

INDUCED HYDRATION RATE DEVELOPMENT OF OBSIDIANS FROM THE COSO VOLCANIC FIELD: A COMPARISON OF EXPERIMENTAL PROCEDURES

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ABSTRACT

In the present study, hydration rate determinations for obsidians from the Coso volcanic field have been developed at elevated temperature and pressure. The completion of the experiment resulted in a hydration rate of $10.9 \mu\text{m}^2/1000$ years for West Sugarloaf and $28.5 \mu\text{m}^2/1000$ years for Sugarloaf Mountain at an effective hydration temperature of 20 degrees C. A comparison of the hydration rate for Sugarloaf Mountain with other rates developed for the same glass indicated varying degrees of correspondence. Possible reasons for the differences in the hydration rate are discussed.

INTRODUCTION

The Coso volcanic field is located at the southern extension of the Basin and Range province, immediately to the east of the Sierra Nevada. It is a region that has experienced active pre-Pleistocene volcanism that began approximately 6 m.y.a. with more active eruptive periods occurring between 4.0 and 2.5 m.y.a., and 2.0 and 1.8 m.y.a. (Duffield et al. 1980). Pleistocene volcanism (1.04 to 0.06 m.y.a.) resulted in the formation of nearly aphyric, high silica rhyolite domes and flows with accompanying basaltic flows (Bacon et al. 1981). The rapid quenching of the silica rich lava at the margins of these flows resulted in the formation of obsidian deposits. These sources of natural glass were

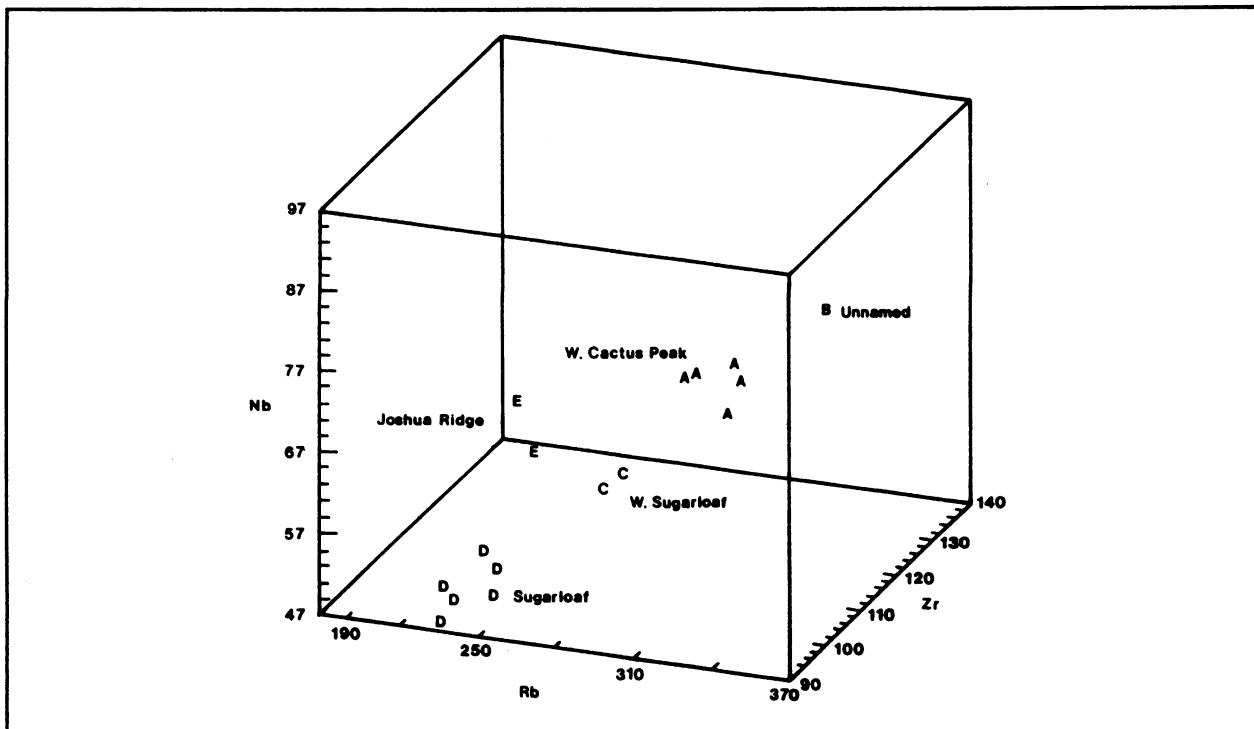
exploited by prehistoric peoples in the manufacture of stone tools and therefore can be used to date archaeological sites by the obsidian hydration dating method. In this analysis, two samples of obsidian from the Coso volcanic field have been selected for the development of hydration rate constants.

Obsidian Sources in the Coso Volcanic Field

In their study of the petrogenic and eruptive history of the Coso volcanic field, Bacon et al. (1981) analyzed 39 silicic localities for their major, minor, and trace element constituents. Up to 44 element and oxide determinations were conducted on each sample. The suite of samples was then partitioned into seven compositional groups using the multivariate procedure of cluster analysis.

Sixteen of the characterized samples were obsidian fragments. An inspection of the cluster dendrogram of Bacon et al. (1981) indicates that five compositionally distinct groups of volcanic glass are present within the Coso field. Although highly similar on the basis on their major and minor elements they exhibit some variability in their trace element profiles. Eight trace elements were selected from the larger set of determinations and the samples were again partitioned into groups using cluster analysis. An average link algorithm using an euclidian distance measure between unstandardized

FIGURE 1
CLUSTER ANALYSIS OF COSO OBSIDIAN



Graphical representation of the cluster analysis solution demonstrating Coso obsidian compositional types based on the parts per million concentration of trace elements.

values was used to determine if the the results of Bacon et al. (1981) could be replicated using a fewer number of attributes. The results of the cluster analysis (Figure 1) indicate that their analytical solution can be replicated using eight data points per sample instead of the forty-four used in the initial study.

A recent survey and geochemical analysis of the Coso volcanic field obsidian sources has been conducted by Hughes (1988). Based on a visual examination of the quality of the material at the source locations Hughes suggested that that only four obsidians of knappable quality are present within the Coso field. These sources have been named Sugarloaf Mountain, West Sugarloaf, Joshua Ridge, and West Cactus Peak (Hughes 1988: 258-260). X-ray fluorescence of samples from each of these sources indicated that the outcrops may be differentiated on the basis of their Zr/Rb concentration values.

The two samples provided by Wirth Environmental Services were selected from the southwest corner of Sugarloaf Mountain (Sample 1-1) and from a locality approximately 4 km to the northeast (Sample 4-1). X-ray fluorescence analysis of the samples by Hughes indicated that Sample 1-1 belongs to the West Sugar-

loaf Mountain source and that Sample 4-1 belongs to Sugarloaf Mountain. Sample 4-1 also corresponds to chemical Group 7 of Bacon et al. (1981).

THE HYDRATION PROCESS

The hydration of obsidian is controlled by the diffusion of atmospheric moisture into the core of the obsidian artifact. When a freshly fractured piece of obsidian is created, ambient water is attracted to the surface. Hydronium ions diffuse into the glass from the surface and exchange for alkali ions, notably sodium, within the alumino-silicate network. The alkali ions counter-diffuse to the surface and are removed. The replacement of sodium ions by hydronium ions results in a thin rim of residual stress which is manifested by optical birefringence when viewed in transmission with polarized light. The rate of hydration rim development (i.e. the hydration rate) is a function of glass composition and the thermal environment to which it has been exposed. It is therefore possible to accelerate the hydration process by raising the temperature of the hydration environment.

Archaeological studies of the hydration process

and leaching studies conducted by individuals in the fields of glass science and nuclear waste management (Michels and Tsong 1980; Hench et al. 1980; Doremus 1979) have repeatedly demonstrated that the diffusion of water into glass follows the equation:

$$x=kt^{1/2} \quad (1)$$

where: x=thickness of the hydration rim
k=a rate constant for each glass composition
t=time

HYDRATION RATE DEVELOPMENT

The diffusion of water into glass is a temperature dependent process that exhibits an Arrhenius relationship:

$$K= Ae^{E/RT} \quad (2)$$

where: K=hydration rate ($\mu\text{m}^2/1000$ years)
A=preexponential ($\mu\text{m}^2/\text{day}$)
E=activation energy (J/mole)
R=universal gas constant (J/mole)
T=temperature (Kelvin)

The development of a hydration rate (K) requires that the activation energy (E) and the preexponential (A) be known. These values for a particular glass composition were determined at elevated temperature under the following experimental conditions.

Freshly fractured obsidian flakes were hydrated in a two liter Parr pressure reactor in 500 ml of distilled deionized water and 1.0 gm of amorphous silica. Powdered silica was added to bring the solution to saturation thereby preventing surface dissolution of the developing hydration rim. Eight separate reaction runs were completed. Temperature ranges for individual runs ranged between 130°C and 190°C for durations up to 18 days (Table 1). At the end of each reaction period, the flake was removed from the solution and a

**TABLE 1
EXPERIMENTAL CONDITIONS AND RIM WIDTHS FOR THE
INDUCED HYDRATION EXPERIMENT**

Sample No.	Lab No.	Temperature(°C)	Duration	Rim Width(μm)	S.D.
Sugarloaf Mountain (Sample 4-1)					
1	87-66	160	3 Day	3.72	0.11
2	87-60	160	6 Day	5.05	0.07
3	87-56	160	12 Day	6.90	0.09
4	87-50	160	18 Day	8.90	0.14
5	87-74	130	12 Day	2.95	0.06
6	87-164	140	12 Day	3.77	0.05
7	87-89	170	12 Day	8.76	0.13
8	87-96	190	12 Day	—Too Diffuse—	
West Sugarloaf (Sample 1-1)					
1	87-67	160	3 Day	2.38	0.07
2	87-61	160	6 Day	3.58	0.08
3	87-55	160	12 Day	5.02	0.09
4	87-49	160	18 Day	5.34	0.07
5	87-73	130	12 Day	2.12	0.03
6	87-163	140	12 Day	2.41	0.05
7	87-88	170	12 Day	4.82	0.06
8	87-97	190	12 Day	—Too Diffuse—	

* Measurements made at 800x or 2000x

TABLE 2
HYDRATION RATE CONSTANTS FOR COSO OBSIDIANS

Obsidian *	Method	Preexponential	Activation Energy	Rate (20°C)
1) W. Sugarloaf	Induced	2.10 (160°C)	84170 J/mole	10.9
2) Sugarloaf	Induced	7.17 (200°C)	70450 J/mole	10.8
3) Sugarloaf ?	Induced	5.02 (172°C)	149781 J/mole	0.0014
4) Sugarloaf	Index	————	————	25-34
5) Sugarloaf	Induced	4.20 (160°C)	82201 J/mole	28.5
6) Coso Hot Springs	Induced	3.0178x10 ¹⁵	80603 J/mole	13.4

* 1: This analysis; 2: Michels (1983); 3: Ericson (1981); 4: Friedman and Long (1976);
5: This analysis; 6: Friedman and Long (1976).

* ? - No compositional data available to confirm obsidian source assignment.

* The Coso Hot Springs source presented by Friedman and Long (1976) was referred to as "Cosco Hot Springs." This spelling is believed to be a typographical error.

period, the flake was removed from the solution and a petrographic thin section prepared. The artificially induced hydration rims were measured at 800x or 2000x under polarized light with a Watson image-splitting measurement instrument. Hydration rims were readily identified and could be measured using traditional measurement techniques on specimens that were hydrated at temperatures equal to or less than 180°C. At 190°C the diffusion front of the hydration rim became poorly defined and an exact boundary region could not be identified.

The hydration rate constants were then calculated for each glass. Samples 1 through 4 were used to calculate the preexponential (A) and Samples 3, 5, 6, and 7 were used to calculate the activation energy (E). This resulted in a preexponential value of 2.1 $\mu\text{m}^2/\text{day}$ for West Sugarloaf and a value of 4.2 $\mu\text{m}^2/\text{day}$ for Sugarloaf Mountain (Table 2). The activation energies were 84170 J/mole and 82201 J/mole respectively. Hydration rates were then calculated at 20°C for each obsidian. This resulted in a hydration rate of 10.9 $\mu\text{m}^2/1000$ years for West Sugarloaf (Sample 1-1) and a rate of 28.5 $\mu\text{m}^2/1000$ years for Sugarloaf Mountain (Sample 4-1).

A COMPARISON OF HYDRATION RATE CONSTANTS

Obsidians from the Coso volcanic field have been the subject of several rate development studies. Induced hydration rate experiments have been conducted by Ericson (1981, [this volume]), Michels (1983), and Friedman and Long (1976). The compositional profiles published by Bacon et al. (1981) also permit hydration rate estimates using the Chemical Index of Friedman and Long (1976). The results of the rate development procedures from previous studies and the results of this study are compared and evaluated.

More than a decade ago, Friedman and Long (1976) introduced the induced hydration rate approach. Twelve chemically different obsidians were hydrated at elevated temperature in saturated steam for periods of up to three years. At the end of the experimental runs the activation energy (E) and the preexponential (A) for each source were calculated from the widths of the induced rims. The researchers then correlated the compositional profiles of the obsidians with their corresponding rates to produce the rate prediction equation which they named the Chemical Index:

$$\text{Chemical Index} = \text{SiO}_2 - 45(\text{CaO} + \text{MgO}) - 20(\text{H}_2\text{O}^*)$$

(3)

A hydration rate at a particular temperature may then be estimated from the conversion graphs provided by Friedman and Long (1976:351). Alternately, the hydration rate constants may be estimated from regression constants. Using the experimental data of Friedman and Long (1976), Smith (1977) computed the best fit line describing the relationship between the Chemical Index and each of the hydration rate constants (A, E). Using this method the preexponential and activation energy may be estimated for obsidians with a Chemical Index of 50 or less.

The compositional data for the Coso volcanic field developed by Bacon et al. (1981) permit hydration rate estimates for the five obsidian types defined by a cluster analysis of the trace element profiles (see also Hughes [1988: Table IV]). An examination of Table 3

indicates that the index values range between 45.75 and 59.25. The values of SiO₂, CaO, and MgO for all the samples are very similar. Variation in the index values are primarily a result of the larger range of values for H₂O⁺.

Hydration rates for each glass were calculated at 20°C. The hydration rates for the five groups range between 12.76 μm²/1000 years to approximately 38.0 μm²/1000 years. The hydration rate for Sugarloaf Mountain ranges between 25 and 34 μm²/1000 years (Table 3). It should be noted that the index values for almost all of the Coso obsidians are much higher than those used in the study by Friedman and Long (1976). The upper limit of the index values in that study was 48.9. Therefore, the rate estimates for the Coso glasses with a Chemical Index greater than 50 could not be

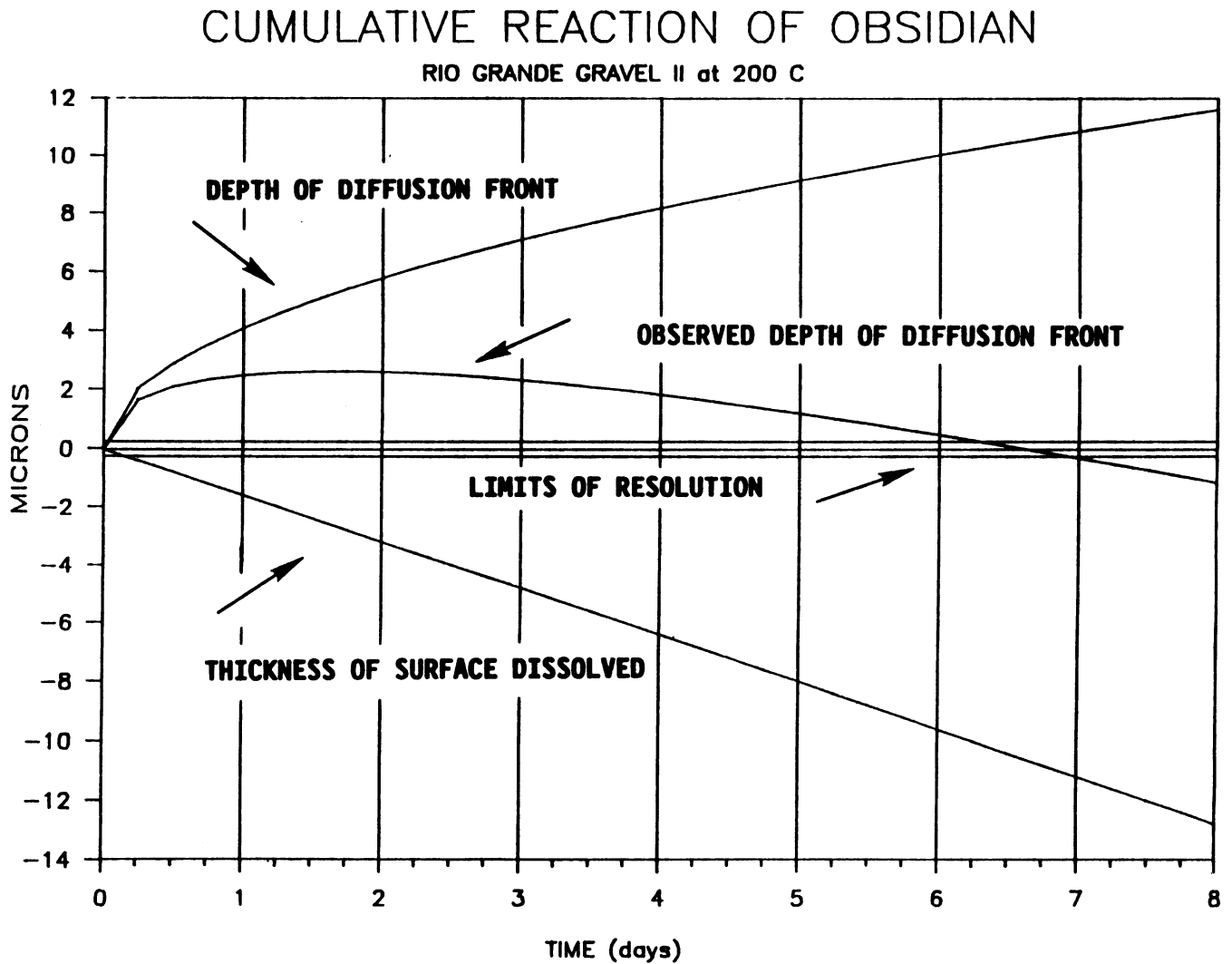
TABLE 3
CHEMICAL INDEX VALUES AND ESTIMATED HYDRATION RATES FOR COSO VOLCANIC FIELD OBSIDIANS

Sample No.	Group	SiO ₂	CaO	MgO	H ₂ O ⁺	Index	Rate(20°C)
13	3	76.9	0.35	0.01	0.19	56.9	35
10 West	3	76.9	0.39	0.01	0.21	54.7	31
14 Cactus	3	76.6	0.35	0.01	0.29	54.6	31
15 Peak	3	76.2	0.39	0.02	0.22	53.35	27
19	3	76.9	0.35	0.02	0.08	58.65	38
5	4	76.9	0.32	0.01	0.14	59.25	38
*16 West	5	76.2	0.43	0.02	0.51	45.75	12.76
*20 Sugarloaf	5	76.4	0.44	0.02	0.28	50.10	17.53
*24 Joshua	6	76.5	0.42	0.02	0.37	49.3	16.78
25 Ridge	6	76.7	0.41	0.02	0.19	53.55	27
4	7	77.0	0.31	0.02	0.23	57.55	34
6	7	76.6	0.36	0.01	0.11	57.75	34
27 Sugarloaf	7	77.0	0.38	0.03	0.27	53.15	27
17 Mountain	7	76.8	0.42	0.03	0.22	52.15	25
18	7	77.5	0.41	0.02	0.17	54.75	31
26	7	76.4	0.37	0.02	0.31	52.65	25

1) Sample Numbers, Group Numbers, and chemical data after Bacon et al. (1981); source names after Hughes (1988).

2) * Hydration rates for starred specimens have been calculated using the regression constants of Smith (1977). The hydration rates for all remaining specimens have been estimated from the conversion graphs of Friedman and Long (1976: 351).

FIGURE 2
OBSERVED THICKNESS OF THE HYDRATION RIM FOR SAMPLES REACTED IN
DISTILLED DEIONIZED WATER



Graphical representation of the observed thickness of the hydration rim for samples reacted in distilled deionized water as a function of linear surface dissolution subtracted from hydration proceeding at the square root of time. the limit of optical resolution associated with the measurement of the hydration rim is 0.25 μm .

calculated from the regression constants of Smith (1977) and required large visual extrapolations from the rate estimation graphs. They should therefore be considered as only very general estimates of the hydration rate. A hydration rate for Sugarloaf Mountain of $10.8 \mu\text{m}^2/1000$ has also been developed by Michels (1983). A listing of all hydration rate determinations on Coso glasses is presented in Table 2.

The hydration rates range from quite slow (Michels) to very fast (this analysis). At this point in time it is difficult to provide an exact explanation as to why apparently similar experimental conditions should result in a wide range of rate constants. However, slight differences of the reaction vessel conditions and the methods of induced hydration rim measurement offer some insights into the problem.

The exchange of alkali ions for hydronium ions in obsidian will occur when moisture is present. However, the form of the water may significantly effect the hydration process. The samples of Friedman and Long (1976) were hydrated in saturated steam. Under these conditions alkali ions are removed from the glass without dissolving the surface of the glass (Doremus 1979). For obsidians hydrated in a bath of distilled deionized water, the reaction solution acts as a corrosive media and dissolves the surface of the glass until the water is saturated with silica (White 1983). Under these conditions the hydration rate develops at the square root of time while surface dissolution precedes linearly with time. Therefore, the resulting hydration rim does not reflect the true hydration history of the sample (Figure 2). Samples reacted by Michels (1983), for the Sugarloaf Mountain source in distilled deionized water may have experienced substantial surface dissolution at the higher temperature runs (200°C - 250°C). This may account for the slower rates compared to rates developed in this analysis and by Friedman and Long (Table 2).

The addition of amorphous (powdered) silica to the distilled deionized water will inhibit the corrosion of the experimental samples. The finely powdered silica will be preferentially dissolved until saturation of the solution is achieved, thereby allowing the hydration rim to develop. The hydration rates for the Coso samples 1-1 and 4-1 were developed in this manner. The rate for the Sugarloaf Mountain source, Sample 4-1, ($28.5 \mu\text{m}^2/1000$ years) is comparable to that estimated from the Chemical Index ($25\text{-}34 \mu\text{m}^2/1000$ years). The hydration rate for West Sugarloaf is slightly slower than that predicted by the Chemical Index.

A portion of the experimental error associated with the induced hydration rate experiment is also contributed by the optical measurement of the induced hydration rims. The accuracy and reproducibility of a

measurement is related to the resolving power of the optical system, the instrument used in the measurement process, the clarity and definition of the diffusion front, and the focusing methods of the operator.

Resolution is the ability to distinguish between two closely spaced objects. Typical optical systems used in the measurement of hydration rims have a resolution of approximately $0.25 \mu\text{m}$. Measurement instruments such as the filar screw are very susceptible to the limits of resolution because the wire is seen with more clarity than the image of the hydration rim. The error associated with each measurement cannot be less than $0.25 \mu\text{m}$. In the computation of a hydration rate using the Arrhenius equation the measurement errors are compounded and can result in a total error of $-30/+70\%$ (Scheetz and Stevenson 1988).

The use of an image-splitting instrument can reduce the measurement error to less than $0.2 \mu\text{m}$ (Dyson 1960). The image-splitting measurement instrument was developed to measure the width of objects with identical or nearly identical opposite edges (i.e. blood cells, wires). When these objects are sheared the edges may be superimposed and very precise measurements achieved. For hydration rims however, these conditions are rarely met. The outer edge of the specimen has a sharp, well-defined boundary while the diffusion front is often represented by a grey band of finite width. As a result, no established stopping point is present and the inner boundary of the diffusion front is dependent upon the judgment of the operator. In spite of this problem measurement error associated with the image-splitting method is less than the resolution of the typical optical system.

Alternate techniques of focusing on the hydration rim can result in different hydration rim width determinations. An inter-laboratory blind test by Green (1986) indicated that substantially different rim width measurements on the same thin section may be provided by different laboratories. In other blind tests, the correspondence between laboratories has been quite close (Jackson 1984: 111-113; Kelly 1987). Where differences do occur they most probably stem from the techniques used to focus the hydration rim under high magnification. An operator may focus on the surface of the thin section or he may focus into the specimen which, in some cases, may better define the optical image. The problem with the latter approach is that the width of the hydration rim can significantly change with the depth of focus and that objective criteria (other than rim clarity) cannot be used to establish a stopping point. For measurements made on the surface of the thin section the objective is moved toward the specimen until the instant when the outer edge of the thin section becomes a sharp clear black line.

SUMMARY AND DISCUSSION

Recent geochemical studies of the Coso volcanic field have identified four chemically distinct obsidian sources used by prehistoric populations. These sources may be distinguished on the basis of their Zr/Rb concentrations (Hughes 1988). Hydration rates for Sugarloaf Mountain and West Sugarloaf have been developed under conditions of elevated temperature and pressure. The completion of the experiment resulted in a hydration rate of $10.9 \mu\text{m}^2/1000$ years for West Sugarloaf and $28.5 \mu\text{m}^2/1000$ years for Sugarloaf Mountain at an effective hydration temperature of 20 degrees C. A comparison of the hydration rate for Sugarloaf Mountain with other rates developed for the same glass indicated varying degrees of correspondence. The hydration rates for Sugarloaf Mountain and West Sugarloaf developed in this study are in general agreement with the hydration rates estimated by the Chemical Index. However, the rates developed by these methods are substantially faster than a hydration rate for Sugarloaf Mountain developed by Michels. The conditions within the reaction vessel and techniques of hydration rim measurement are suggested as possible explanations for the different rate determinations.

It is clear that additional criteria are needed to determine the best set of experimental methods used in rate development studies. 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 error and best replicates the natural hydration process. As a first step in establishing the preferred experimental procedure, a comparison of dates generated by the different rate constants with independent archaeological data should be completed.

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ACKNOWLEDGEMENTS

Funding for this study was provided by James Cleland of Wirth Environmental Services, San Diego, California.