained by reviewing the glass science literature is applied, we can suggest that: (1) during our cumulative experiments in which solution was replaced after each run, solution pH and degree of saturation were in effect reduced upon initiation of the next run (conditions characterized as "pulsed-flow"). Michels, in contrast, conducting non-cumulative experiments, generated an increasingly basic and saturated solution (conditions characterized as "static"); and (2) our experiments contained a greater number of samples than Michels', which should represent an increased SA/V ratio, in effect increasing solution pH and saturation. It may be that between these two differences in procedure and condition, a counter-balance in effect is achieved. It can be pointed out that if results at 225°C are excluded from comparison, the range in differences between Set 1 and Michels' results are much smaller; ranging from 0.04-2.31 microns, with the average difference being 0.68 ±0.73.

A repeat set of experiments (Set 2) was conducted, for which initial and final pH of solution were monitored. Table 8 presents measurements for samples reacted at 150, 175, and 200°C (reactions at 225 and 250°C were discontinued). Comparing these measurements with the initial set (see Table 9), differences were observed ranging from 0.0 to 2.1 microns, with the average difference being 0.98 ± 0.70. The greatest differences were exhibited for the longer reactions at 200°C.

Table 8. Average Hydration Measurements for Accelerated Experiment Set 2

A: 200 degrees C for 1 to 6 days

Day	$\overline{BL}$	n	s	$\overline{N}$	n	s	$\overline{K}$	n	s	$\overline{A}$	n	s
1	2.5	1	-	2.1	2	0.07	2.0	3	0.10	1.7	1	-
2	2.8	3	0.12	2.2	2	0.00	2.2	2	0.21	1.5	2	0.00
4	3.6	3	0.10	2.7	3	0.06	2.5	3	0.06	-		-
6	4.2	4	0.17	3.2	4	0.10	3.3	3	0.10	2.2	3	0.26

B: 4 day runs at varying temperatures

Temp	$\overline{BL}$	n	s	$\overline{N}$	n	s	$\overline{K}$	n	s	$\overline{A}$	n	s
150	1.9	4	0.03	1.6	4	0.06	1.6	4	0.05	1.2	4	0.02
175	3.2	4	0.15	2.4	4	0.08	2.4	4	0.10	1.6	4	0.29

Reacted in deionized water. Measurements in microns.

What explains the observed differences for these repeat experiments (Sets 1 and 2)? Solution pH again may provide a key to these differences. Table 10 presents initial and final solution pH for specified reaction conditions. For reaction of samples at 150 and 175°C, final solution pH readings did not increase significantly from

Table 9. Differences between Repeated Experiments: Sets 1 and 2

A: 200 degrees C for 1 to 6 days

Day	BL	N	K	A
1	1.0	0.6	0.7	0.7
2	1.2	0.8	0.9	1.0
4	2.0	2.0	2.1	-
6	1.7	1.9	1.9	1.7

B: 4 day runs at varying temperatures

Temp	BL	N	K	A
150	0.2	0.0	0.0	0.1
175	0.3	0.5	0.5	0.7

Differences in microns.

Table 10. Solution pH for Experiment Set 2

Temp	Days	Initial	Final
150	4	6.2	7.0
175	4	6.5	6.7
200	1	5.8	8.0
200	1	5.8	7.8
200	2	5.2	7.8
200	2	6.1	8.5

initial pH readings, with solution remaining essentially neutral. Final solution pH readings for reaction of samples at 200 °C ranged from 7.8 to 8.5. Das (1980:169), in reacting glass samples at temperatures ranging from 1 to 69 °C, found "the higher the pH of the leaching solution, the more silica was extracted, and that this effect was much more pronounced at pH greater than 9." If this is the case at lower temperatures, what might the effect be at higher temperatures?

Solutions which attain pH levels of 8.5 may be affecting surface reactions significantly, producing variable results.

An additional repeat experiment Set 3 was conducted, with the exception of reactions at 225 and 250 ^{o}C. Table 11 presents hydration measurements for this set. A comparison of these data with those of experiment Set 2 is presented in Table 12. Differences between these sets are very slight, ranging from 0.0 to 0.6 microns. The average difference is 0.24 ± 0.19 microns. If repeat experiment Sets 2 and 3 show essentially no difference, then can differences between Sets 1 and 2 be attributed to high pH attainment and associated problems with silica dissolution?

Table 11. Average Hydration Measurements for Accelerated Experiment Set 3

A: 200 degrees C for 1 to 6 days

Day	$\overline{\text{BL}}$	n	s	$\overline{\text{N}}$	n	s	$\overline{\text{K}}$	n	s	$\overline{\text{A}}$	n	s
1	2.9	5	0.07	2.3	5	0.04	2.3	5	0.04	1.7	4	0.05
2	2.8	5	0.00	2.3	5	0.05	2.3	4	0.08	1.7	5	0.04
4	4.2	5	0.04	2.9	5	0.05	2.9	5	0.05	2.4	5	0.13
6	4.2	5	0.05	2.8	5	0.05	2.8	5	0.04	2.1	4	0.06

B: 4 day runs at varying temperatures

Temp	$\overline{\text{BL}}$	n	s	$\overline{\text{N}}$	n	s	$\overline{\text{K}}$	n	s	$\overline{\text{A}}$	n	s
150	2.4	5	0.08	1.7	5	0.11	1.8	5	0.09	1.3	5	0.04
175	3.4	5	0.07	2.7	5	0.05	2.7	5	0.05	2.2	4	0.06

Reacted in deionized water. Measurements in microns.

What explains why experiment Sets 2 and 3 are so different from Set 1, when in theory, results were produced under the same conditions and procedures? In retrospect, and after much deliberation, it was determined that in reality, the flaked obsidian samples utilized in

Table 12. Differences between Repeated Experiments: Sets 2 and 3

A: 200 degress C for 1 to 6 days

Day	BL	N	K	A
1	-0.4	-0.2	-0.3	0.0
2	0.0	-0.1	-0.1	-0.2
4	-0.6	-0.2	-0.4	-
6	0.0	0.4	0.5	0.1

B: 4 day runs at varying temperatures

Temp	BL	N	K	A
150	-0.5	-0.1	-0.2	-0.1
175	-0.2	-0.3	-0.3	-0.6

Differences in microns.

Table 13 . Weights of Obsidian used in Experiment Sets 1, 2, 3, & 4

Temp	1	2	3	4
150	56.6	36.6	37.1	29.8
175	67.6	37.8	33.8	28.1
200	82.9	50.6	37.8	27.8
225	46.4	33.9		33.4
250	68.4	41.1		35.2

Weight in grams.

these experiments were not standard in size and that perhaps this variability (reflecting differences in SA/V) could explain the differences observed between experiment sets. Table 13 presents weights of obsidian used in experiments Sets 1, 2, 3, and 4 (the set described in the following paragraph). It can be seen that weights of obsidian used in Sets 2 and 3 more closely correspond than those of Set 1. Future experiments may possibly be improved by better controlling SA/V ratios.

Given evident dissolution at higher temperatures and high solution pH for reactions at 200^{o} C, we elected to investigate steps taken by Stevenson and Scheetz (in press) to avoid such problems (i.e., lowering temperature and saturating solution with silica). A subsequent experiment Set 4, confined reactions to temperatures of 200^{o} C and less, and included water saturated with amorphous silica, in an effort to inhibit silica dissolution.

If the saturation of water with silica is inhibiting surface dissolution, then greater depth of hydration should be expected. Table 14 presents hydration measurements for experiment Set 4. These measurements are **significantly** greater than either of the first three sets, suggesting that surface dissolution is being inhibited. Differences between experiment Sets 3 and 4 are presented in Table 15. Differences range from 0.6 to 6.5 microns, with the average difference being 2.87 ± 1.8 microns. Final solution pH remained essentially unchanged from initial pH, as shown in Table 16.

Table 14. Average Hydration Measurements for Accelerated Experiment Set 4
A: 200 degrees C for 1 to 6 days

Day	$\overline{BL}$	n	s	$\overline{N}$	n	s	$\overline{K}$	n	s	$\overline{A}$	n	s
1	4.8	4	0.06	3.8	4	0.05	3.8	3	0.00	3.0	4	0.08
2	6.2	3	0.06	5.3	4	0.05	-		-	4.2	3	0.12
4	8.6	4	0.10	7.7	3	0.00	7.7	2	0.07	5.8	3	0.12
6	10.7	4	0.13	8.7	4	0.10	8.7	4	0.18	6.6	4	0.08

B: 4 day runs at varying temperatures

Temp	$\overline{BL}$	n	s	$\overline{N}$	n	s	$\overline{K}$	n	s	$\overline{A}$	n	s
150	3.0	4	0.10	2.4	4	0.13	2.7	4	0.06	2.0	4	0.08
175	5.3	4	0.17	4.5	4	0.08	4.5	4	0.06	3.6	4	0.08

Reacted in deionized water saturated with amorphous silica.
Measurements in microns.

Table 15. Differences between Repeated Experiments: Sets 3 and 4*

A: 200 degrees C for 1 to 6 days

Day	BL	N	K	A
1	-1.9	-1.5	-1.5	-1.3
2	-3.4	-3.0	-	-2.5
4	-4.4	-4.8	-4.8	-3.4
6	-6.5	-5.9	-5.9	-4.5

B: 4 day runs at varying temperatures

Temp	BL	N	K	A
150	-0.6	-0.7	-0.9	-0.7
175	-1.9	-1.8	-2.8	-1.4

Differences in microns.
* Set 3: Reaction in deionized water
Set 4: Reaction in silica saturated deionized water

Table 16. Solution pH for Experiment Set 4

Temp	Days	Initial	Final
150	4	6.2	6.3
175	4	6.0	6.8
200	1	6.2	6.6
200	1	6.1	6.1
200	2	5.8	6.4
200	2	5.8	6.2

Implications of Accelerated Experiments for Absolute Dating

What conclusions can be drawn from the preceding findings? A primary question articulated in the research design, asks whether experimental results are reproducible. Although findings are not conclusive, and at first glance may appear discouraging, close scrutiny allows a positive interpretation. The two most comparable experiment sets, 2 and 3, produced very similar results, differences being within the range of measurement error. It appears that if all variables which potentially affect results are held constant, results are reproducible.

What factors account for the variability observed between experiment sets? Briefly, between experiment Set 1 and Michels', it was postulated that: (1) differences in solution pH caused by (2) differences in SA/V ratios and the replacement of solution between cumulative runs, may have contributed to (3) differences in hydration development. For Sets 1 and 2, it was determined that differences in the size of samples (as evidenced by weight differences in Table 13) may have contributed to differences in hydration results. Between Sets 2 and 3, little difference was observed. Between Sets 3 and 4, large differences were attributed to the composition of solutions which contrasted deionized water with silica-saturated deionized water.

What do results imply regarding experimental design? First, it was found that high temperature reactions of 225 and 250 °C produced samples covered with a gritty residue and yielding poorly defined hydration rims, attributable to surface dissolution. Reactions at 200 °C produced solutions attaining high pH levels. Differences exhibited between hydration developed under these conditions and hydration developed in a silica-saturated solution, indicate that substantial surface dissolution occurs in deionized water at 200 °C. Based on these findings, a maximum temperature, as recommended by Stevenson and Scheetz (in press), seems justified. They suggest that reactions should be confined to temperatures of 180 °C or less.

Secondly, should solutions be saturated with amorphous silica? Although findings are not definitive, it appears that silica saturation acts to inhibit surface dissolution and maintain the initial solution pH level. For these reasons, silica saturation might be considered an improvement. An alternative design, as previously mentioned, reacts glass in vapor in contrast to a liquid-phase. Bates et al. (1988), reacting obsidian in both liquid and vapor phases, find that birefringent layers formed in vapor were always thicker and more clearly defined compared to hydrothermally reacted samples (differences are attributed to the dissolution which occurs during hydrothermal experiments).

What assessment can be made for the use of accelerated hydration experiments to absolutely date obsidian artifacts? Based upon the overview of glass surface reaction studies and results of our accelerated experiments, several issues are identified as yet unresolved:

(1) The appropriateness of applying condition-specific rate constants derived from high-temperature essentially closed-system experiments, to field conditions, needs to be assessed;

(2) In a related issue, additional confirming evidence is needed to support the extrapolation of hydration rate constants from high temperatures to ambient temperatures; and

(3) Further understanding of the kinetics of natural glass weathering in near-surface soil contexts is needed before a descriptive equation on long-term time dependence can be agreed upon.

As such, it is in our opinion, difficult to endorse the use of accelerated experiments for absolute dating.

Although we conclude that dating in an absolute sense is yet premature, the issues we raise are recognized not to discourage, but to encourage a new rigour. From a practical standpoint, for the time being, accelerated hydration experiments may be more useful for relative dating purposes, as first suggested by Ericson in 1977. An investigation exploring this potential, as presented below, was undertaken as another objective of this thesis.

Application of Accelerated Experiments for Relative Dating

Many archaeological sites in California contain obsidian specimens that derive from multiple geochemical sources, reflecting distribution systems developed by social networking between prehistoric groups. Analyzing source frequency distributions of these obsidians over time can lead to the formation of hypotheses regarding shifts in procurement strategy, shifts in obsidian use and intensity, and shifts in relations with other socio-political groups. To conduct such analyses and draw conclusions of this nature, it is necessary to temporally order these source-specific artifacts. However, with the well-documented difficulties involved in obtaining source-specific rates of hydration that yield reliable dates, temporal ordering through the absolute dating of obsidian is viewed as problematic.

Alternatively, archaeologists choosing to utilize a relative dating approach to obsidian have been analytically limited by their inability to make reliable cross-source comparisons of hydration data, given differences in geochemical composition contributing to variability in rates. To circumvent this limitation, attempts have been made to calibrate hydration measurements. Implicitly assuming that relative calibrations can be achieved by equating depths of hydration developed for source-specific obsidians during equivalent lengths and conditions of exposure, some researchers have asserted temporal equivalencies based upon archaeological evidence.

Kaufman (1980:81) attempted a cross-source comparison of Borax Lake and Konocti obsidians, assuming temporal equivalencies based upon stratigraphic associations of data at LAK-381. He equated Konocti and Borax Lake obsidian hydration measurements at a ratio of 1:1.61. Origer (1987:51) estimated hydration measurement ratios for Napa Glass Mountain and Annadel obsidians with temporal equivalencies determined based upon projectiile point forms and radiocarbon dates. He found that the ratio of Annadel to Napa Glass Mountain is on the order of 1:1.20.

G. White (1984:114) generated hydration data obtained from features at stratigraphic breaks at LAK-510 which provided clear units of contemporaneity; he also employed projectile point types with assumed contemporaneity to equate hydration rim measurements for Borax Lake, Napa, and Konocti obsidians. He found Borax Lake obsidian hydrates faster than Konocti or Napa obsidian, with Konocti hydrating slowest. For example, as derived from his Table 11, readings of hydration for these sources would be equated in ratio form as BL:N:K = 1:0.85:0.35.

T. Jackson (1986:71), based on admittedly tenuous data, observed that "Mt. Konocti obsidian hydrates at about the same rate as Napa Valley obsidian. Borax Lake obsidian hydrates relatively more quickly." He suggested that approximately 2.4 microns of hydration for Borax Lake obsidian is roughly equivalent to 1.8 microns of hydration for Napa Valley obsidian in the southern interior North Coast Ranges.

Reasoning that accelerated hydration experiments might provide a more rigorous means for establishing relative calibrations, Tremaine and Fredrickson (1988) conducted an investigation (based on the preliminary results of this thesis) to study the covariation of hydration development for obsidians over time, given the certainty of temporal equivalency and constant temperature history. It was hypothesized that if the relationship between hydration development for any two source-specific obsidians was found constant and could be defined, a relative calibration could be established, providing the ability to make cross-source comparisons.

Accelerated hydration experiment Sets 1 and 2 were used by Tremaine and Fredrickson (1988) to determine the nature of the relationship between co-reacting obsidians. Specifically, was the relationship constant and definable? Ratios of temporally equivalent rim widths derived from experiment Sets 1 and 2 were compared and found to be very consistent regardless of reaction time or temperature, as shown in Table 17.

Data from all experiments conducted to date were subsequently examined to determine hydration measurement ratios for the six possible

Table 17. Ratios of Temporally Equivalent Hydration Measurements: Comparisons within and between Experiment Sets 1 and 2

Temp	Days	BL:N 1	BL:N 2	BL:K 1	BL:K 2	BL:A 1	BL:A 2
150	4	1:0.76	1:0.84	1:0.76	1:0.84	1:0.62	1:0.63
175	4	1:0.82	1:0.75	1:0.83	1:0.75	1:0.66	1:0.50
200	1	1:0.77	1:0.84	1:0.77	1:0.80	1:0.69	1:0.68
200	2	1:0.75	1:0.79	1:0.78	1:0.79	1:0.63	1:0.54
200	4	1:0.84	1:0.75	1:0.82	1:0.69	1:0.66	-
200	6	1:0.86	1:0.76	1:0.88	1:0.79	1:0.66	1:0.52
n		6	6	6	6	6	5
average		1:0.80	1:0.79	1:0.81	1:0.78	1:0.65	1:0.57
st. dev.		0.05	0.04	0.05	0.05	0.03	0.08

paired-source combinations; BL:N, BL:K, BL:A, N:K, N:A, and K:A. Twenty-five sets of data per source-pair were compiled and are given as hydration measurement ratios in Table 18. These data sets represent average hydration measurements for four to five samples of each source per specified circumstance, representing a maximum of 108 sets of measurements per source in total. Average hydration measurement ratios for the different paired sources indicate that BL:N = 1:0.79; BL:K = 1:0.79; BL:A = 1:0.62; N:K = 1:1; N:A = 1:0.77; and K:A = 1:0.77. Standard deviations for these hydration measurement ratios were 0.06 or less. These low standard deviations lend support to the earlier conclusion that the relationship between co-hydrating source-specific obsidians remains constant **regardless** of reaction condition (i.e., time, temperature, SA/V, solution pH, and solution composition). On a qualifying note, further experiments are currently being conducted reacting these same obsidian sources hydrothermally at temperatures below 150°C and in vapor-phase conditions, which may provide differing results.

Because the relationship between co-reacting obsidians appears to be consistent under varying conditions, cross-source comparisons are potentially enabled, circumventing the need to quantify the extent to which particular conditions affect hydration rates as warranted in absolute dating. To achieve a relative calibration of hydration measurements for two obsidian sources, a cross-source **comparison constant** is derived from the quotient or inverse quotient of the temporally equivalent hydration ratio. Hydration measurements obtained for one source may then be equated to hydration measurements of the other by multiplying by the given comparison constant. A case example

Table 18. Ratios of Temporally Equivalent Hydration Measurements According to Experiment Set

*Each ratio represents average measurements for 4-5 samples/source

Paired-Sources	Temp	Time	Set 1	Set 2	Set 3	Set 4
BORAX LAKE:	150	4	1:0.76	1:0.84	1:0.71	1:0.80
NAPA VALLEY	175	4	1:0.82	1:0.75	1:0.79	1:0.85
	200	1	1:0.77	1:0.84	1:0.79	1:0.79
	200	2	1:0.75	1:0.79	1:0.82	1:0.85
	200	4	1:0.84	1:0.75	1:0.69	1:0.90
	200	6	1:0.86	1:0.76	1:0.67	1:0.81
Total Average	1:0.79 +/- 0.06					
BORAX LAKE:	150	4	1:0.76	1:0.84	1:0.75	1:0.90
MT. KONOCTI	175	4	1:0.83	1:0.75	1:0.79	1:0.85
	200	1	1:0.77	1:0.80	1:0.79	1:0.79
	200	2	1:0.78	1:0.79	1:0.82	-
	200	4	1:0.82	1:0.69	1:0.69	1:0.90
	200	6	1:0.88	1:0.79	1:0.67	1:0.81
Total Average	1:0.79 +/- 0.06					
BORAX LAKE:	150	4	1:0.62	1:0.63	1:0.54	1:0.67
ANNADEL	175	4	1:0.66	1:0.50	1:0.65	1:0.68
	200	1	1:0.69	1:0.68	1:0.59	1:0.63
	200	2	1:0.63	1:0.54	1:0.61	1:0.68
	200	4	1:0.66	-	1:0.57	1:0.67
	200	6	1:0.66	1:0.52	1:0.50	1:0.62
Total Average	1:0.62 +/- 0.06					
NAPA VALLEY:	150	4	1:1.00	1:1.00	1:1.06	1:1.13
MT. KONOCTI	175	4	1:1.00	1:1.00	1:1.00	1:1.00
	200	1	1:1.00	1:0.95	1:1.00	1:1.00
	200	2	1:1.03	1:1.00	1:1.00	-
	200	4	1:0.98	1:0.93	1:1.00	1:1.00
	200	6	1:1.02	1:1.03	1:1.00	1:1.00
Total Average	1:1 +/- 0.04					
NAPA VALLEY:	150	4	1:0.81	1:0.75	1:0.76	1:0.83
ANNADEL	175	4	1:0.79	1:0.68	1:0.81	1:0.80
	200	1	1:0.89	1:0.81	1:0.74	1:0.79
	200	2	1:0.83	1:0.68	1:0.74	1:0.79
	200	4	1:0.79	-	1:0.83	1:0.75
	200	6	1:0.76	1:0.69	1:0.75	1:0.76
Total Average	1:0.78 +/- 0.05					
MT. KONOCTI:	150	4	1:0.81	1:0.75	1:0.72	1:0.74
ANNADEL	175	4	1:0.79	1:0.67	1:0.81	1:0.80
	200	1	1:0.89	1:0.85	1:0.74	1:0.79
	200	2	1:0.81	1:0.68	1:0.74	-
	200	4	1:0.80	-	1:0.83	1:0.75
	200	6	1:0.75	1:0.67	1:0.75	1:0.76
Total Average	1:0.77 +/- 0.06					

illustrates this procedure in a subsequent section.

Comparison constants for North Coast Ranges obsidians* (derived from temporally-equivalent hydration measurement ratios) are given in Table 19. The comparison constants obtained indicate, for example, that to equate Borax Lake measurements with Napa measurements, Borax Lake measurements are multiplied by 0.79. For the reverse, to equate Napa measurements with Borax Lake measurements, Napa readings are multiplied by 1.27.

Comparison constants may potentially enhance the relative dating technique. However, we suggest that comparison constants be used conscientiously. Importantly, it is cautioned that applications are necessarily restricted to compare samples of sources which have been exposed to similar temperature histories and conditions (i.e., reflecting parallel reactions). A definition of situations which satisfy this provision is inevitably vague given our current state of understanding regarding the affects of near-surface soil conditions to rates of hydration. Many archaeologists have observed reasonable hydration patternings and internal consistency for data found within sites and across sites exposed to moderate climates, which have left them comfortable with assuming insignificant effects for variations within these contexts. With temporizing acceptance of this premise, comparison constants may pragmatically enhance the analytical potential

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* Hughes (1988) has recently identified at least four distinctive geochemical varieties within the Coso volcanic field, Inyo County, southern California. He points out that intrasource geochemical differences may potentially cause hydration rate variability. Given these findings, it is important to qualify that the comparison constants presented reflect obsidian samples obtained from single parent specimens. Future investigations may reveal that intrasource geochemical variabilities exist for these North Coast Ranges obsidians.

Table 19. Comparison Contants** for North Coast Ranges Obsidians*

BL X 0.79 = N or vice versa N X 1.27 = BL
BL X 0.79 = K K X 1.27 = BL
BL X 0.62 = A A X 1.61 = BL
N X 1.00 = K K X 1.00 = N
N X 0.77 = A A X 1.30 = N
K X 0.77 = A A X 1.30 = K

* Borax Lake (BL); Napa Valley (N); Mt. Konoct (K); Annadel (A)

** These constants, although based on a very large sample size, should be regarded as provisional. Reactions of these sources at 120 C and in vapor-phase are currently underway. These conditions have produced better quality slides (better optical resolution for measuring), probably as a result of reducing problems associated with higher temperature experiments.

of hydration data when applied to site- and locality-specific contexts. Means are thus provided: to establish whether obsidians present at a site are reflective of coeval activities or different time periods; to allow the elucidation of diachronic shifts in source useage and intensity; to infer changes in obsidian access or procurement strategy; and to hypothesize regarding changes in socio-political relations with neighboring peoples.

Case Example

As a hypothetical case, assume an obsidian lithic scatter has been test excavated. A total of 500 flakes are recovered and geochemically traced. Ten percent of this population is selected and subjected to hydration analysis. A number of samples from each source represented (Borax Lake, Napa Valley, Mt. Konocti, and Annadel), are chosen to exact information regarding diachronic shifts in source useage.

Resulting hydration measurements are presented in raw form, as shown in Figure 2. Temporal comparisons can not be made at this point, as it is not known how these data are related. Figure 3 presents these same data adjusted for temporal comparison. A relative calibration is achieved by positioning Napa Valley, Mt. Konocti, and Annadel micron values in relation to Borax Lake micron values, using the comparison constants provided in Table 19.

Cross-source comparisons are now possible. It can be observed, for example, that a shift in use of obsidians occurs at one point in time. During the earliest period reflected (BL micron range ˜ 6.4-10.0), only Napa Valley, Mt. Konocti, and Annadel obsidians are represented. During the later period (BL micron range ˜ 3.2-6.2), Mt. Konocti and Annadel obsidians are no longer used. Napa Valley obsidian use tapers off, while use of Borax Lake obsidian is initiated.

The above observations can be used to articulate research questions and formulate hypotheses regarding possible prehistoric scenarios within local and regional contexts. It may be postulated that changes in access to obsidian occurred, or that changes in procurement strategy were made. Because obsidian was a highly valued resource, this material was often accessed or procured through the social networking between prehistoric peoples. Therefore, it follows, that shifts in obsidian use may reflect changes in relations between socio-political groups.

Inferences on the intensity of obsidian useage over time may also be made. As Bramlette (1989) points out, however, it is important that numbers of source-specific samples reflect proportions representative

Figure 2. Case Example: Raw Data

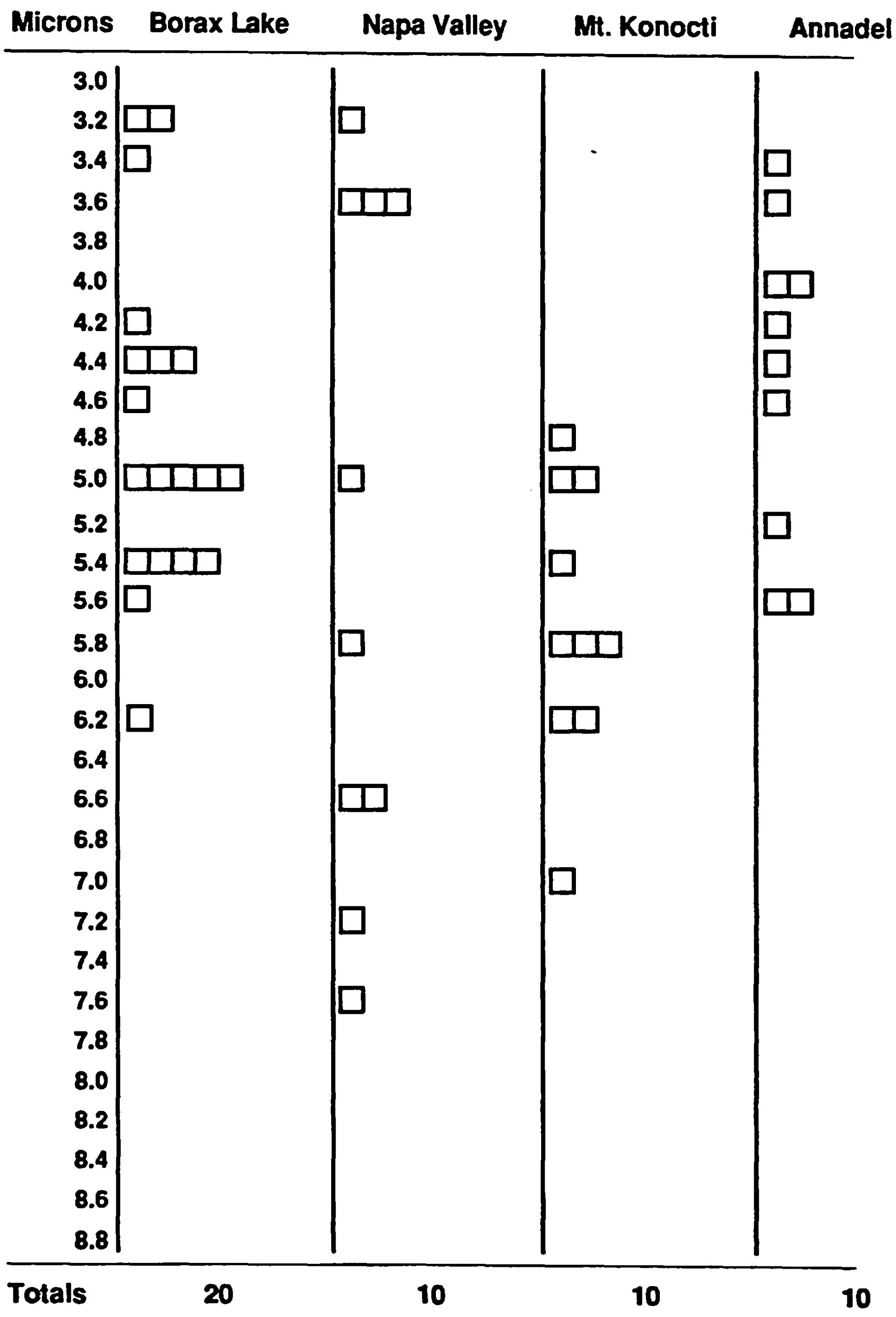
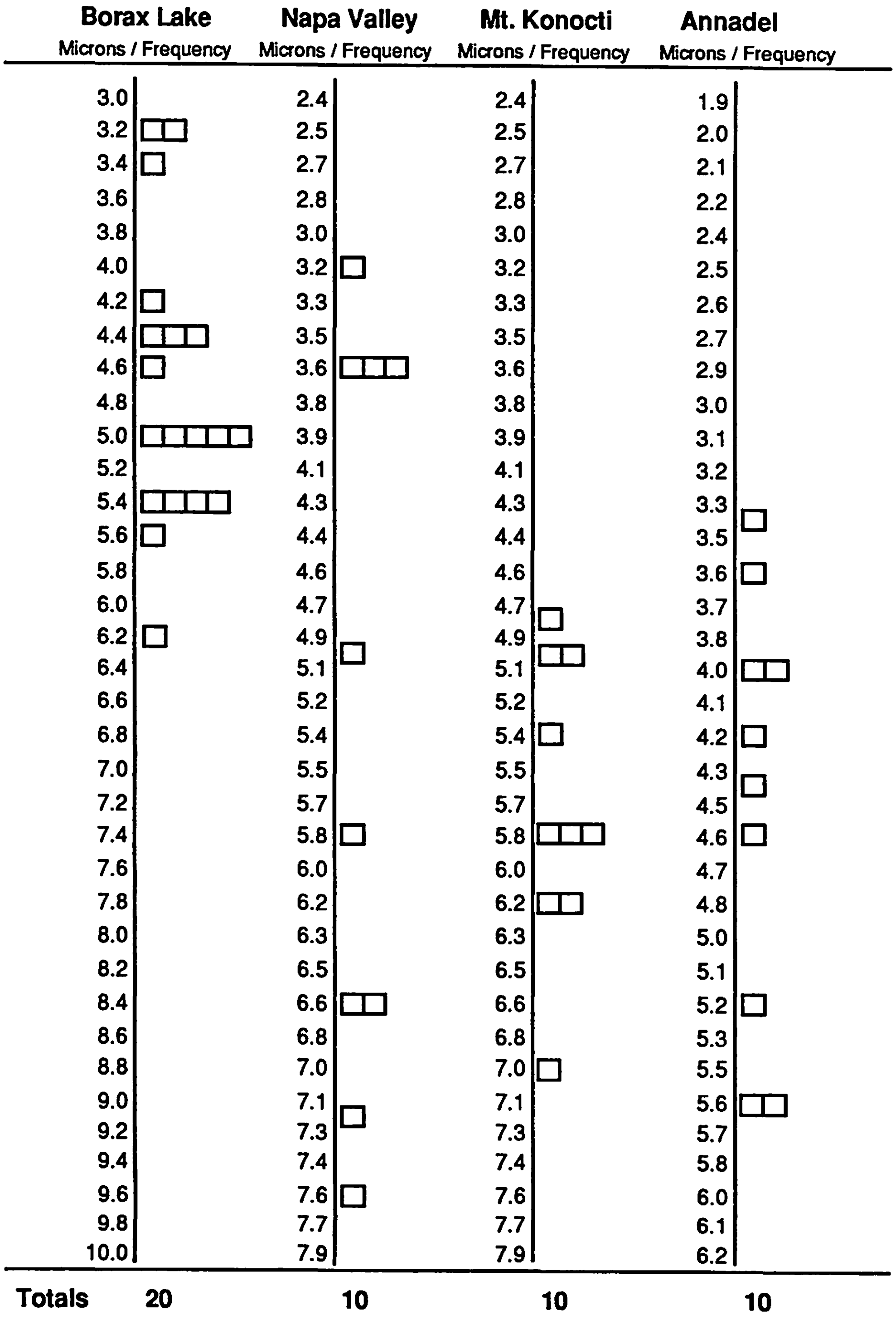


Figure 3. Case Example: A Relative Calibration *



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* Calibration achieved by equating Napa Valley, Mt. Knocti, and Annadel hydration measurements with Borax Lake using comparison constants.

of the entire population. As he notes, sampling selections seldom reflect true proportions of source distribution. Therefore, some sources can be over-represented, while others can be under-represented. To deal with this problem, Bramlette (1989) proposes a simple weighting scheme to reduce sampling bias.

It is hoped that this brief case example serves to illustrate the potential of cross-source comparison constants for enhancing the analytical abilities of relative dating.

Chapter 5

SUMMARY

As an initial objective of this thesis, a large body of literature on the physical-chemistry of glass surface reactions was examined with the intent to synthesize and integrate this information into the extant methodical and theoretical foundation for obsidian dating studies in archaeology. I found that glass scientists have made considerable advances in their understanding of glass weathering kinetics. In an overview of their findings, basic glass surface reactions (i.e., outward leaching of alkali ions, inward diffusion of water, silica dissolution, and precipitation) and factors which affect these reactions (i.e., solution pH, solution composition, SA/V, relative humidity, and temperature), were described. Further, a "classic" model and more recent discussions regarding models of glass weathering were presented.

Models

It is clear, from the studies examined, that glass weathering is a complex phenomenon, and that the current hydration model commonly held by archaeologists is probably too simplistic. A matter of vital importance to the dating of obsidian (in absolute age-estimates) is the rate expression most appropriately describing long-term glass weathering. Archaeologists have long debated this issue. Glass scientists apparently haven't resolved this point either. The "classic" model proposes a two-stage process, where a short term initial parabolic reaction rate ($t^{0.5}$) is observed, followed by a long-term linear rate of reaction. More recent models attempt to integrate

rate-limiting effects such as solution saturation and precipitation which may occur under certain conditions, apparently causing incongruent weathering ($t^{n<1}$).

Silica Dissolution

Silica dissolution, a reaction found to compete with hydration and therefore of concern for obsidian dating, was discussed in two respects: as it affects obsidian hydration under (1) natural and (2) experimental conditions. The significance of silica dissolution to obsidian hydrating under **natural** conditions appears to be uncertain, although findings by Bunker et al. (1983) are encouraging, showing that silica dissolution is negligible when compared to alkali leaching even when leaching kinetics are linear with time.

Under high temperature **experimental** conditions, such as those produced by Michels to develop hydration rate constants, there is strong evidence to suggest that significant dissolution occurs. Revised experimental designs have been formulated in order to combat this affect: (1) reacting glasses in silica-saturated solutions at temperatures below 180 ^{o}C (Stevenson and Scheetz in press); and (2) reacting in vapor rather than liquid-phase (Bates et al. 1988).

Factors Affecting Glass Reactions

Because many factors have been shown to affect glass surface reactions, their potential significance on rates of hydration under field and experimental conditions is naturally of concern. It was determined that to fully assess implications for obsidian dating in its absolute chronometric capacity, the extent to which specific variables affect rates of hydration (individually and in combiniation) need to be quantified. I suggested, in addition, that field measurements be taken of specific variables (e.g., soil moisture, pH, SA/V, groundwater composition, groundwater flow rate, and relative humidity of soil air) to determine the expected ranges of variations for near-surface soils characterizing archaeological sites. Parametric studies on glass reactions could perhaps then be utilized to estimate, with greater confidence, the extent to which each variable affects hydration within this defined context (expected field conditions).

Accelerated Hydration Experiments

As a further objective of this thesis, accelerated hydration experiments were conducted to investigate applications for both absolute and relative dating. These experiments indicated that test results are reproducible if test conditions are held constant. Variability observed in hydration development between experiment sets was attributed to differences in SA/V and solution composition.

Problems were encountered when reacting obsidian at temperatures greater than 200 °C. These samples yielded hydration rims poorly defined, difficult or impossible to measure, and covered with a gritty residue attributed to silica dissolution. In an attempt to avoid dissolution problems, samples were reacted in silica-saturated solutions. Results showed that significantly larger hydration rims were developed during these tests, supporting the suggestion that silica-saturated solutions inhibit surface dissolution.

These experiments and the literature reviewed indicate that hydration rate constants (derived from high-temperature essentially closed-system tests) are condition-specific. Therefore, the appropriateness of applying such rate constants to field conditions was questioned. This issue, in conjunction the with lack of agreement on a rate expression to best describe long-term weathering, left an endorsement of the application of accelerated hydration experiments for **absolute** dating difficult to justify.

The use of data generated from accelerated experiments for **relative** dating was consequently explored. By developing a reliable means to make cross-source comparisons, the relative dating approach could be enhanced. It was reasoned that if depths of hydration, developed for source-specific obsidians over equivalent lengths and conditions of exposure, could be equated, relative calibrations could be achieved. Accelerated hydration experiments were considered an ideal means to study the co-variation of hydration development of obsidians over time given the certainty of temporal equivalency and constant temperature history.

Test results suggested that the relationship between co-hydrating obsidians is consistent regardless of reaction time or condition of exposure. It was proposed that temporally equivalent hydration measurement ratios, when expressed as quotients or inverse quotients, can serve as cross-source comparison constants, enabling the relative calibration of hydration measurements. Applications can be made to compare samples of sources exposed to similar temperature histories and conditions, which in a temporizing action, may be considered as data found in site- and locality-specific contexts of moderate climate. These comparison constants allow the temporal ordering of co-occuring obsidians from different geochemical sources without resorting to calibration in calendar years. Means are thus provided: to establish whether obsidians present at a site are reflective of coeval activities or different time periods; to allow the elucidation of diachronic shifts in source useage and intensity; to infer changes in obsidian access or procurement strategy; and to hypothesize regarding changes in socio-political relations with neighboring peoples.

Although it was concluded that the absolute dating of obsidian remains less than secure, due to the uncertainties identified during the course of this thesis, this should not be cause for discouragement. It is hoped that this assessment is taken with positive spirit and is regarded as encouragement towards a new rigour. The nuclear waste management industry (having funding, instrumentation, and manpower) is currently conducting a massive and intensive research program on the weathering of glass on a scale which archaeologists could never dream of. We have a unique and unparalled opportunity to gain from their findings, and improve our abilities to date obsidian.

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APPENDIX:
MEASUREMENTS OF INDUCED OBSIDIAN HYDRATION

Thin Section Preparation and Measurement Technique

Preparations were completed at the Sonoma State University Obsidian Hydration Laboratory, an adjunct of the Anthropological Studies Center, Department of Anthropology. A description of these procedures is taken from Origer (1987).

Obsidian specimens were examined in order to locate two or more surfaces that would yield edges perpendicular to the microslide to which they were adhered when preparation was completed. After location of such a locus, two parallel cuts were made with a water-cooled diamond impregnated circular saw blade. The result of the cut normally was a pie-shaped wedge with a thickness of approximately one millimeter.

The wedge was broken free of the specimen and mounted with heat-softened Lakeside cement to a pre-numbered microslide. Reduction of the thickness of the wedge was accomplished by hand-held grinding with a slurry of #600 corundum abrasive on a glass plate. Grinding motion followed a figure-eight pattern to insure even wear. Initial grinding removed approximately 2/5 of the wedge thickness, eliminating microchips caused by the saw blade during the cutting process. The slide was reheated, the Lakeside cement softened, and the wedge inverted. The newly exposed surface was then ground until a thickness of 30-50 microns was attained. The final thickness was measured by the "touch" technique whereby a finger was run over the glass surface onto the wedge and the difference estimated by feel. A second technique employed for determining the proper final thin-section thickness is termed the "transparency" test whereby the slide is held against a strong light source to observe whether passage of light is readily allowed.

When the desired thickness of the thin-section was attained, the slide was again heated, which cleared the obsidian wedge perimeter of corundum abrasive and scratches in the Lakeside cement. A glass coverslip was affixed over the wedge to the microslide with piccolyte, a mounting media having properties similar to those of Canada balsam.

Examination and measurement of the hydration bands was accomplished with an American Optical petrographic microscope. Measurement of hydration band thickness was made with a Bausch and Lomb 12.5 power filar micrometer eyepiece, and a 45 power objective. Five to six measurements were taken at up to six loci on each specimen. All completed microslides and their respective hydration band measurements are curated at the Obsidian Hydration Laboratory, Anthropological Studies Center, Sonoma State University.

Explanations for Abbreviations and Phrases used on the following pages:

A = Annadel obsidian
bev or beveled = specimen mounted or ground at angle
BL = Borax Lake obsidian
C = degrees Centigrade
d = day
dh = diffuse hydration
difficult = hydration band difficult to measure
discont. = discontinuous band
double band = a specimen exhibiting two hydration band thicknesses
dw = deionized water
faint = faint hydration band
gen. poor = generally poor resolution
Group Mean = the average hydration measurement for group of samples
Indiv.Mean = the average hydration measurement obtained for one specimen
K = Mt. Konocti obsidian
N = Napa Valley obsidian
not meas = hydration was not measurable due to unidentified problems
nvb = no visible band
one side only = only one of two edges possible exhibits measurable hyd.
poor = (regarding preparation of slide)
res = resolution
sd = standard deviation
slightly diffuse = hydration band measurable, but definition not best
step fractured = (regarding thin-section preparation)
too thin = (regarding thin-section preparation)
variable band = hydration band exhibiting varying thickness
weathered = hydration edge appears to be deteriorating,
difficult to define

MEASUREMENTS OF INDUCED OBSIDIAN HYDRATION

Experiment: SET 1
Temperature: 150 C
Reaction Time: 4 d
Solution: dw
Initial pH:
Final pH:

OH Lab #	Readings (microns)					Indiv.Mean	Group Mean	sd	Source	Remarks
5A4	2.1	2.1	2.1	2.1	2.2	2.1			BL	
B	2.0	2.0	2.1	2.1	2.2	2.1				
C	2.0	2.0	2.1	2.2	2.2	2.1				
D	2.1	2.1	2.2	2.2	2.2	2.2				thin
E	2.1	2.1	2.1	2.1	2.2	2.1	2.1	.03		
6A4	1.6	1.6	1.8	1.8	1.8	1.7			N	
B										nvb
C	1.5	1.5	1.6	1.6	1.8	1.6				
D	1.4	1.5	1.5	1.6	1.6	1.5				
E	1.5	1.5	1.5	1.6	1.6	1.5	1.6	.07		
7A4									K	nvb
B	1.5	1.5	1.6	1.6	1.6	1.6				
C	1.6	1.6	1.6	1.8	1.8	1.7				
D	1.5	1.5	1.5	1.6	1.6	1.5				
E	1.5	1.5	1.5	1.6	1.6	1.5	1.6	.07		
8A4	1.2	1.3	1.3	1.3	1.3	1.3			A	
B	1.3	1.4	1.4	1.4	1.4	1.4				
C	1.3	1.3	1.4	1.4	1.4	1.4				
D	1.3	1.3	1.3	1.4	1.4	1.3				
E	1.2	1.3	1.4	1.4	1.4	1.3	1.3	.04		

Lab Accession No.: 87-H594
Slide Preparer: K. Tremaine
Reader: T. Origer
Date: Jan 88

Comments:

MEASUREMENTS OF INDUCED OBSIDIAN HYDRATION

Experiment:	SET 1
Temperature:	175 C
Reaction Time:	4 d
Solution:	dw
Initial pH:	
Final pH:	

OH Lab #	Readings (microns)					Indiv.Mean	Group Mean	sd	Source	Remarks
9A4	3.4	3.6	3.6	3.6	3.6	3.6			BL	faint
B	3.5	3.5	3.6	3.6	3.7	3.6				
C	3.5	3.5	3.5	3.5	3.6	3.5				
D	3.4	3.5	3.5	3.6	3.7	3.5				
E	3.5	3.5	3.5	3.6	3.6	3.5	3.5	.05		
10A4	2.9	2.9	3.0	3.0	3.1	3.0			N	
B										dh
C	2.9	2.9	2.9	3.0	3.0	2.9				
D	2.7	2.7	2.7	2.9	3.0	2.8				
E	2.9	3.0	3.0	3.1	3.2	3.0	2.9	.10		
11A4	2.7	2.9	2.9	3.0	3.0	2.9			K	
B	2.7	2.9	2.9	3.0	3.0	2.9				
C	2.7	2.7	2.9	3.1	3.1	2.9				
D	2.7	2.7	2.7	3.0	3.0	2.8				
E	2.7	2.9	3.0	3.0	3.0	2.9	2.9	.04		
12A4	2.2	2.2	2.3	2.3	2.4	2.3			A	
B	2.2	2.2	2.3	2.3	2.3	2.3				
C	2.1	2.2	2.3	2.3	2.4	2.3				
D	2.2	2.3	2.3	2.3	2.3	2.3				
E	2.1	2.2	2.3	2.3	2.3	2.2	2.3	.04		

Lab Accession No.:	87-H594
Slide Preparer:	K. Tremaine
Reader:	T. Origer
Date:	Jan 88

Comments:

MEASUREMENTS OF INDUCED OBSIDIAN HYDRATION

Experiment: SET 1
Temperature: 200 C
Reaction Time: 1 d
Solution: dw
Initial pH:
Final pH:

OH Lab #	Readings (microns)					Indiv.Mean	Group Mean	sd	Source	Remarks
1A1	3.4	3.4	3.5	3.5	3.6	3.5			BL	slightly diffuse
B	3.2	3.4	3.4	3.5	3.6	3.4				faint
C										dh
D	3.4	3.6	3.6	3.6	3.6	3.6				
E	3.2	3.4	3.4	3.5	3.6	3.4	3.5	.10		
2A1	2.8	2.8	2.8	2.9	2.9	2.8			N	
B	2.6	2.6	2.7	2.7	2.7	2.7				
C	2.7	2.7	2.7	2.7	2.9	2.7				
D	2.6	2.6	2.7	2.7	2.8	2.7				
E	2.7	2.8	2.8	2.8	2.9	2.8	2.7	.05		
3A1	2.6	2.7	2.8	2.8	2.8	2.7			K	
B	2.6	2.6	2.7	2.7	2.7	2.7				
C	2.6	2.6	2.6	2.6	2.7	2.6				
D	2.7	2.7	2.8	2.8	2.8	2.8				
E	2.6	2.8	2.8	2.9	2.9	2.8	2.7	.08		
4A1	2.2	2.3	2.4	2.4	2.4	2.3			A	
B	2.2	2.2	2.3	2.4	2.4	2.3				
C	2.3	2.4	2.4	2.5	2.5	2.4				
D	2.3	2.4	2.4	2.5	2.5	2.4				
E	2.3	2.3	2.4	2.4	2.5	2.4	2.4	.05		

Lab Accession No.: 87-H594
Slide Preparer: K. Tremaine
Reader: T. Origer
Date: Jan 88

Comments:

MEASUREMENTS OF INDUCED OBSIDIAN HYDRATION

Experiment: SET 1
Temperature: 200 C
Reaction Time: 2 d
Solution: dw
Initial pH:
Final pH:

OH Lab #	Readings (microns)					Indiv.Mean	Group Mean	sd	Source	Remarks
1A2	3.9	3.9	4.0	4.0	4.0	4.0			BL	discont. band
B	3.9	4.0	4.0	4.0	4.1	4.0				faint
C	3.9	4.0	4.0	4.1	4.2	4.0				very faint
D	3.9	3.9	3.9	4.0	4.0	3.9				discont., faint
E	3.8	3.9	4.0	4.0	4.2	4.0	4.0	.04		best band in gr
2A2	2.9	2.9	3.0	3.0	3.0	3.0			N	
B	2.9	2.9	3.0	3.0	3.1	3.0				
C	2.9	2.9	3.0	3.2	3.2	3.0				
D	3.0	3.1	3.1	3.1	3.2	3.1				
E	3.0	3.0	3.0	3.1	3.1	3.0	3.0	.04		
3A2	3.1	3.1	3.2	3.2	3.2	3.2			K	
B	3.0	3.0	3.0	3.1	3.2	3.1				
C	2.9	2.9	2.9	3.0	3.0	2.9				
D	2.9	2.9	3.0	3.1	3.2	3.0				
E	3.1	3.1	3.1	3.1	3.2	3.1	3.1	.11		
4A2	2.5	2.5	2.6	2.6	2.7	2.6			A	
B	2.4	2.4	2.5	2.5	2.5	2.5				
C	2.5	2.5	2.5	2.5	2.5	2.5				
D	2.3	2.4	2.5	2.5	2.5	2.4				
E	2.5	2.5	2.6	2.7	2.7	2.6	2.5	.08		

Lab Accession No.: 87-H594
Slide Preparer: K. Tremaine
Reader: T. Origer
Date: Jan 88

Comments:

MEASUREMENTS OF INDUCED OBSIDIAN HYDRATION

Experiment:	SET 1
Temperature:	200 C
Reaction Time:	4 d
Solution:	dw
Initial pH:	
Final pH:	

OH Lab #	Readings (microns)					Indiv.Mean	Group Mean	sd	Source	Remarks
1A4	5.5	5.5	5.5	5.6	5.6	5.5			BL	
B										dh
C	5.5	5.6	5.6	5.7	5.7	5.6				
D	5.5	5.6	5.6	5.6	5.6	5.6				
E	5.5	5.5	5.6	5.7	5.8	5.6	5.6	.04		
2A4	4.6	4.7	4.7	4.7	4.8	4.7			N	
B	4.6	4.6	4.7	4.7	4.7	4.7				
C	4.6	4.6	4.7	4.7	4.8	4.7				
D	4.5	4.6	4.7	4.8	4.8	4.7				
E	4.6	4.7	4.7	4.7	4.7	4.7	4.7	.01		
3A4	4.6	4.7	4.7	4.8	4.8	4.7			K	
B	4.4	4.5	4.5	4.6	4.6	4.5				
C	4.5	4.5	4.6	4.6	4.7	4.6				
D	4.4	4.5	4.6	4.7	4.7	4.6				
E	4.6	4.6	4.7	4.8	4.8	4.7	4.6	.09		
4A4	3.6	3.7	3.8	3.8	3.8	3.7			A	
B	3.7	3.8	3.8	3.8	3.8	3.8				
C	3.6	3.7	3.8	3.8	3.8	3.7				
D	3.6	3.6	3.7	3.8	3.8	3.7				
E	3.7	3.7	3.7	3.8	3.8	3.7	3.7	.03		

Lab Accession No.:	87-H594
Slide Preparer:	K. Tremaine
Reader:	T. Origer
Date:	Jan 88

Comments:

MEASUREMENTS OF INDUCED OBSIDIAN HYDRATION

Experiment:	SET 1
Temperature:	200 C
Reaction Time:	6 d
Solution:	dw
Initial pH:	
Final pH:	

OH Lab #	Readings (microns)					Indiv.Mean	Group Mean	sd	Source	Remarks
1A6	5.7	5.8	5.8	5.8	5.8	5.8			BL	
B	5.8	5.8	5.8	5.8	5.8	5.8				
C	6.0	6.0	6.2	6.3	6.3	6.2				
D	6.0	6.0	6.0	6.0	6.0	6.0				
E	5.8	5.8	5.8	5.9	6.0	5.9	5.9	.16		
2A6	4.8	4.9	5.1	5.2	5.2	5.0			N	
B	4.9	5.1	5.1	5.2	5.2	5.1				
C	4.9	4.9	5.1	5.1	5.4	5.1				
D	4.9	5.1	5.2	5.3	5.3	5.2				
E	5.1	5.1	5.1	5.3	5.3	5.2	5.1	.06		faint
3A6	5.2	5.2	5.2	5.2	5.3	5.2			K	
B	5.1	5.2	5.2	5.3	5.4	5.2				
C	5.1	5.1	5.2	5.3	5.3	5.2				
D	5.2	5.3	5.3	5.3	5.3	5.3				
E	4.9	5.1	5.1	5.2	5.2	5.1	5.2	.07		
4A6	4.0	4.0	4.1	4.1	4.1	4.1			A	gen. poor, faint
B	3.8	3.8	3.8	4.0	4.0	3.9				gen. poor, faint
C	3.8	3.8	4.0	4.0	4.1	3.9				gen. poor, faint
D	3.6	3.6	3.6	3.6	3.7	3.6				gen. poor, faint
E	3.6	3.6	3.8	3.8	4.0	3.8	3.9	.17		gen. poor, faint

Lab Accession No.:	87-H594
Slide Preparer:	K. Tremaine
Reader:	T. Origer
Date:	Jan 88

Comments:

MEASUREMENTS OF INDUCED OBSIDIAN HYDRATION

Experiment:	SET 1
Temperature:	225 C
Reaction Time:	4 d
Solution:	dw
Initial pH:	
Final pH:	

OH Lab #	Readings (microns)					Indiv.Mean	Group Mean	sd	Source	Remarks
13A4									BL	dh
B										dh
C										dh
D										dh
E										dh
14A4	6.0	6.0	6.2	6.2	6.3	6.1			N	faint
B	6.2	6.2	6.5	6.5	6.6	6.4				dh
C	6.2	6.4	6.5	6.5	6.6	6.4				too thin
D	5.9	5.9	5.9	6.0	6.2	6.0				faint
E							6.2	.21		dh
15A4	5.4	5.4	5.6	5.7	5.8	5.6			K	faint
B	5.6	5.6	5.6	5.7	5.8	5.7				faint
C										dh
D										dh
E							5.7	.07		dh
16A4	4.2	4.3	4.3	4.3	4.8	4.4			A	
B	3.2	3.3	3.5	3.5	3.6	3.4				
C	3.2	3.5	3.5	3.6	3.6	3.5				
D										dh
E							3.8	.55		dh

Lab Accession No.:	87-H594
Slide Preparer:	K. Tremaine
Reader:	T. Origer
Date:	Jan 88

Comments:

MEASUREMENTS OF INDUCED OBSIDIAN HYDRATION

Experiment:	SET 1
Temperature:	250 C
Reaction Time:	4 d
Solution:	dw
Initial pH:	5.9
Final pH:	8.7

OH Lab #	Readings (microns)	Indiv.Mean	Group Mean	sd	Source	Remarks
17A4					BL	dh
B						nvb, thin
C						dh
D						too thin
E						dh
18A4					N	dh
B						dh
C						dh
D						dh
E						dh
19A4					K	dh
B						dh
C						dh
D						dh
E						dh
20A4					A	dh
B						dh
C						dh
D						dh
E						dh

Lab Accession No.:	87-H594
Slide Preparer:	K. Tremaine
Reader:	T. Origer
Date:	Jan 88

Comments:

MEASUREMENTS OF INDUCED OBSIDIAN HYDRATION

Experiment:	SET 2
Temperature:	150 C
Reaction Time:	4 d
Solution:	dw
Initial pH:	6.2
Final pH:	7.0

OH Lab #	Readings (microns)					Indiv.Mean	Group Mean	sd	Source	Remarks
25A4	1.9	2.0	2.0	2.0	2.0	2.0			BL	
B	1.8	1.9	1.9	1.9	2.0	1.9				
C	1.8	1.9	1.9	2.0	2.0	1.9				
D	1.9	1.9	1.9	1.9	2.0	1.9	1.9	.03		
26A4	1.6	1.6	1.6	1.8	1.8	1.7			N	
B	1.5	1.5	1.6	1.6	1.8	1.6				
C	1.5	1.5	1.5	1.6	1.6	1.5				
D	1.5	1.6	1.6	1.8	1.8	1.7	1.6	.06		
27A4	1.6	1.6	1.6	1.8	1.8	1.7			K	
B	1.5	1.5	1.6	1.6	1.8	1.6				
C	1.5	1.6	1.6	1.6	1.6	1.6				
D	1.5	1.5	1.6	1.8	1.8	1.6	1.6	.05		
28A4	1.1	1.1	1.2	1.2	1.2	1.2			A	
B	1.1	1.1	1.2	1.2	1.3	1.2				
C	1.0	1.1	1.1	1.2	1.3	1.1				1st band
	1.6	1.6	1.8	1.9	1.9	1.8				2nd band
D	1.1	1.1	1.1	1.2	1.3	1.2	1.2	.02		

Lab Accession No.:	87-H594
Slide Preparer:	K. Tremaine
Reader:	T. Origer
Date:	Jan 88

Comments:

MEASUREMENTS OF INDUCED OBSIDIAN HYDRATION

Experiment: SET 2
Temperature: 175 C
Reaction Time: 4 d
Solution: dw
Initial pH: 6.52
Final pH: 6.70

OH Lab #	Readings (microns)					Indiv.Mean	Group Mean	sd	Source	Remarks
29A4	14.0	14.0	14.0	14.5	15.0	14.3			BL	faint
B	14.0	14.0	14.5	14.5	15.0	14.4				faint
C	14.0	14.0	14.5	14.5	14.5	14.3				faint
D	14.0	14.0	14.0	15.0	15.0	14.4	3.15	.15		
30A4	10.5	10.5	11.0	11.0	11.5	10.9			N	
B	10.0	10.0	11.0	11.5	11.5	10.8				
C	10.5	10.5	11.0	11.0	11.0	10.8				
D	10.5	10.5	10.5	10.5	11.5	10.7	2.35	.08		
31A4	10.0	10.0	10.5	11.0	11.0	10.5			K	
B	10.5	10.5	10.5	11.0	11.0	10.7				
C	10.0	10.5	10.5	11.0	11.5	10.7				
D	10.5	10.5	10.5	11.0	11.0	10.7	2.35	.10		
32A4	7.0	7.0	7.5	7.5	8.0	7.4			A	
B	7.0	7.0	7.0	7.0	7.5	7.1				
C	7.5	7.5	7.5	8.0	8.0	7.7				
D	6.5	7.0	7.0	7.5	7.5	7.1	1.55	.29		

Lab Accession No.: 87-H594
Slide Preparer: K. Tremaine
Reader: T. Origer
Date: Jan 88

Comments:

MEASUREMENTS OF INDUCED OBSIDIAN HYDRATION

Experiment: SET 2
Temperature: 200 C
Reaction Time: 1 d
Solution: dw
Initial pH: 5.8
Final pH: 8.0

OH Lab #	Readings (microns)					Indiv.Mean	Group Mean	sd	Source	Remarks
21A1	2.4	2.4	2.5	2.5	2.5	2.5			BL	slightly diffuse
B										dh, faint
C										dh, faint
D							2.5	.00		too thin
22A1									N	too thin
B										dh, thin
C	1.8	1.8	2.1	2.1	2.1	2.0				faint
D	2.1	2.1	2.1	2.2	2.3	2.2	2.1	.07		faint
23A1	1.8	1.8	1.8	1.9	2.1	1.9			K	faint
B										dh, faint
C	1.9	1.9	2.1	2.1	2.1	2.0				dh, faint
D	1.9	2.1	2.1	2.1	2.2	2.1	2.0	.10		dh, faint
24A1	1.6	1.6	1.7	1.8	1.8	1.7			A	dh, faint
B										nvb
C										dh, faint
D							1.7			nvb

Lab Accession No.: 87-H594
Slide Preparer: K. Tremaine
Reader: T. Origer
Date: Jan 88

Comments:

MEASUREMENTS OF INDUCED OBSIDIAN HYDRATION

Experiment: SET 2
Temperature: 200 C
Reaction Time: 2 d
Solution: dw
Initial pH: 5.8
Final pH: 7.8

OH Lab #	Readings (microns)					Indiv.Mean	Group Mean	sd	Source	Remarks
21A2	2.7	2.7	2.7	2.8	2.8	2.7			BL	
B	2.8	2.9	2.9	3.0	3.1	2.9				
C	2.6	2.7	2.7	2.7	2.8	2.7				
D							2.8	.12		too thin
22A2	2.1	2.2	2.2	2.3	2.4	2.2			N	
B										too thin
C	2.2	2.2	2.2	2.3	2.3	2.2				
D							2.2	.00		poor
23A2	2.1	2.2	2.2	2.3	2.5	2.3			K	
B										too thin
C										too thin
D	1.9	2.0	2.0	2.0	2.1	2.0	2.2	.21		
24A2	1.4	1.5	1.6	1.6	1.6	1.5			A	
B										too thin
C	1.4	1.5	1.6	1.6	1.6	1.5				
D							1.5	.00		too thin

Lab Accession No.: 87-H594
Slide Preparer: K. Tremaine
Reader: T. Origer
Date: Jan 88

Comments:

MEASUREMENTS OF INDUCED OBSIDIAN HYDRATION

Experiment:	SET 2
Temperature:	200 C
Reaction Time:	4 d
Solution:	dw
Initial pH:	5.2
Final pH:	7.8

OH Lab #	Readings (microns)					Indiv.Mean	Group Mean	sd	Source	Remarks
21A4									BL	too thin
B	3.6	3.6	3.7	3.7	3.7	3.7				
C	3.4	3.4	3.5	3.6	3.8	3.5				faint
D	3.5	3.6	3.6	3.6	3.6	3.6	3.6	.10		faint
22A4	2.6	2.7	2.7	2.7	2.8	2.7			N	
B	2.5	2.6	2.7	2.7	2.8	2.7				
C										
D	2.5	2.6	2.7	2.7	2.7	2.6	2.7	.06		
23A4									K	poor
B	2.4	2.4	2.5	2.5	2.5	2.5				
C	2.4	2.5	2.5	2.5	2.5	2.5				
D	2.4	2.6	2.7	2.7	2.8	2.6	2.5	.06		
24A4									A	poor
B										poor
C										poor
D										poor

Lab Accession No.:	87-H594
Slide Preparer:	K. Tremaine
Reader:	T. Origer
Date:	Jan 88

Comments:

MEASUREMENTS OF INDUCED OBSIDIAN HYDRATION

Experiment:	SET 2
Temperature:	200 C
Reaction Time:	6 d
Solution:	dw
Initial pH:	6.1
Final pH:	8.5

OH Lab #	Readings (microns)						Indiv.Mean	Group Mean	sd	Source	Remarks
21A6	4.0	3.9	4.1	4.3	4.3	4.1	4.1			BL	thin
B	4.0	3.9	4.1	3.9	4.0	4.1	4.0				
C	4.5	4.4	4.4	4.3	4.3	4.4	4.4				
D	3.9	4.2	4.0	4.1	4.0	4.1	4.1	4.2	.17		
22A6	3.0	3.2	3.1	2.9	3.2	3.1	3.1			N	
B	3.2	3.0	3.1	3.2	3.1	3.2	3.1				
C	3.3	3.2	3.0	3.2	3.0	3.2	3.2				
D	3.5	3.2	3.6	3.0	3.2	3.0	3.3	3.2	.10		thin
23A6	3.4	3.5	3.4	3.5	3.2	3.2	3.4			K	
B	3.2	3.2	3.2	3.5	3.6		3.3				
C	3.2	3.1									thin
D	3.4	3.2	3.1	3.2			3.2	3.3	.10		thin
24A6	1.7	1.9	1.9	2.1						A	difficult
B	2.1	1.8	1.9	2.1	1.9		2.0				difficult
C	2.5	2.6	2.3	2.5	2.6	2.6	2.5				difficult
D	1.8	2.2	2.2	2.0	2.1	2.3	2.1	2.2	.26		difficult

Lab Accession No.:	87-H594
Slide Preparer:	K. Tremaine
Reader:	K. Tremaine
Date:	July 88

Comments:

MEASUREMENTS OF INDUCED OBSIDIAN HYDRATION

Experiment: SET 3
Temperature: 150 C
Reaction Time: 4 d
Solution: dw
Initial pH: 5.9
Final pH: 8.5

OH Lab #	Readings (microns)						Indiv.Mean	Group Mean	sd	Source	Remarks
86A4	2.2	2.5	2.4	2.2	2.4	2.3	2.3			BL	
B	2.4	2.5	2.3	2.4	2.4	2.5	2.4				
C	2.5	2.5	2.5	2.4	2.4	2.5	2.5				
D	2.5	2.2	2.4	2.4	2.3	2.5	2.4				bev one side
E	2.2	2.4	2.2	2.4	2.2	2.5	2.3	2.4	.08		beveled
87A4	1.6	1.6	1.6	1.6	1.7		1.6			N	
B	1.7	1.8	1.8	1.9	1.9		1.8				
C	1.7	1.7	1.7	1.7	1.7		1.7				beveled
D	1.4	1.4	1.5	1.6	1.7		1.5				beveled
E	1.6	1.6	1.7	1.7	1.8		1.7	1.7	.11		
88A4	2.2	1.9	1.6	1.8	1.6	1.8	1.8			K	
B	1.7	1.9	1.7	1.9	1.9	1.7	1.8				
C	1.9	1.9	1.9	1.8	1.7	1.8	1.8				
D	1.8	1.6	1.7	1.9	1.8	1.9	1.8				
E	1.9	1.8	2.2	2.1	1.8	2.1	2.0	1.8	.09		
89A4	1.3	1.3	1.3	1.3	1.3		1.3			A	beveled
B	1.3	1.3	1.3	1.3	1.4		1.3				beveled
C	1.4	1.4	1.4	1.4	1.7		1.5				
D	1.2	1.2	1.3	1.3	1.3		1.3				
E	1.3	1.3	1.3	1.3	1.4		1.3	1.3	.04		

Lab Accession No.: 87-H594
Slide Preparer: Kim Tremaine
Reader: Kim Tremaine
Date: Aug 88

Comments: Difficulties measuring Napa and Annadel specimens

MEASUREMENTS OF INDUCED OBSIDIAN HYDRATION

Experiment: SET 3
Temperature: 175 C
Reaction Time: 4 d
Solution: dw
Initial pH: 6.2
Final pH: 8.6

OH Lab #	Readings (microns)						Indiv.Mean	Group Mean	sd	Source	Remarks
90A4	3.3	3.6	3.2	3.2	3.6	3.2	3.4			BL	
B	3.6	3.4	3.3	3.4	3.2	3.4	3.4				
C	3.6	3.7	3.3	3.6	3.4	3.3	3.5				
D	3.4	3.3	3.4	3.3	3.4	3.4	3.4				
E	3.2	3.3	3.3	3.6	3.2	3.4	3.3	3.4	.07		
91A4	2.5	2.7	2.7	2.6	2.4	2.5	2.6			M	
B	2.6	2.7	2.5	2.7	2.8	2.5	2.6				
C	2.7	2.8	2.5	2.8	2.7	2.6	2.7				
D	2.8	2.7	2.7	2.7	2.5	2.8	2.7				
E	2.9	2.7	2.6	2.6	2.7	2.6	2.7	2.7	.05		
92A4	2.7	2.5	2.8	2.9	2.7	2.7	2.7			K	
B	2.9	2.6	2.6	2.5	2.7	2.9	2.7				
C	2.9	2.9	2.6	2.8	2.8	2.6	2.8				
D	2.6	2.5	2.7	2.6	2.9	2.8	2.7				
E	2.8	2.8	2.8	2.7	2.9	2.7	2.8	2.7	.05		
93A4	2.3	2.1	2.2	2.2	1.9	1.6	2.1			A	
B	2.1	2.2	2.3	2.2	2.1	2.2	2.2				
C	2.3	2.2	2.2								poor res
D	1.9	2.2	1.9	2.1	2.3	2.1	2.1				
E	2.2	2.3	2.3	1.9	2.3	2.2	2.2	2.2	.06		

Lab Accession No.: 87-H594
Slide Preparer: Kim Tremaine
Reader: Kim Tremaine
Date: Aug 88

Comments:

MEASUREMENTS OF INDUCED OBSIDIAN HYDRATION

Experiment: SET 3
Temperature: 200 C
Reaction Time: 1 d
Solution: dw
Initial pH: ?
Final pH: 8.1

OH Lab #	Readings (microns)						Indiv.Mean	Group Mean	sd	Source	Remarks
81A1	2.9	2.8	2.8	3.0	2.6	2.9	2.8			BL	
B	2.9	2.9	2.9	3.0	3.0		2.9				difficult
C	2.9	3.0	3.0	3.1	2.8	3.1	3.0				
D	2.8	2.9	2.6	3.1	3.1	2.9	2.9				
E	2.8	2.8	3.0	3.0	2.8	2.9	2.9	2.9	.07		
83A1	2.2	2.2	2.2	2.2	2.4	2.4	2.3			K	
B	2.3	2.0	2.1	2.1	2.2	2.2	2.2				difficult
C	2.3	2.2	2.4	2.5	1.9	2.3	2.3				bev
D	2.2	2.4	2.2	2.2	2.1	2.4	2.3				
E	2.2	2.1	2.4	2.4	2.2	2.3	2.3	2.3	.04		bev
84A1	1.6	1.7	1.7	1.8	1.8		1.7			A	poor
B	1.6	1.6	1.6	1.7	1.8		1.7				poor, bev
C	1.6	1.7	1.7	1.7	1.8		1.7				poor, bev
D	1.8	1.7	1.6	1.7	1.7	1.6	1.7				step-fractured
E	1.4	1.6	1.6	1.6	1.7		1.6	1.7	.05		bev
85A1	2.4	2.3	2.5	2.5	2.4	2.4	2.4			N	
B	2.4	2.3	2.3	2.3	2.3	2.3	2.3				
C	2.4	2.4	2.4	2.2	2.2	2.3	2.3				bev, difficult
D	2.2	2.3	2.2	2.3	2.4	2.4	2.3				
E	2.2	2.4	2.2	2.4	2.3	2.2	2.3	2.3	.04		

Lab Accession No.: 87-H594
Slide Preparer: K. Tremaine
Reader: K. Tremaine
Date: Aug 88

Comments: Problems with quality of Annadel, as well as difficulties with Konocti specimen

MEASUREMENTS OF INDUCED OBSIDIAN HYDRATION

Experiment: SET 3
Temperature: 200 C
Reaction Time: 2 d
Solution: dw
Initial pH: 5.9
Final pH: 8.3

OH Lab #	Readings (microns)						Indiv.Mean	Group Mean	sd	Source	Remarks
81A2	2.9	2.8	2.6	2.9	2.7	2.9	2.8			BL	
B	2.7	2.7	2.9	3.0	2.8	2.7	2.8				
C	2.8	2.6	2.6	2.9	3.0	2.9	2.8				
D	2.8	2.9	3.0	2.7	2.7	2.8	2.8				
E	3.0	2.8	2.8	2.7	2.9	2.8	2.8	2.8	.00		
83A2	2.2	2.2	2.4	2.3	2.2	2.4	2.3			K	
B	2.3										beveled
C	2.3	2.2	2.4	2.2	2.4	2.4	2.3				difficult
D	2.4	2.0	2.0	2.1	2.3	2.3	2.2				beveled
E	2.3	2.4	2.4	2.2	2.4	2.4	2.4	2.3	.08		poor
84A2	1.8	1.8	1.8	1.8	1.8		1.8			A	weathered
B	1.6	1.7	1.8	1.8	1.8		1.7				weathered
C	1.7	1.7	1.7	1.8	1.8		1.7				weathered
D	1.7	1.7	1.7	1.8	1.8		1.7				beveled
E	1.6	1.7	1.7	1.8	1.8		1.7	1.7	.04		poor res
85A2	2.5	2.5	2.4	2.2	2.2	2.3	2.4			N	
B	2.4	2.2	2.4	2.2	2.3	2.4	2.3				
C	2.5	2.3	2.3	2.4	2.4	2.2	2.4				
D	2.3	2.3	2.4	2.4	2.2	2.3	2.3				
E	2.4	2.4	2.5	2.2	2.2	2.3	2.3	2.3	.05		

Lab Accession No.: 87-H594
Slide Preparer: K. Tremaine
Reader: K. Tremaine
Date: Sept 88

Comments: Difficulties with quality of Konocti and Annadel obsidian

MEASUREMENTS OF INDUCED OBSIDIAN HYDRATION

Experiment: SET 3
Temperature: 200 C
Reaction Time: 4 d
Solution: dw
Initial pH: 6.6
Final pH: 7.8

OH Lab #	Readings (microns)						Indiv.Mean	Group Mean	sd	Source	Remarks
81A4	4.2	4.1	4.1	4.1	4.1	4.3	4.2			BL	
B	4.1	3.9	4.1	4.3	4.4	4.5	4.2				
C	4.0	4.3	4.5	4.2	4.4	4.2	4.3				
D	4.1	3.9	4.4	4.2	4.5	4.1	4.2				
E	4.2	4.2	4.0	4.5	4.1	4.2	4.2	4.2	.04		
83A4	2.8	2.8	3.0	3.0	3.1	3.1	3.0			K	
B	2.8	2.8	2.9	2.8	3.0	2.9	2.9				
C	2.9	3.1	2.9	2.9	2.8	3.0	2.9				
D	3.1	3.0	2.9	2.9	2.9	3.1	3.0				
E	2.9	3.0	2.8	3.0	3.0		2.9	2.9	.05		
84A4	2.3	2.3	2.2	2.1	2.3	2.5	2.3			A	poor res
B	2.4	2.6	2.6	2.4	2.7	2.6	2.6				
C	2.5	2.6	2.5	2.3	2.4	2.4	2.5				
D	2.4	2.2	2.3	2.2	2.4	2.5	2.3				2.5 best res
E	2.4	2.6	2.5	2.4	2.4	2.6	2.5	2.4	.13		
85A4	2.8	2.8	2.8	2.9	2.8	3.0	2.9			N	
B	2.8	2.8	2.8	2.8	3.0	3.0	2.9				
C	3.1	2.9	2.7	3.2	3.3		3.0				variable band, dh
D	2.7	2.8	2.8	3.0	3.0	2.8	2.9				
E	3.1	2.8	2.9	3.0	3.1	2.9	3.0	2.9	.05		

Lab Accession No.: 87-H594
Slide Preparer: K. Tremaine
Reader: K. Tremaine
Date: Sept 88

Comments:

MEASUREMENTS OF INDUCED OBSIDIAN HYDRATION

Experiment:	SET 3
Temperature:	200 C
Reaction Time:	6 d
Solution:	dw
Initial pH:	6.2
Final pH:	8.6

OH Lab #	Readings (microns)						Indiv.Mean	Group Mean	sd	Source	Remarks
81A6	4.5	4.4	4.1	4.1	4.3	4.4	4.3			BL	difficulty
B	4.2	4.4	4.1	4.3	4.1		4.2				difficulty
C	4.1	4.3	4.3	4.2	4.4		4.3				4.1 best res
D	4.1	4.1	4.3	4.4	4.1	4.3	4.2				poor res
E	4.3	4.1	4.3	4.2	4.1	4.4	4.2	4.2	.05		
83A6	2.9	2.8	2.7	2.6	2.9	2.8	2.8			K	
B	2.6	2.8	2.7	2.9	2.8	2.7	2.8				
C	2.8	2.7	2.9	2.7	2.8	2.8	2.8				
D	2.8	2.6	2.8	2.7	2.8	2.9	2.8				
E	2.9	2.8	2.9	2.9	2.8	2.9	2.9	2.8	.04		
84A6	2.0	2.0	2.0	2.1	2.1		2.0			A	poor res
B	2.0	2.0	2.0	2.0	2.0		2.0				poor res
C	2.0	2.0	2.1	2.3	2.3		2.1				poor res
D	2.0	2.0	2.0	2.1	2.3		2.1				poor res
E								2.1	.06		too poor res
85A6	2.8	3.0	2.9	2.8	2.9	2.7	2.9			N	
B	2.8	3.0	2.6	2.8	2.9	2.6	2.8				poor res
C	2.7	2.9	2.9	2.7	2.9	2.7	2.8				
D	2.9	2.9	2.7	3.0	2.8	3.0	2.9				
E	2.8	2.7	2.9	2.8	2.8	3.0	2.8	2.8	.05		best res

Lab Accession No.:	87-H594
Slide Preparer:	K. Tremaine
Reader:	K. Tremaine
Date:	Sept 88

Comments:

MEASUREMENTS OF INDUCED OBSIDIAN HYDRATION

Experiment:	SET 4
Temperature:	150 C
Reaction Time:	4 d
Solution:	dw w/ si gel
Initial pH:	6.2
Final pH:	6.3

OH Lab #	Readings (microns)						Indiv.Mean	Group Mean	sd	Source	Remarks
53A4	3.2	3.0	3.0	3.1	3.2	3.2	3.1			BL	
B	3.1	3.2	2.9	3.2	3.0	3.0	3.1				
C	2.8	3.0	2.9	2.8	3.0	2.9	2.9				thin
D	3.0	3.1	3.0	3.0			3.0	3.0	.10		one side only
54A4	2.6	2.3	2.6	2.3	2.4	2.4	2.4			N	
B	2.2	2.2	2.7	2.6	2.6		2.5				diffuse
C	2.2	2.6	2.1	2.1	2.2		2.2				
D	2.3	2.4	2.4	2.4	2.6	2.5	2.4	2.4	.13		best res 2.4
55A4	2.5	2.6	2.7	2.7	2.8	2.6	2.7			K	
B	2.4	2.6	2.7	2.7	2.8	2.7	2.7				
C	2.4	2.4	2.5	2.7	2.7	2.6	2.6				
D	2.7	2.6	2.7	2.6	2.7	2.5	2.6	2.7	.06		
56A4	1.9	1.9	2.1	1.7	1.9	1.9	1.9			A	
B	1.8	2.1	1.9	1.9	2.2		2.0				
C	1.9	2.1	2.1	2.0	2.1	2.2	2.1				
D	1.9	2.1	1.9	1.9	2.1		2.0	2.0	.08		

Lab Accession No.:	87-H594
Slide Preparer:	K. Tremaine
Reader:	K. Tremaine
Date:	Aug 88

Comments:

MEASUREMENTS OF INDUCED OBSIDIAN HYDRATION

Experiment:	SET 4
Temperature:	175 C
Reaction Time:	4 d
Solution:	dw w/ si gel
Initial pH:	6.0
Final pH:	6.8

OH Lab #	Readings (microns)						Indiv.Mean	Group Mean	sd	Source	Remarks
49A4	5.4	5.5	5.4	5.5	5.2	5.3	5.4			BL	
B	5.6	5.5	5.0	5.1	5.4		5.3				
C	5.1	5.0	5.0	5.0	4.8	5.2	5.0				
D	5.3	5.1	5.2	5.1	5.5	5.7	5.3	5.3	.17		
50A4	4.6	4.6	4.5	4.4	4.4	4.6	4.5			N	
B	4.5	4.3	4.4	4.2	4.3	4.5	4.4				
C	4.3	4.2	4.6	4.7	4.6		4.5				
D	4.5	4.2	4.5	4.9	4.8	4.5	4.6	4.5	.08		
51A4	4.5	4.4	4.3	4.2	4.9	4.4	4.5			K	
B	4.3	4.5	4.6	4.2	4.5	4.4	4.4				
C	4.5	4.3	4.3	4.4	4.5	4.7	4.5				difficult
D	4.4	4.3	4.4	4.4	4.6	4.5	4.4	4.5	.06		
52A4	3.7	3.7	3.2	3.5	3.6	3.2	3.5			A	
B	3.8	3.7	3.7	3.5	3.6	3.6	3.7				
C	3.6	3.5	3.2	3.6	3.7	3.7	3.6				
	6.9	7.0					7.0				double band
D	3.5	3.7	3.6	3.5	3.5	3.7	3.6	3.6	.08		

Lab Accession No.:	87-H594
Slide Preparer:	K. Tremaine
Reader:	K. Tremaine
Date:	July 88

Comments:

MEASUREMENTS OF INDUCED OBSIDIAN HYDRATION

Experiment: SET 4
Temperature: 200 C
Reaction Time: 1 d
Solution: dw w/ si gel
Initial pH: 6.2
Final pH: 6.6

OH Lab #	Readings (microns)						Indiv.Mean	Group Mean	sd	Source	Remarks
57A4	4.8	4.5	4.9	4.8	4.9	4.9	4.8			BL	
B	4.8	4.8	4.6	4.5	4.8	4.8	4.7				diffuse
C	4.9	4.9	4.8	4.8	4.8		4.8				
D	4.8	4.5	4.5	4.5	4.9	4.8	4.7	4.8	.06		
58A4	3.7	4.0	3.7	4.0	3.6	3.7	3.8			N	best res 3.7
B	3.9	3.8	3.6	3.6	3.9	3.8	3.8				
C	3.9	3.9	3.8	3.8	4.0	3.8	3.9				
D	3.9	3.8	3.6	3.9	3.8	3.7	3.8	3.8	.05		
59A4										K	too thin
B	3.7	3.7	3.8	3.9	3.9		3.8				faint
C	3.7	3.7	3.7	3.8	3.9		3.8				faint
D	3.6	3.7	3.8	4.0	3.8	3.8	3.8	3.8	.00		
60A4	3.0	2.9	3.0	3.0	2.8	2.9	2.9			A	
B	2.9	2.9	3.0	2.9	3.2	3.2	3.0				
C	3.2	2.9	3.1	3.2	3.0	3.0	3.1				
D	3.0	3.0	2.9	3.0	3.2	3.1	3.0	3.0	.08		

Lab Accession No.: 87-H594
Slide Preparer: K. Tremaine
Reader: K. Tremaine
Date: Aug 88

Comments:

MEASUREMENTS OF INDUCED OBSIDIAN HYDRATION

Experiment: SET 4
Temperature: 200 C
Reaction Time: 2 d
Solution: dw w/ si gel
Initial pH: 6.1
Final pH: 6.1

OH Lab #	Readings (microns)						Indiv.Mean	Group Mean	sd	Source	Remarks
57A2	5.9	6.2	6.0	6.3	6.0	6.0	6.1			BL	
B	5.8	5.8									too thin
C	6.3	6.5	6.0	6.3	6.0	6.0	6.2				
D	5.9	6.3	6.2	6.3	5.9	6.4	6.2	6.2	.06		
58A2	5.5	5.1	5.4	5.2	5.2	5.5	5.3			N	
B	5.5	5.2	5.4	5.4	5.3	5.2	5.3				
C	5.3	5.2	5.3	5.4	5.5	5.4	5.4				diffuse
D	5.4	5.5	5.2	5.2			5.3	5.3	.05		thin
59A2										K	not meas
B	5.4										too thin
C											not meas
D											too thin
60A2	3.9	4.1	4.1	4.1			4.1			A	
B	3.9	4.2	4.5	4.2	4.5		4.3				poor res
C	3.9	4.1	3.9	4.3	4.1	4.2	4.1				best res 4.1
D	3.9							4.2	.12		not meas

Lab Accession No.: 87-H594
Slide Preparer: K. Tremaine
Reader: K. Tremaine
Date: Aug 88

Comments: Trouble with Konocti measurements.

MEASUREMENTS OF INDUCED OBSIDIAN HYDRATION

Experiment: SET 4
Temperature: 200 C
Reaction Time: 4 d
Solution: dw w/ si gel
Initial pH: 5.8
Final pH: 6.4

OH Lab #	Readings (microns)						Indiv.Mean	Group Mean	sd	Source	Remarks
57A4	8.7	8.5	8.7	8.6	8.3		8.6			BL	
B	8.4	8.6	8.3	8.7	8.6	8.4	8.5				thin
C	8.7	8.7	8.1	8.7	8.3		8.5				thin, diffuse
D	8.2	8.8	8.4	9.1	8.9		8.7	8.6	.10		
58A4	7.8	7.8	7.8	7.7	7.5	7.5	7.7			N	
B	7.6	7.6	7.5	7.8	7.7	7.7	7.7				
C	7.5	7.5	7.8	7.8			7.7				diffuse, poor res
D								7.7	.00		too thin
59A4	7.5	7.7	8.0	7.8	7.6	7.7	7.7			K	diffuse, poor res
B											too thin
C	7.5	7.5	7.5	7.8	7.8		7.6				diffuse, faint
D	7.3	7.7	7.8					7.7	.07		diffuse
60A4	6.2	6.0	5.6	6.0	5.9	5.7	5.9			A	
B	5.7	5.5	5.7	5.8	5.7	5.7	5.7				
C	5.6	5.8	5.6	5.7	5.6	5.7	5.7				
D								5.8	.12		no thin section

Lab Accession No.: 87-H594
Slide Preparer: K. Tremaine
Reader: K. Tremaine
Date: Aug 88

Comments: Konocti specimens generally poor quality

MEASUREMENTS OF INDUCED OBSIDIAN HYDRATION

Experiment: SET 4
Temperature: 200 C
Reaction Time: 6 d
Solution: dw w/ si gel
Initial pH: 5.8
Final pH: 6.2

OH Lab #	Readings (microns)						Indiv.Mean	Group Mean	sd	Source	Remarks
57A6	10.8	10.8	10.6	10.7	10.5	10.7	10.7			BL	
B	10.6	10.8	10.8	10.6	10.9	10.6	10.7				
C	10.6	10.6	10.4	10.4	10.3	10.6	10.5				
D	10.6	10.6	10.8	10.9	10.8	11.1	10.8	10.7	.13		
58A6	8.7	8.6	8.7	8.5	8.7		8.6			N	faint, difficult
B	8.6	8.6	8.6	8.6	8.5	8.9	8.6				
C	9.0	8.5	8.7	9.1	8.6	8.6	8.8				8.6 best res
D	8.4	8.7	8.5	9.0	8.6	8.7	8.7	8.7	.10		
59A6	8.7	8.9	8.9	8.9	8.9	8.9	8.9			K	
B	8.6	8.5	8.9	8.3	8.6	8.2	8.5				double band
C	8.3	9.0	8.8	8.9			8.8				faint
D	8.5	8.3	8.7	8.6	8.7	9.0	8.6	8.7	.18		
60A6	6.8	6.6	6.6	6.8	6.6	6.7	6.7			A	
B	6.5	6.7	6.5	6.5	6.7	6.5	6.6				
C	6.5	6.5	6.6	6.4	6.6	6.3	6.5				
D	6.8	6.5	6.6	6.6			6.6	6.6	.08		faint

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