OBSIDIAN HYDRATION AS AN INDEPENDENT DATING TECHNIQUE

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THESIS

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ABSTRACT

The purpose of this work is to test the validity of a method developed by Friedman and Long (1976) for calculating the ages of archaeological sites by obsidian hydration dating. According to Friedman and Long, hydration ages can be calculated if the following are known: 1) the hydration rind thickness of the obsidian; 2) the chemical composition of the obsidian; 3) soil temperature regimes where the obsidian was buried. Obsidian hydration is a potentially important dating technique. Obsidian is a common raw material in Alaskan archaeological sites, some of which cannot be reliably dated by other methods.

A test for Friedman and Long's method was devised using obsidian from the stratified Dry Creek archaeological site near Healy, Alaska. The hydration ages calculated using this method were at variance with the radiocarbon ages by as much as 20,000 years. The results of the test indicate that parts of Friedman and Long's method require revision, particularly those involving the relationship between chemical composition and hydration rates of the obsidian.

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CHAPTER I

INTRODUCTION.

The introductory chapter outlines the purpose of this work. Obsidian, a natural volcanic glass, is put into perspective among the other igneous rocks. Obsidian hydration as a dating technique is defined and placed within the larger framework of prehistory and chronology.

A. PURPOSE

Until recently, hydration rates used in obsidian hydration dating have been calculated from archaeological obsidians whose ages are known through their association with organics that have been dated by radiocarbon dating. This <u>modus</u> <u>operandi</u>, unfortunately, partially ignores what are currently believed to be the critical variables that affect hydration rates--soil temperature and chemical composition of the obsidian. Recently, Friedman and Long (1976) proposed a quantitative method for relating chemical composition to hydration rates. Hence, if soil temperatures and chemical composition of the obsidian are known, we should be able to calculate hydration rates independently of radiocarbon dates.

The purpose of this work is to test Friedman and Long's method through careful consideration of soil temperatures and chemical composition using the stratified and well-dated Dry Creek archaeological site as a test case. -1If Friedman and Long's method is correct, the implications are that sites without reliable radiocarbon dates can be dated by obsidian hydration alone. This could prove to be useful to archaeologists working in the arctic and subarctic where sites are, in many cases, shallow and lack suitable organics for radiocarbon dating. Obsidian hydration could also be used as a "back-up" dating method where radiocarbon dates are suspect on stratigraphic, typological, or other grounds.

B. OBSIDIAN'S PLACE IN NATURE

What is obsidian? To answer this question, we must step back and look at igneous rocks in general, which are formed by the cooling and solidification of magmas. The <u>intrusive</u> igneous rocks are those found in sills, dikes, laccoliths, and batholiths while <u>extrusive</u> igneous rocks are associated with surficial volcanic activity. Extrusives include lava flows, pumice, ashes, tuffs, and volcanic glasses (Bayly 1968:43-48).

An alternate classification of igneous rocks which encompasses both the intrusives and extrusives is based on the amount of silica (SiO_2) in the rocks and the grain size. Acidity and viscosity of the parent magma are proportional to silica content. High viscosity restricts ionic migration, and, as a concomitant, crystal growth, during cooling. The amount of crystal growth determines the grain size, commonly referred to as texture in petrological terminology.

The texture of the rock, then, depends upon the silica content and the rate of cooling of the magma. That is to say, the finestgrained rocks form from rapidly cooled acidic magmas. Non-granular rocks have a vitreous (glassy) luster, exhibit a conchoidal fracture, and have no crystal structure except as highly localized inclusions. A rock with these characteristics is normally called obsidian. For our purposes, further discussion of igneous rock terminology can be summarized as in Figure 1.

		increasing sil	lica content-		\rightarrow		
	ca. 50% silica	ca. 60%	% silica	ca. 72	2% silica		
Texture	Basic (or mafic)*	Basic Interme (or mafic)*			Acid (or felsic)*		
coarse	gabbro	diorite	syenite	grano- diorite	granite		
medium	micro- gabbro	micro- diorite	micro- syenite	micro- grano- diorite	micro- I granite		
fine	basalt	andesite	trachyte	dacite	rhyolite		
glassy	basaltic glass (very ra	andesitic glass re)**	trachytic obsidian (rare)	dacitic obsidian (more common)	rhyolitic obsidian (most common)		
	in	creasingly vis	cous parent m	na gma s			

* For purposes of geologic mapping, it is common to divide the volcanic rocks into two classes, mafic and felsic.

** These designations of relative abundance refer only to the glassy rocks.

Figure 1. Igneous rock terminology. (after Rosenfeld 1965:75)

Andesitic and basaltic glasses form only when cooling is extremely rapid, otherwise some crystallization will occur as these lavas are of low viscosity. Some basaltic glasses are known from Hawaii and Iceland (Morgenstein and Rosendahl 1976:141) where lavas may flow directly into the ocean. Of the obsidians, rhyolitic obsidian is the most common since it forms from highly viscous magmas; the temperature drop need not be so extreme for its formation. Even so, obsidians normally comprise only a small percentage of the total volume of acidic lava flows. Occasionally, large viscous flows can solidify into obsidian, e.g., Obsidian Cliff in Yellowstone Park. Most acidic lavas are, however, saturated with volatile gasses (predominantly water vapor) and "...at the same time so viscous, that they are blown to fragments on reaching the surface and give rise to pumice, ash, or glowing clouds" (Rittmann 1962:202-203). The rarity of obsidian is compounded by the fact that obsidian older than the late Tertiary Period usually becomes devitrified, i.e., crystallized (Marshall 1961; Jack 1976:185) although older obsidians are known.

C. OBSIDIAN'S PLACE IN PREHISTORY

Obsidian is one of the more easily flaked rocks and, due to its glassy texture, extremely sharp cutting edges can be produced. These qualities have made it a common item, despite its rarity relative to other raw materials, in the tool kits of prehistoric peoples inhabiting volcanic areas of the world, <u>e.g.</u>, the Pacific Rim and Southwestern Asia.

Prehistorians pay particular attention to obsidian for two main reasons. First, it has certain properties that allow it to be used in a dating method known as obsidian hydration dating, the subject of this paper. Second, analysis of minor chemical elements can tell us the geological source of archaeological obsidians. This provides a basis for inference about trade networks or movements of people to procure obsidian. Appendix I is a brief summary of what is readily available on known and possible Alaskan obsidian sources.

Throughout the history of archaeology, chronology has been a major concern. Indeed, one of the goals of modern archaeology, according to Hole and Heizer (1973:11), is "(t)o attain knowledge of sequences of events and chronologies in the absence of written documents." Until the mid-twentieth century, archaeological assemblages could only be dated relative to one another by their vertical provenience within a stratified site or by detailed and often tortuous comparison of artifact types from unstratified sites to those known from stratified sites. A possible exception to this statement is the use

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of tree ring dating, or dendrochronology, by the late 1930's, but this is of limited spatial and temporal applicability. Archaeology was considerably changed about 1950 with the advent of radiocarbon dating; archaeological cultures could at last be related to one another within an absolute time framework. Unfortunately, radiocarbon dating is not the answer to all of the archaeologist's chronology-oriented prayers. This can be illustrated by several problems commonly encountered by, but by no means restricted to, archaeologists working in Alaska.

The majority of known Alaskan sites are surficial or shallow; datable organics can readily be contaminated by more recent rootlets, humic acids, caribou urine, etc. Cryoturbation can reduce what were once well defined hearths filled with charcoal to dark blurs that may be indistinguishable from the results of fires of natural origin. Finally, wood and bone artifacts are rarely preserved, except in the more recent sites, leaving the investigator with stone implements and charcoal that are not always of demonstrably equal age. In short, there is in some cases, using radiocarbon dating alone, uncertainty as to just what is being dated.

The above comments are not meant to imply that radiocarbon dating is to be abandoned, but that it is often desirable to use another dating technique in conjunction with it. Given that obsidian is found in the majority of known Alaskan archaeological sites, obsidian hydration dating is a logical adjunct to radiocarbon dating.

The premise on which obsidian hydration dating is based is simply that obsidian absorbs water at a freshly exposed surface; this process is known as hydration. The depth to which water has penetrated is measurable with an optical microscope by examining a thin section cut at right angles to the surface of the specimen. The thin hydrated shell is visible under normal or polarized light and is known as the hydration rim or rind. If the thickness of the hydration rind and the hydration rate are known, the age of the specimen can be calculated. This is discussed in detail in the next chapter.

The majority of obsidian hydration studies have been on obsidians from California (Clark 1961; Michels 1965), Mesoamerica (Dixon 1966; Meighan, Foote, and Aiello 1968; Michels 1971; Stross et al. 1976), and Japan (Katsui and Kondo 1965, 1976; Morlan 1967) but are occasionally attempted in areas as diverse as Easter Island (Evans 1965) and Alaska (Davis 1976). Most of these studies emphasize obsidian hydration as an absolute dating technique but it is also useful for relative dating to establish horizontal stratigraphy (Layton 1973) and vertical stratigraphy within undifferentiated deposits. Artifact re-use can be detected because the re-used portion will show a thinner hydration rind (Katsui and Kondo 1976:138; Michels 1969).

Geologists have used obsidian hydration to approximate the age of obsidian flows (Friedman 1968; Friedman and Peterson 1971) and glacial events (Friedman et al. 1973; Pierce, Obradovich, and Friedman 1976). Obsidian nodules caught in glacial ice sometimes develop stress cracks where hydration can begin. The advantages of obsidian hydration dating are that there are no contamination problems and the artifact itself is dated. The disadvantage is that the rate of hydration is dependent on soil temperatures and the obsidian's chemical composition. Predicting past soil temperatures is no easy task and cannot, as yet, be done with precision. Our current knowledge of how to relate the chemical composition to the hydration rate is limited. Keeping these problems in mind, it should, however, be possible to estimate the age, within substantial margins of error, of archaeological obsidian specimens independently of radiocarbon dates.

CHAPTER II

THE DEVELOPMENT OF OBSIDIAN HYDRATION DATING.

This chapter is an examination of the history and theory of obsidian hydration dating up to the present. The critical variables that affect hydration rates and how hydration ages are calculated are discussed. Previous work in the arctic and subarctic is reviewed.

A. THE DEVELOPMENT OF OBSIDIAN HYDRATION DATING UP TO 1976

Geologists have been aware of the phenomenon of obsidian hydration since the first decade of this century, but not enough was known until the late 1950's to use it as a dating method. In 1960, Irving Friedman and Robert Smith of the United States Geological Survey proposed the use of obsidian hydration to the archaeological community in <u>American Antiquity</u>. This was followed by an archaeological evaluation of the method by Clifford Evans and Betty Meggers (1960). In their preliminary paper, Friedman and Smith reported that obsidian hydrates at a rate determined by petrologic and climatic factors and that the thickness of the hydration rind and the age of the specimen are related by the diffusion law

$R = K\sqrt{t}$

where R is the hydration rind thickness in microns, K is the hydration rate, and t is the age of the specimen in years. Dividing through by K and squaring both sides, we get the normal working form of the

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equation:

$$R^2 = kt$$
 (2-1)

where R and t are the same as above and k equals K^2 . The hydration rate, k, is expressed in microns squared per thousand years, <u>i.e.</u>, $\mu^2/1000$ yrs.

Based on studies of hundreds of archaeological obsidian specimens associated with radiocarbon dated organics, Friedman and Smith (1960: 492) suggested hydration rates for different climatic regions as follows:

Region	Hydration Rate ($\mu^2/1000$ yrs)
Coastal Ecuador	11
Egypt	8.1
Temperate No.1	6.5
Temperate No.2	4.5
Subarctic	0.82
Arctic	0.36

A flurry of enthusiasm followed; here was a new dating technique that cost only a few dollars per sample. But as archaeologists began to apply the method, they often found that the regional rates did not give hydration dates comparable to radiocarbon dates. The obvious solution to that problem was that Friedman and Smith's rates had to be adjusted somewhat to fit a particular area. A year later, however, Clark (1961) had studied a well-dated series of obsidian artifacts from a stratified site in California and found that if k was to be a constant, the only R-t relationship that could reconcile the radiocarbon dates and the hydration rind measurements was

$$R = kt^{3/4}$$
 (2-2)

Katsui and Kondo's (1965) work on Hokkaido supported Friedman and Smith's original R-t relationship. They also found that hydration rates for Hokkaido averaged about 1.8 $\mu^2/1000$ yrs, midway between Friedman and Smith's Temperate No.2 and Subarctic rates.

Realizing their incomplete knowledge of the hydration process, Friedman and Smith, in collaboration with William Long (1966), conducted a series of laboratory experiments wherein obsidian was hydrated rapidly in constant-temperature ovens set at 100°C. Their data supported the R-t relationship expressed by Equation 2-1. They further noted (Friedman, Smith, and Long 1966:324) that the hydration rate, k, is related to temperature by the Arrhenius equation for temperature-dependent chemical reactions

$$k = Ae(-E/R)(1/T)$$
 (2-3)

where A is a constant characteristic of the reaction, E is the activation energy in calories/mole, R is the universal gas constant equal to 1.99 cal/mole-degree (not to be confused with R in Equation 2-1), and T is the absolute temperature in degrees Kelvin. This equation simply shows that the reaction rate, k, increases exponentially as temperature increases and that A and E are different for different chemical reactions. Presumably, A and E could be related to petrologic factors but exactly how remained unknown.

Despite the fact that Equation 2-3 clearly shows that hydration rates vary with temperature, archaeologists continued to assume that

constant regional or local hydration rates existed, no matter how deeply the obsidian specimens in question were buried. This assumption could only be true if all the obsidian artifacts within a region were buried at the same depth, which is unlikely, and if soil temperatures within a region were the same at that depth, which they probably are not, or if all the artifacts within a region were found on the surface and the air temperature within that region was everywhere the same. Choosing to ignore the fact that soil temperatures vary with depth (see for example Figures 7a, 7b, and 8B.) and that constant regional hydration rates exist only in special cases, <u>i.e.</u>, surface sites with identical air temperature curves, archaeologists continued to look for new R-t relationships.

Meighan, Foote, and Aiello (1968) concluded from their work in Mexico that R and t were linearly related, as follows:

$$R = kt$$
(2-4)

Johnson's (1969) work in the Klamath Basin of California again supported Friedman and Smith's 1960 R-t relationship, Equation 2-1. However, Findlow et al. (1975:347) found that out of all possible R-t relationships,

$$R^2 - R = kt$$
 (2-5)

best fit their Southwest data. Using data from a site in Mexico, Kimberlin (1976:75) found that

$$R = kt^{1/3}$$
 (2-6)

best accounted for his results. Noting that there were now at least five different R-t relationships in the literature, Kimberlin proposed

that

$$R = kt^{X}$$

where k and x must be determined empirically for each geological obsidian source. Ambrose (1976), working in the laboratory with New Zealand obsidian, produced evidence that strongly supported Friedman, Smith, and Long's 1966 model as expressed by Equations 2-1 and 2-3. He pointed out (Ambrose 1976:100) that it is necessary to quantify soil temperatures at each site since they are variable within a region and obsidian hydration is a temperature-dependent reaction. Therefore, there is no such thing as a single, constant hydration rate for a region or a geological source. However, an average k can be calculated for each depth using temperature curves and Equation 2-3.

In conclusion, it should be noted that all those who have conducted controlled laboratory studies have shown that the relationship between R, the rind thickness, and t, the age of the specimen, is of the form

$$k^2 = kt$$
 (2-1)

Those who have proposed other R-t relationships have not adequately accounted for temperature variations and continued to assume that the hydration rate, k, must be a constant. It follows that this procedure would yield an infinite number of R-t relationships all of which fail to reflect reality unless it can be demonstrated that soil temperatures are the same at all depths within a site. This could occur only at surface sites.

On the other hand, even if attempts are made to account for temperature variation by using the Arrhenius equation 14

(2-7)

$$k = Ae(-E/R)(1/T)$$
 (2-3)

the reader will note that two variables, A and E, remain unaccounted for. Before this is discussed, a summary of current knowledge of the hydration process at the molecular level is necessary.

Î

B. CURRENT METHOD AND THEORY IN OBSIDIAN HYDRATION DATING The Hydration Process.

A better understanding of the hydration of obsidian can be acquired through a brief look at its chemical composition and structure. As mentioned earlier, the most common type of obsidian is rhyolitic obsidian. The chemical composition of a world-wide sample of rhyolitic obsidians (most abundant constituents only) is shown in Table I. From the table, it is clear that the predominant component of obsidian is silicon dioxide or SiO_2 . In glasses, silicon and oxygen atoms are thought to be arranged as follows:



(after Becker and Wentworth 1973:32 and Scholze 1966:624)

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TABLE	I Chem	ical Compo	sition of	a World-	Wide Samp	le of Rhy	olitic Ob	sidians	
Source Area	Si02	A1203	Fe ₂ 0 ₃	Fe0	MgO	CaO	Na ₂ 0	K20	H ₂ 0 ⁺
California	75.78	12.39	0.22	1.25	0.31	0.81	4.00	4.64	0.41
New Mexico	76.20	13.17	0.34	0.73	0.19	0.42	4.31	4.46	0.33
Wyoming	74.70	13.72	1.01	0.62	0.14	0.78	3.90	4.02	0.62
Wyoming	72.59	13.49	1.58	1.32	1.65	2.12	4.63	2.52	0.18
Mexico	75.23	12.36	0.96	1.24	0.01	1.00	4.00	4.62	0.73
Nicaragua	76,68	14.49	n.d.	1.09	0.84	1.53	3.92	1.20	0.36
Colombia	75.87	14.35	0.22	0	0.29	0	3.96	4.65	0.33
Ecuador	76.33	12.89	1.17	0.32	0.08	0.72	5.45	2.49	0.35
Ecuador	73.07	11.78	2.30	n.d.	0.39	2.02	1.19	6.84	2.24
Now Zoaland	75.46	11.27	1.17	2.05	0.27	0.53	3.45	4.88	0.28
New Zealand	73 37	9.69	4.48	n.d.	0.37	1.14	4.38	5.91	0.58
New Zearand	75.72	12.55	0.44	1.43	tr.	1.41	2.73	4.81	0.36
Java	74 80	14 32	0.88	1.00	tr.	1.26	3.38	3.28	1.24
Java	74.00	12 88	1 34	1.53	0.15	1.44	3.29	4.16	0.29
Admiralty Is.	73.55	13.19	0.89	1.49	0.37	0.96	4.45	4.32	0.37

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TABLE	I (contir	nued)	(data f	rom Washi	ington 191	17; all f	igures are	e percent	by weight)
Source Area	SiO2	A1203	Fe ₂ 0 ₃	Fe0	MgO	CaO	Na ₂ 0	K20	H20 ⁺
Sumatra	78.15	11.94	0.72	0.33	0.20	1.32	0.67	5.71	0.14
Japan	74.41	13.33	0.08	0.86	0.43	1.90	2.99	4.30	0.23
Iceland	75.01	12.27	0.80	2,78	0.08	1.87	3,36	2.80	0.25
Iceland	73.40	12.90	3.70	n.d.	0.14	2.35	3.83	2.99	0.43
Ascension Is.	71.42	14.90	1.41	2.32	0.08	0.80	6.01	3.52	0.85
Canary Is.	73.05	14.67	0.89	n.d.	0.26	0.97	3.99	5.11	0.91
Ethiopia	72.46	13.96	1.65	0.89	tr.	0.81	5.69	5.16	0.17
Aeolian Is.	74.37	12.65	2.58	n.d.	0.20	1.22	3.87	4.57	0.22
Aeolian Is.	72.19	12.56	3.65	'n.d.	0.85	2.52	4.41	3.35	0.40
Sardinia	74.61	12.68	0.09	1.36	0.21	0.69	3.68	4.77	1.37
Hungary	72.79	13.77	1.69	n.d.	0,28	1.24	3,39	4.38	2.41
mean	74.46	13.01	1.37	1.19	0.30	1.22	3.81	4.21	0.62
S.D.	1.60	1.15	1.16	0.69	0.35	0.62	1.14	1.20	0.59
n	26	26	25	19	26	26	26	26	26

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1000 1000 1000 1000 1000

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This amorphous structure (really that of a supercooled liquid whose viscosity approaches infinity) is found in artificial and natural glasses. Rigidity comes from the sequential -Si-O-Si- bonds (Becker and Wentworth 1973:31).

The second most abundant component of obsidian is alumina or Al_2O_3 , but it not clear exactly where it fits into the structure as represented on the previous page. It is probable that in at least some obsidians it replaces silicon at some points in the structural network (Ericson, Mackenzie, and Berger 1976:27).

The exact mechanism of hydration in glasses is not fully understood. Two models have been proposed for water transport:

> Whole water molecules diffuse into the silicon-oxygen network where the reaction

> > $= Si - O - Si = + H_2 O \rightarrow = Si - OH_{HO} - Si =$

occurs (Moulson and Roberts 1961:1215; Marshall 1961:1151). Because of the irregular structure of glasses, a continuous range of interionic bond strengths exists. Diffusing water would react at the weakest bonds first.

2. Water travels in the form of H⁺ and OH⁻ groups that alternately jump from one Si-O bond to the next. First, an =Si-O-Si= bond is broken at the surface of the glass to form two silanol groups (see a. below). Then, protons (H⁺) and hydroxyl radicals (OH⁻) alternately jump to the next =Si-O-Si= bond to form two new silanols and allowing the old ≡Si-O-Si≡ bond to reform (b. and c. below) (Ericson, Mackenzie, and Berger 1976:29).

a.
$$\equiv \text{Si-O-Si} + \text{H}^+ + \text{OH}^- \rightarrow \equiv \text{Si}^- \frac{\text{OH}}{\text{HO}} - \text{Si} \equiv$$

b.
$$\equiv Si - OH - Si = 0 - Si \equiv \longrightarrow \equiv Si - O - Si \equiv HO - Si = 0$$

c. $\equiv Si - 0$, Si = 0, Si = 0,

some manufactured glasses.

In both models, the net result is the same--water breaks the Si-0 bonds to form silanols as it penetrates, weakening the structure! Perhaps hydration occurs by both mechanisms simultaneously. In any case, hydration involves more than simple diffusion. Water is reacting with structural components and, according to Weyl and Marboe (1964:720), is increasing the diffusion rate. This is known as an autocatalytic reaction wherein water acts as both a reactant and a catalyst. The hypothesis that hydration shows characteristics of diffusion and chemical reactions is supported by Friedman, Smith, and Long's (1966) bimodal model as expressed by Equation 2-1, the diffusion law, and Equation 2-3, the Arrhenius equation for temperature

Perlite is believed to be the end product of obsidian hydration (Ross and Smith 1955:107; Haller 1960:46; Friedman, Smith, and Long 1966). Perlite is typically highly fractured and contains at least twice as much water as obsidian. Most of the water in perlite is meteoric (absorbed during hydration); most of the water in obsidian is magmatic (Friedman and Smith 1958:218).

dependent chemical reactions.

The surface of glass has a strong affinity for water (Weyl and Marboe 1964:720). As long as the vapor pressure, p, is greater than zero, the surface remains saturated with water molecules and hydration rates are limited only by Equation 2-3, the Arrhenius equation. Vapor pressure is determined by the Clausius-Clapeyron equation

$$p = Ae^{(-\Delta H/R)(1/T)}$$
(2-8)

where ΔH is the heat of vaporization, R is the universal gas constant, T is the temperature in degrees Kelvin, and A is a constant characteristic of water (Becker and Wentworth 1973:371). By this model, vapor pressure, and hence, hydration rates, approach zero only when the temperature approaches absolute zero, <u>i.e.</u>, -273.18°C.

Chemical Composition and Hydration Rates.

From the above, it seems that Friedman, Smith, and Long's 1966 model is consistent with what is known about the hydration process. But how does obsidian's chemical composition affect hydration rates? That it does in some way has been known since 1960 when Friedman and Smith observed different rates for Egyptian obsidians of differing chemical compositions even though these obsidians had experienced comparable temperature regimes. It was not until 1976 when Friedman and Long published the results of a long-term experiment on the subject that much could be said about the quantitative relationship between chemical composition and hydration rates. Friedman and Long hydrated obsidian samples of known chemical composition (major components) at elevated temperatures for periods up to four years. This technique allows better control over the temperature variable than is possible for archaeological obsidian. By writing Equation 2-3 in natural logarithmic form,

$\ln k = (-E/R)(1/T) + \ln A$

and plotting ln k versus (1/T), the slope of the resultant line is equal to (-E/R) and the vertical intercept is ln A. The results of this procedure are summarized in Table II. In attempting to relate the chemical composition to hydration rates, Friedman and Long (1976: 347) found that

(a) combination of components expressed as $SiO_2 - 45(CaO + MgO) - 2O(H_2O^+)$ (all percentages by weight; the H_2O^+ is water liberated above 110 °C) is more closely related to hydration rate... than is silica content alone. We refer to this parameter as the chemical index. This chemical index was derived empirically by varying the coefficients to fit the smoothest curve to the experimental hydration rates.

The chemical index, referred to here as CI, ranges from 0.9 to 48.9 for Friedman and Long's samples. As CI increases, the hydration rate increases. Friedman and Long offer no explanation as to why increasing SiO₂ content increases k and increasing CaO, MgO, and H_2O^+ decreases k. Perhaps higher SiO₂ content increases the number of potential binding sites for migrating water. MgO and CaO may compete with water for the \equiv Si-O-Si \equiv binding sites while increasing H_2O^+ could slow down diffusion as in hydration model 1 (pg. 19) or interfere with H⁺ and OH⁻ migration as in model 2.

It is my impression that some archaeologists feel that hydration rates are different for different geological sources. Sources,

TADLE II AITI		<u>101</u> <u>Mile</u>	Mor ch Aller I	
Locality	<u>A</u>	<u>1n A</u>	E/R	Chemical Index
Xalpazquillo	1.832×10^{16}	37.45	10,550	30.5
Clear Lake	1.494×10^{16}	37.24	10,670	17.9
Big Obsidian Flow	1.488 x 10 ¹⁶	37.24	10,750	10.2
Love Quarry	1.172×10^{16}	37.00	10,900	0.9
American Falls	9.000 x 10 ¹⁵	36.74	10,140	42.6
Obsidian Cliff	6.457 x 10 ¹⁵	36.40	9,851	46.3
Panum Dome	6.279 x 10 ¹⁵	36.38	10,070	41.0
Grassy Lake	4.601 x 10 ¹⁵	36.07	9,923	43.9
Cosco Hot Springs	3.017 x 10 ¹⁵	35.64	9,687	48.9

TABLE II Arrhenius Equation Parameters for Nine North American Obsidians

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however, can only be identifed by trace elements, which have no known affect on hydration rates. Further, it is not possible to assign a hydration rate to archaeological obsidians known to be from the same source, even if temperatures are equivalent, since the chemical composition within the souce may vary considerably (Rittmann 1962:106).

Using the data from Table II, A and E/R can be plotted against CI to derive a quantitative relationship as shown in Figure 2. The data points fall into two distinct groups and each group was treated separately. Equations for these relationships were found by using the least squares method (Sokal and Rohlf 1973:228). These equations are

	$A = 2.085 \times 10^{14} \text{ CI} + 1.186 \times 10^{16}$			
0 < CI < 35	E/R = -11.613 CI + 10,890.24			
35 < CI < 40	NO DATA			
	$A = -4.667 \times 10^{14} \text{ CI} + 2.666 \times 10^{16}$	(2 10)		
40 (1 (50	E/R = -54.028 CI + 12,340.60	(2-10)		

From the chemical composition we can calculate the chemical index and from the chemical index we can calculate the Arrhenius equation parameters A and E/R. Figure 3 shows graphically how the hydration rate varies with temperature and chemical index.

Then, if the temperature regime, T, to which the obsidian specimens have been exposed is known, in addition to the chemical parameters above, all of the variables known to affect hydration rates are accounted for. Given the body of theory outlined in this chapter,







<u>Figure 3</u>. A plot of hydration rate versus temperature for chemical indices from 0 to 50. Note how the hydration rate becomes increasingly temperature-sensitive as the chemical index and temperature increase.

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it should be possible to calculate hydration rates and the ages of archaeological obsidian specimens independently of radiocarbon dates.

C. PREVIOUS WORK IN THE ARCTIC AND SUBARCTIC

Work with obsidian hydration dating in the arctic and subarctic begins with the preparation of Friedman and Smith's 1960 paper. They requested that archaeologists working in these areas send them obsidian samples from strata with reliable radiocarbon dates. Louis Giddings responded with material from the Iyatayet site, Cape Denbigh, and Richard MacNeish sent ten specimens from the southwest Yukon. From these samples, Friedman and Smith suggested hydration rates for the arctic and subarctic of 0.36 and 0.82 $\mu^2/1000$ yrs, respectively, as shown on page 11. In the early 1960's, MacNeish (1964:305) decided to try hydration dating on a larger scale by using material from 14 sites in the southwest Yukon. However, when the archaeological components were ordered in terms of hydration rind thicknesses, they did not match the temporal ordering provided by radiocarbon dating and stratigraphic evidence. The obsidian dating project was discontinued. It appears that there were obsidians from several different sources (MacNeish 1964:308), possibly of different chemical compositions, in his samples. This could explain the discrepancies, but, at the time, almost nothing was known about the effects of chemical composition on hydration rates.

Bandi (1969:52) reported a hydration date of 8400 B.P. for the Campus site. This date was based on a small number of rind measurements performed by Yoshio Katsui at Bandi's request (Edward Hosley, written communication of March 28, 1977). This date, according to Cook (1969:

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297) "...is to be looked at askance...since there is no valid (hydration) rate established for Alaska." Further, Bandi reported neither the hydration rind thicknesses nor the hydration rate used in deriving this date. Jason Smith (1971), working in British Columbia, used a rate of $1.4 \,\mu^2/1000$ yrs. This was suggested to him by W. B. Koch (unpublished) who was working with obsidian from Onion Portage (Anderson 1968). John Cook's unpublished hydration rind measurements from Healy Lake show considerable intra-level scatter but when these values are averaged, they show in a general way that the deeper an artifact is buried, the older it is. While the reader may not find this result particularly profound, it is important to note that it is an example of the information to be gained from obsidian hydration in sites where clear-cut stratigraphy is absent.

At the Chemi site in the Southwest Yukon, William Workman (1974) found that the hydration rind thicknesses clustered fairly well within cultural levels, but the ages calculated using rates of 0.7, 0.8, and $0.9\mu^2/1000$ yrs show some discrepancies with the radiocarbon ages. It appears that Leslie Davis and Donald Clark, who worked on the obsidian from Chemi, suggested these rates but the data on which the rates are based are not specified. In Davis' (1976) report on obsidian hydration dating for the Alyeska Archaeology Project, he calculated two rates of 1.19 and $0.32\mu^2/1000$ yrs based on radiocarbon dated organics associated with the obsidian specimens. The intra-site ages computed with these rates are scattered. Davis has done other work with obsidian from the Koyukuk River area for Donald Clark but this, to my knowledge, is unpublished.

Finally, Workman (1976:145) reported obsidian hydration rind measurements from the Gulkana (GUL-077) site. Fourteen of these clustered between 0.5 and 0.8 microns but four others ranged from 1.5 to 4.2 microns. Two of the high readings are from flakes recovered from hearths. Workman suggests that the two other more-hydrated flakes were made at a much earlier date and brought to the site in late prehistoric times. These flakes could also have higher chemical indices. The rind measurements made on flakes from hearths should be treated with caution since the heat of the fire can cause extremely rapid hydration and thus increase rind thicknesses. Also, burned flakes often show diffuse, uneven hydration rinds that are difficult to measure accurately (Nancy S. Marshall, written communication of January 14, 1977).

To summarize, it is fair to say that the use of hydration dating in the arctic and subarctic is characterized by a fruitless search for valid rates coupled with well-placed skepticism about hydration dating as a whole. Perhaps the most lucid summary is from Workman (1976:145):

Attempts to read calendar years in the thickness of hydration rinds on obsidian flakes cannot be taken too seriously in the subarctic as yet.

CHAPTER III

METHODS.

This chapter outlines the methods used to test the body of theory on using obsidian hydration as an independent dating technique as described in the previous chapter. It includes pertinent data on the test site (Dry Creek), chemical analysis, soil temperature modeling, hydration rind measurement, and computer programming.

A. INTRODUCTION

This work is basically a test of a new model proposed by Friedman and Long (1976) for predicting hydration rates. Should this model provide accurate hydration dates, the methodology which follows can also be applied to other sites. However, some of the procedures, particularly estimating soil temperatures, are site-specific and will have to be modified accordingly. The sections on hydration rind measurement and chemical analysis describe standardized laboratory techniques; these are of general applicability.

Some procedures are presented in what may seem to be tedious detail, but it is necessary to do so to give the reader a feeling for what is involved in testing and using this model. The sections are presented in a rough "chronological" order, from field recovery of obsidian specimens to computation of hydration ages.

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B. OBSIDIAN AT DRY CREEK

While the methods proposed here are meant for eventual use in shallow, undated sites, they must first be tested in a stratified, well-dated site. In view of this, the Dry Creek site (HEA-005) was chosen as a test case for the following reasons:

- 1. The 1976 excavations recovered about 800 obsidian specimens, mostly unretouched flakes.
- Dry Creek is a multi-component site with obsidian in two of three archaeological components.
- 3. Radiocarbon dates have been obtained that will serve as a standard of comparison for the hydration dates.
- Close vertical and horizontal proveniences were recorded for most of the obsidian pieces. In a few cases, high flake densities precluded this. Then, the clusters were bagged as a unit with the closest possible provenience recorded.

The Dry Creek site is located about 180 km southwest of Fairbanks, Alaska, near the town of Healy. It is atop a 25 m bluff that overlooks Dry Creek, a tributary of the Nenana River. The bluff, composed of outwash gravels from the Healy Glaciation, is capped by 2 m of eolian deposits. As shown in Figure 4, these sediments are composed of seven loess units and four sand units; five buried paleosol complexes are found within the section (Thorson and Hamilton 1977:153) as well as three archaeological components. At the close of the 1974 season, it was thought that four archaeological components existed, based on depth measurements alone. After Thorson and Hamilton carefully mapped the profile and defined the eleven lithological units, it could be shown that the two middle components were, in fact, one. This temporary misinterpretation resulted from the fact that

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Figure 4. Generalized stratigraphic section, Dry Creek archaeological site, Healy, Alaska. Obsidian is found in Components 2 and 3. Paleo-sols 1, 2, and 3 are tundra soils; Paleosols 4a and 4b are forest soils. Redrawn from Thorson and Hamilton (1977:Figure 4).

the lithological units are not at a constant depth below surface throughout the profile (W. Roger Powers, personal communication). My own experience at the site during the 1976 season supports Dr. Powers' conclusion.

The obsidian recovered in 1976 is from Components 2 and 3 and, when mapped horizontally as in Figure 5, falls into five spatially distinct groups. Inspection with a 70X binocular microscope revealed that the obsidian is homogeneous within groups but heterogeneous between groups. Besides the horizontal distribution, the following observations support this grouping:

Group I Component 2, depth 133-141 cm

luster: vitreous texture: glassy, but slightly granular groundmass color: transparent, colorless banding: distinct gray bands; form ranges from straight, parallel bands to irregular sinusoidal ones inclusions: many small bubbles, opaque black particles, (quartz?) microcrystallites visible on fractured surfaces general: thicker flakes are opaque black

Group II Component 2, depth 137-147 cm

luster: vitreous
texture: glassy
groundmass color: transparent, gray
banding: none
inclusions: occasional black opaque particles
general: thin flakes completely clear to naked eye

Group III Component 3, depth 49-57 cm

luster: vitreous
texture: glassy
groundmass color: transparent, gray
banding: diffuse and irregular when present
inclusions: numerous small black and a few brown particles
general: thin flakes appear slightly gray



Figure 5. Horizontal distribution of obsidian at the Dry Creek site, 1976 excavations. The stippled areas are dense obsidian flake concentrations. Each group is believed to be the result of a single, separate flaking event. Group III is from Component 3; the others are from Component 2.

Group IV Component 2, depth 137-145 cm

Group V Component 2, depth 126-137

luster: vitreous
texture: glassy
groundmass color: transparent, colorless
banding: distinct, numerous black wavy bands
inclusions: numerous black particles
general: thin flakes appear speckled to the naked eye, thicker
flakes are opaque black

This grouping is also verified by the chemical analysis (vide infra).

Because of the horizontal distribution, <u>i.e.</u>, tight spatial clustering, and within-group petrological homogeneity, the author believes that each group represents a single flaking event. Therefore, all the flakes in any one group are thought to have been manufactured at a single time and from the same piece of raw material. The flakes from the five groups very likely come from five different pieces of raw material given the differences in banding, inclusions, etc. These five pieces may or may not be from the same source; the characteristics described above and the type of chemical analysis that I have had done are not reliable indicators of source.

As can be seen in Figures 6a, 6b, and 6c, there has been some vertical movement of specimens within each group. The maximum vertical separation ranges from eight to eleven centimeters with the average for all five groups being nine centimeters. These vertical distribu-



Figure 6a. Vertical distribution of obsidian at the Dry Creek site, 1976 excavations. Groups I and II. East-west cross-sections are shown. Each dot represents a single obsidian specimen. Hydration rind thicknesses are known for specimens marked by +. The boxes are flake clusters that were recovered en mass. The number of small dots within the boxes is roughly equal to the number of obsidian flakes recovered from the clusters.







tions are attributed to four main factors:

- 1. Frost heaving (Price 1972:27; Washburn 1973:65).
- Faulting. In Figure 4, the reader will note faults running vertically through the section. These faults are common in all areas where obsidian was recovered. The easternmost part of the distribution of Group V, shown in Figure 6c, is particularly suggestive of this (W. Roger Powers, personal communication).
- The ancient surface on which the flakes were dropped was propably not level.
- 4. It is likely that the inhabitants of the site stepped on the flakes a few times, pushing some deeper into the ground than others.

The five groups contained 177, 235, 79, 196, and 109 obsidian specimens, respectively. A 10% sample was selected from each group and sent to the Pennsylvania Obsidian Dating Laboratory for hydration rind measurement. The samples selected include specimens from the entire depth range where possible. In some cases, flakes at the top or bottom of the distribution were too small to be thin sectioned by the laboratory. Sampling was done in this non-random way to test the null hypothesis that, within any one group, there is no correlation between depth and hydration rind thickness. The alternate hypothesis is that temperature variations are sufficient over about nine centimeters to cause observable differences in rind thickness. Using the methods described in Sokal and Rohlf (1973:261-275) for tests of significance in correlation, it was found that that the null hypothesis (no correlation) was accepted at the 0.01 level of confidence for all five groups. The implication of this result is that it is valid to analyze the flakes in any group as if temperature variation over nine

centimeters was negligible.

The reader will note from Table III that that there is variability in hydration rind thickness within each group. This could be attributed to microvariation in chemical composition within the piece of raw material but there is neither confirming nor negating evidence on this. There is evidence to show that the temperature of pieces of obsidian exposed to direct sunlight gets much higher than that of pieces in the shade or immediately below the surface (Friedman and Long 1976:351). Obsidian, being black, is a good absorber of solar radiation. Therefore, the rind thickness variability within groups could be attributed to differential exposure of the flakes to direct sunlight shortly after being dropped at the sight.

C. CHEMICAL ANALYSIS

As seen in Chapter II, it is necessary to know the percentages by weight of SiO₂, MgO, CaO, and H_2O^+ in order to calculate the chemical index and, hence, hydration rates for the obsidian samples. The State Division of Geological and Geophysical Surveys laboratory on the Fairbanks campus was provided with a randomly selected 3.5 gm sample from each of the five groups for determination of these components. Silicon, magnesium, and calcium were determined by both atomic absorption and X-ray techniques so that each could act as a crosscheck for the other. The State laboratory was unable to do the H_2O^+ determination, so they returned the remaining samples and these were sent to the Chemical and Geological Laboratories of Alaska, Inc., Anchorage. H_2O^+ was determined by gravimetric techniques. All three techniques are described below.

Atomic Absorption.

Atomic absorption works on the principle that atoms of a particular element absorb light of a specific wavelength. This wavelength, known as the resonant wavelength, is unique to each atomic species and is determined by the energy needed to elevate the electrons of a species from the ground state to an excited state. Therefore, when a beam of monochromatic light at the resonant wavelength and of known intensity is passed through atoms of the element in question, light is absorbed in an amount proportional to the abundance of that element. Free atoms are produced by dissolving the sample in

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strong acids and spraying the solution into a nitrous oxide-acetylene flame. The sheet of flame acts as a reservoir for free atoms while absorbance is measured. In practice, the absorbance of the sample is compared to that of a standard solution of known concentration. An appropriate resonant wavelength light source is required for each element being analyzed.

X-ray Emission Spectrography.

When matter is bombarded with X-rays of sufficient energy, electrons in the inner shells of atoms comprising that matter are elevated to higher energy levels. Since this is an unstable condition, electrons from the outer shells drop down to refill the inner shells. To do so, the outer shell electrons must loose energy; this leaves the atoms as <u>secondary X-rays</u>. Most of the energy given off is concentrated into a few wavelengths that are characteristic of each element. In practice, samples of unknown composition are ground into a fine powder, compressed into uniform pellets, and bombarded with X-rays. The wavelengths and intensities of the secondary X-rays emitted are recorded on a chart recorder. By comparing these values to those for standards of known composition, the elements present and their abundance can be calculated. More detailed descriptions of atomic absorption and X-ray emission spectrography are found in Maxwell (1968:497-531), Volborth (1969:194, 235) and Wainerdi and Uken (1971:205-270).

Gravimetric Methods.

Rocks contain two kinds of water, H_20^+ and H_20^- . The H_20^- is

moisture absorbed from the air or soil and is not chemically combined with the rock. It can be driven off by heating the powdered sample to 120°C for two days. The H_20^+ is water that could not escape before the magma solidified. It is also known as the water of crystallization. It can be driven off by heating the sample to 900°C for twenty minutes. If the sample is carefully weighed before and after the second heating in the presence of a dessicant, the difference in weight is equal to the weight of the H_20^+ . There are a number of ways to determine H_20^+ but they all involve the basic procedures of heating and weighing. These are described in more detail in Jeffery (1975:262-279).

The results of these determinations were as follows (all figures are % by weight):

	Si02*	Mg0*	CaO*	H ₂ 0 **
Group I	78.5	0.04	0.66	0.98
Group II	79.0	0.11	0.53	0.49
Group III	75.7	0.23	0.81	0.38
Group IV	78.2	0.07	0.67	0.38
Group V	75.4	0.03	0.63	0.38

* N. Veach and H. Potworowski, analysts

** T. Hill, analyst

Using these figures, the chemical index is calculated from Friedman and Long's (1976:347) formula

 $CI = Si0_2 - 45(Mg0 + Ca0) - 20(H_20^+)$

Hence, the chemical indices for these samples are as follows:

Group	I	27.4
Group	II	40.4
Group	III	21.3
Group	IV	37.3
Group	٧	38.1

Groups IV and V fall between 35 and 40 where there is no data (see Figure 2), so A and E/R had to be determined by a less exact method. The author drew a curve on Figure 3 midway between the curves for CI = 35 and CI = 40 which was assumed to represent CI = 37.5. Hydration rate values (vertical axis) were measured from the graph for temperature values (horizontal axis) between 0° and 26°C and substituted into the logarithmic form of the Arrhenius equation

 $\ln k = (-E/R)(1/T) + \ln A$

to find values for A and E/R. These values fell directly on the line extrapolated back from CI = 40 (Figure 2), so the equations for CI between 40 and 50 (Equation 2-10) were used to find values for A and E/R corresponding to the chemical indices 37.3 and 38.1. As we shall see in Chapter IV, the hydration ages calculated for Groups IV and V were not particularly aberrant. It is assumed that this extrapolation was valid.

D. ESTIMATING SOIL TEMPERATURES

In order to evaluate hydration rates, it is necessary to develop a predictive model for soil temperatures. For Alaska, this has been done for the Barrow area only (Nakano and Brown 1972). The area around Dry Creek lies in the zone of discontinuous permafrost (Stearns 1966:3; Ferrians, Kachadoorian, and Greene 1969:2); the site itself is underlain by permafrost. Soil temperature curves for permafrost regimes are available for Fort Yukon (Aitken 1962) and Northway, Alaska (Aitken 1964), and Skovorodino (Muller 1947:19) in the Trans-Baikal region of Siberia. These curves are shown in Figures 7a and 7b.

No suitable soil temperature records could be found for the Healy area. However, the gross features of soil temperatures in permafrost regimes can be estimated by the equation

$$T = -T'_{o} + A_{o}e^{-Z\sqrt{\pi/4P_{y}}} \sin(2\pi t/P_{y} - Z\sqrt{\pi/4P_{y}})$$
(3-1)
where T is the temperature in degrees C at depth Z in meters at a
given time of the year t, -T'_{o} is the mean annual air temperature, A_

given time of the year t, $-T_o$ is the mean annual air temperature, A. is the amplitude of yearly air temperature fluctuations, Py is the period (one year), and \ll (alpha) is the thermal diffusivity (Gold and Lachenbruch 1973:11). This equation describes a sine curve with a term, $e^{-Z\sqrt{\pi/\measuredangle Py}}$, that attenuates the amplitude with increasing depth and a term, $-Z\sqrt{\pi/\measuredangle Py}$, that approximates the way in which soil temperatures typically lag behind air temperatures. This lag increases with depth. These features are illustrated in Figure 8A which is a graphic representation of the curves generated by Equation 3-1.







Figure 7b. Yearly air and soil temperature curves. Skovorodino, Eastern Trans-Baikal, Siberia. From Muller (1947).



Figure 8. Predicted soil temperature curves for the Dry Creek site, Healy, Alaska. A. Yearly soil temperature curves generated by Equation 3-1. The air temperature curve is from Weather Bureau records. These temperature values are substituted into the Arrhenius equation. B. Observed and predicted soil temperatures at Dry Creek for September 18, 1976. The predicted points are generated by Equation 3-1.

The parameters $-T'_{\circ}$ and A_o were obtained from Healy climatic records². Alpha (\ll), the thermal diffusivity, is related to the thermal conductivity, K, soil density, p, and mass specific heat, C, by

$$C = K/pC \tag{3-2}$$

Alpha is influenced by numerous variables like aspect, moisture content, parent material, snow cover, and vegetation cover (Annersten 1966; Brown 1964; Gold 1967; Hoekstra 1969; Kallio and Sieger 1969; Price 1971; Shul'gin 1965; Smith 1975; Viereck 1973). The current state of knowledge of permafrost soils does not allow reliable estimates of alpha. However, Equation 3-1 can be solved for alpha if soil temperatures are known for any time during the year.

Soil temperatures were measured by the author at the Dry Creek site on September 18, 1976, using a one meter temperature probe connected to a YSI Model 42SC Tele-Thermometer. Thaw depth was also measured with a 1.5 meter frost probe. At some points, the frost table was beyond the reach of the temperature probe, but the temperature at the frost table can generally be taken to be 0°C (C. Theodore Dyrness, personal communication of September 17, 1976). It was found that the frost table had dropped considerably immediately adjacent to the excavation. At about three meters north of the excavation, the frost table was at its normal level for that time of year (about 1.4 meters) so temperatures were recorded along a line four meters north

 These data were secured from the Meteorologist-In-Charge, Weather Service Forecast Office, Anchorage, Alaska. The Healy weather station operated from 1920 to 1944 and their records are out of print.

of the excavation between the grid points E16 and E21 where obsidian had been recovered. These readings were quite consistent, varying by less than one degree C at any depth. The average temperature gradient is shown in Figure 8B. By substituting these temperatures and depths into Equation 3-1 and solving for alpha, it was found that alpha varies with depth in a near-linear fashion. The regression line equation was calculated to be

$$\propto = 1.050 \text{ Z} + 0.236$$
 (3-3)

where Z is the depth below surface in meters. Figure 9 shows a plot of alpha versus depth and the regression line. By substituting values of alpha from this equation into Equation 3-1, holding t constant at a value equivalent to September 18, and varying Z, a temperature gradient was generated that is in good agreement with the observed data as shown in Figure 8B. Equations 3-1 and 3-3 could then be used to compute soil temperatures, T, for any depth at any time of the year for use in the Arrhenius equation, Equation 2-3.





E. HYDRATION RIND MEASUREMENT

Thin Section Preparation.

The technique described here is basically that used to prepare geological thin sections. Slight modifications were made by Friedman and Smith (1960) and Michels and Bebrich (1971) to suit the particular needs of obsidian hydration dating. Nancy Marshall, who prepared and measured the Dry Creek specimens, worked with Michels and Bebrich for several years while at Pennsylvania State University. Her procedures are presented below.

To prepare a thin section, two parallel cuts are made about 5 mm deep and 1 mm apart perpendicular to a worked surface of the specimen. A water-cooled, diamond-impregnated, continuous-rim brass or copper alloy saw blade about 0.4 mm thick and 10 cm in diameter rotating at 3000-3600 RPM is used. This produces thin, smooth cuts with little chipping of the hydrated surface. A razor blade is inserted into the shallower cut and pushed towards the deeper one, snapping off the wedge at its base. Holding the wedge on the moistened ball of the index finger, one of the sawed surfaces is ground smooth on a horizontal lapidary rotating at 300-450 RPM with a slurry of 303-1/2 corundum powder and water. This usually removes chipped areas left by the sawing operation. The wedge, ground side down, is then mounted on a microscope slide with cooked Canada balsam. The unground side is then ground on the same lapidary until the specimen is 30-50 microns thick. The slide is washed with water and protected with a glass cover slide affixed with Canada balsam. It is now ready for reading.

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Three to six thin sections can be prepared per hour with a reject rate as low as 5%. Slides may be rejected for any of the following reasons:

1. No hydration visible; too thin or spalled off in preparation.

- Improper grinding such that saw chipping is not removed or the plane of the wedge is not perpendicular to the worked surface.
- 3. Ground too thick or too thin.
- 4. Improper mounting.
- Samples that have been exposed to intense heat show uneven, diffuse rinds that cannot be measured accurately.

Of 98 Dry Creek specimens submitted for measurement, five were rejected. Three showed no hydration and two were simply too small; they were shattered during the sawing operation.

Reading The Slide.

The thickness of the hydration rind is read on a petrographic microscope equipped with a 100X oil immersion objective and a 15X Vickers image-splitting measuring ocular. The hydrated layer will appear as a faint line parallel to the edge of the specimen under ordinary light. The line is the result of a slight change in refractive index at the hydrated-unhydrated interface. Several measurements are taken along the specimen's edge. These readings are averaged unless re-use is suspected. With the Vickers ocular, the rind thickness can be measured to within ± 0.125 microns (Michels and Bebrich 1971:202-214). In cases where extremely accurate measurements are needed, the error factor can be reduced to ± 0.05 microns by measuring enlarged color photomicrographs (Findlow and De Atley 1976:167). The hydration rind measurements for the Dry Creek samples are shown in Table III³.

3. A single measurement was taken from each flake. At several points in Table III, a catalog number is repeated and followed by the letters a, b, c, etc. Those flakes were from dense clusters and were not cataloged separately.

Dry Creek Archaeolog	ical <u>Site</u> .
<u>Catalog #</u>	Rind Thickness (µ)
UA76-155-3445	2.19
3451	2.16
3663	2.29
3713	2.15
3724a	2.21
3724b	2.27
3724c	2.22
3724e	2.17
3725	2.17
e 3752	2.21
3786	2.34
3810	2.02
3815a	2.12
3815b	2.35
3815c	2.02
3815d	1.96
3815e	2.12
3815f	2.26
3815g	2.49
	mean = 2.20
	S.D. = 0.13
	n = 19
	<u>Catalog #</u> UA76-155-3445 3451 3663 3713 3724a 3724a 3724c 3724c 3725 3752 3786 3810 3815a 3815b 3815b 3815c 3815c 3815d 3815c 3815f 3815f 3815g

TABLE IIIHydration Rind Measurements for Obsidian SpecimensFrom the Dry Creek Archaeological Site.

	Catalog #	Rind Thickness (#)
UA76	-155-1361	2.96
	5335	2.87
	5341	2.73
	5357	2.49
	5413	2.46
	5433	2.81
	5442	2.70
	5446	2.47
	5455	2.48
	5513a	2.51
Group II	5513b	2.80
137-147 cm below surface	5517	2.59
	5518	2.56
	5521a	2.71
	5521b	2.64
	5521c	2.62
	5521d	2.76
	5521e	2.60
	5521f	2.74
	5521g	2.60
	5521h	2.49
	5521i	2.47
	5521j	2.64

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TABLE III (continued)

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	Catalog #	Rind Thickness (H)
Group II (continued)	UA76-155-5521k	2.34
	55211	2.45
	5521m	2.57
	5521n	2.57
	55210	2.46
	5521p	2.70
		mean = 2.61
		S.D. = 0.15
		n = 29

UA	76-155-1047		1.83
Group III 57 cm below surface	1078		1.64
	1092		1.72
	1206		1.48
	1214		1.56
	1216a		1.56
	1216b		1.53
	1216c		1.57
	1216d		1.54
	1292		1.54
		mea	n = 1.60

S.D. = 0.11 n = 10

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	Catalog #	Rind Thickness (µ)
UA76	-155-1353a	1.88
	1353b	1.61
	1355a	1.75
	1355b	1.52
	1355c	1.50
	1355d	1.72
	1355e	1.66
	1355f	2.04
	1355g	1.96
Group IV	1355h	1.78
137-145 cm below surface	1355j	1.86
	1355k	1.73
	13551	1.86
	1356a	1.94
	1356b	2.00
	1420	2.14
	1425	1.79
	1428	1.70
	1430	1.99
	5176	1,90
	5179	1.80
		mean = 1.82
		S.D. = 0.17
		n = 21

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	Catalog #	Rind Thickness (屮)
UA76	5-155-0294	1.94
	0311a	1.90
	03116	2.00
Group V 126-137 cm below surface	4154	1.92
	4155	2.03
	4156	2.15
	4160	2.04
	4162a	2.02
	4162b	2.30
	4162c	2.10
	4166	2.11
	4225	2.12
	5522	2.07
		mean = 2.05
		S.D. = 0.11
		n = 13

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	Group I	Group II	Group III	Group IV	Group V
mean	2.20	2.61	1.60	1.82	2,05
S.D.	0.13	0.15	0.11	0.17	0.11
n	19	29	10	21	13

F. COMPUTATIONS

At this point, it is useful to summarize the methodology and show how chronometric ages are calculated from the various types of data.

1. <u>Chemical</u> <u>Analysis</u>.

Samples are analyzed for SiO_2 , MgO, CaO, and H_2O^+ . From this, a chemical index is computed using the following:

$$CI = SiO_2 - 45(MgO + CaO) - 2O(H_2O^{T})$$

CI is then used to find A and E/R, two of the three variables that affect hydration rates, using the regression equations

0 < CI < 35	$- A = 2.085 \times 10^{14} \text{ CI} + 1.186 \times 10^{16}$
	E/R = -11.613 CI + 10,890.24
35 < CI < 40	NO DATA
10 4 61 4 50	$A = -4.667 \times 10^{14} \text{ CI} + 2.666 \times 10^{16}$
40 (01 (50	E/R = -54.028 CI + 12,340.60

2. Soil Temperature.

Soil temperatures are estimated by

$$T = -T_{o}' + A_{o} e^{-Z\sqrt{\pi/\alpha}P_{y}} \sin(2\pi t/P_{y} - Z\sqrt{\pi/\alpha}P_{y})$$

Values for alpha (\ll) are based on temperature measurements taken at Dry Creek and vary with Z, depth, as follows:

< = 1.050 Z + 0.236</pre>

3. Hydration Rates.

The hydration rate, k, is calculated from the Arrhenius equation

$$k = Ae^{(-E/R)(1/T)}$$

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The hydration rate is calculated at 50 points along the temperature curve with Z equal to zero. These are averaged. Z is increased by one centimeter, 50 more values of T are found, and 50 more values of k are found and averaged. This is repeated until Z equals the depth at which the specimen was recovered. These values of k are then averaged to give a hydration rate that represents the average hydration rate during the specimen's entire archaeological history. The underlying assumption in this procedure is that rates of deposition at Dry Creek have been constant; using the simple average implies that that specimen has spent the same amount of time at Z = 1, 2,n cm, where n equals the recovery depth.

4. Hydration Ages.

Given the hydration rind thickness, R, and the hydration rate, the archaeological age of the specimen is found from

$$t = R^2/k$$

where t equals the hydration age in years. The entire procedure is represented schematically on the following page.



G. ERROR ANALYSIS

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The parameters A, E/R, and alpha are calculated from regression equations. Confidence limits can be set for these for these using standard statistical techniques (Sokal and Rohlf 1969:246). The limits were computed for the 0.32 level of confidence or one standard deviation on either side of the regression line (Figures 2 and 9).

The expression used to find the chemical index may not be univerversally applicable. Friedman and Long's (1976) expression was derived from a small sample. Some of the major constituents like Al_2O_3 and Na_2O were fairly constant in their samples but are more variable when a world-wide sample is considered so their effects on hydration rate may have been masked.

The parameter A, from Equation 3-1 is the amplitude of the yearly air temperature curve and is mainly a function of the latitude and the degree of continentality of Dry Creek's climate. This is not expected to have changed appreciably during the occupation of the site.

Sources of error that cannot easily be quantified are changes in mean annual air temperature, ground cover (which affects soil temperatures), and rates of deposition. Since the premise on which this methodology is based is that Dry Creek is unknown chronologically, the stratigraphic units (Figure 4) cannot easily be correlated with known or hypothesized Pleistocene-Holocene air temperature changes.

-64-

Paleosols 4a and 4b are Subarctic Brown forest soils (Thorson and Hamilton 1977:161). From this, it can be inferred that air temperatures and ground cover were close to present-day conditions during the formation of these soils. Hydration rates for artifacts found above about 65 cm, then, can be evaluated using the present-day parameters in Equations 3-1 and 3-3. This affects Group III most strongly.

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Paleosols 1, 2, and 3 are tundra soils (ibid.). Thorson and Hamilton attribute their formation to a decreased rate of loess deposition, but it is also possible that they result from lower air temperatures. Tundra cover, with its good insulating qualities, tends to lower soil temperatures and raise the frost table. Temperature reductions near the surface are on the order of 4° to 6°C relative to sparsely covered areas (Ng and Miller 1975:225). Whether the tundra soils developed due to cooler air temperatures or a decreased loess rain, the net result is lowered soil temperatures. Recent estimates of Pleistocene air temperatures (Péwé 1975:109; Gates 1976:1142) for interior Alaska indicate that temperatures were 1° to 5°C lower than today. The effects of cooler temperatures or tundra cover can be simulated in the present model by decreasing the mean annual temperature, -T' in Equation 3-1, by a few degrees. To cover the probable range of variation, -T' is set 3.5°C lower than today ±2.5°C below 65 cm. This will most strongly affect Groups I, II, IV, and V all of which are from Component 2.

Figure 4 shows that rates of deposition are not constant. The

stratigraphy reflects numerous episodes of slow deposition (or even erosion), soil formation, and fast deposition. Given this complex picture, it would be difficult to assess the ultimate effects on hydration rates. With the present methodology, it can only be assumed that deposition was constant in a general way. However, if one looks ahead at the radiocarbon dates and plots them versus depth, the result is very nearly a straight line as shown in Appendix II. The uniform deposition assumption, then, would appear to have little effect on the calculated hydration ages.

Errors in measuring hydration rinds and percentages of chemical constituents are assumed to be negligible compared to those discussed above. Given the uncertainties in quantifying a number of the variables affecting hydration rates, it is impossible at present to construct a completely rigorous mathematical model. However, we do have sufficient information to test Friedman and Long's model of hydration. This is done in Chapter IV.

H. THE COMPUTER PROGRAM

A Fortran IV program was written by the author for use on the University of Alaska's Honeywell 66/20 computer. Due to the complexity of the equations involved and the large number of calculations required for each specimen, use of computers seems mandatory for obsidian hydration dating.

The catalog number, chemical index, hydration rind thickness, and recovery depth for each specimen is read from data cards. Starting with depth, Z, equal to zero, the program uses Equations 3-1 and 3-3 to find the temperature at 50 points along the yearly curve. These values are fed into Equations 2-9, 2-10, and 2-3 giving 50 values of k, the hydration rate. The k values are averaged and this represents the hydration rate at Z = 0. The above steps are repeated n times where n is equal to the depth at which the artifact was found with Z being increased by one centimeter at the start of each repetition. When Z reaches 75 cm, the parameters in Equation 3-1 are switched from the cooler tundra soil regime to the present-day one. The n values of k are then averaged and fed into Equation 2-1, giving the age of the specimen. The above procedure simulates the temperature regime that a piece of obsidian would be subject to as it is dropped on the ground and gradually buried by eolian deposition.

Maximal and minimal values of alpha, T, A, E/R, k, and hydration age are calculated in a parallel fashion using values outlined in the previous section. The most probable age is subtracted from the
maximum age to get a plus factor and the minimum age is subtracted from the most probable age to get a minus factor. The plus values are typically larger than minus values due to the exponential form of Equation 2-3. The printout gives catalog number, group, chemical index, rind thickness, depth, and the hydration age with a plus-orminus factor. The above steps are repeated for each specimen. Because of the large number of repetitive calculations, this program costs about \$1 in computer time for each data card. Complete text and a sample printout is shown in Appendix III.

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CHAPTER IV

DENOUEMENT.

This final chapter summarizes the results of the experiment and the conclusions that can be drawn from those results. Following that is a brief summary and suggestions for future research.

A: RESULTS AND CONCLUSIONS

The first computer run using the initial model produced rather discouraging results. The average hydration ages (years, B.P.) are as follows:

	Group I	22,814	+ 8,254 - 6,479
	Group II	16,038	+15,723 - 7,598
Component 2 (radiocarbon age: 10,690 ±250)	Group IV	12,175	+18,602 - 6,896
∼140 cm	Group V	13,467	+18,175 - 7,270
	Groups I,II,IV,V (weighted average)	17,037	+14,208 - 6,971
Component 3 (radiocarbon age: 3,430 ±75 3,655 ±60 4,670 ±95)	Group III	11,222	+ 1,653 - 1,375

~50 cm

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Discussion.

Clearly, the model is inaccurate and imprecise. Even though the error factors are huge, the minimum average Component 2 hydration age of 10,066 (17,037 minus 6,971) overlaps only slightly with the radiocarbon age. The minimum Component 3 hydration age does not even approach the oldest rediocarbon date of 4,670 ±95. What is perhaps more disconcerting is that, given these hydration ages alone, Component 2 cannot be distinguished from Component 3. This is illustrated in Figure 10. The inset in Figure 10 shows, in part, why the error factors for Component 3 are smaller than for Component 2. From 0 to 75 cm, no uncertainty, except for confidence limits on alpha, is built into the temperature model under the assumption that conditions were the same as today. The error factor of ~15% for Component 3 is directly related to confidence limits set for the relationship between the chemical index and the Arrhenius equation parameters A and E/R. Below 75 cm, temperature uncertainty is estimated to be ±2.5°C and the error factors on the hydration ages increase accordingly. For Group I, the error increases to 28-36%; half is from temperature uncertainty and half is from confidence limits on A and E/R. Groups II, IV, and V have higher chemical indices and, as seen in Figure 2, have broader confidence limits. As shown in Figure 3, specimens with higher chemical indices have hydration rates that are also more temperature-sensitive, so the error rises to 50-150%.

All of the hydration dates are too old, indicating that the predicted hydration rates are too slow. Therefore, the predicted



Figure 10. Summary of results with the initial temperature model. Horizontal lines indicate radiocarbon ages of components. <u>Inset</u>: Air temperatures used in initial model. The dotted curve shows Holocene air temperature changes as proposed by Fairbridge (1972). soil temperatures must be too low. In an effort to isolate inaccuracies in the soil temperature model, the author altered the model to roughly fit the Holocene air temperature curve as proposed by Fairbridge (1972:295). This curve shows a climatic optimum or hypsithermal about 6°C warmer than today at about 4000 B.P. It was simple to simulate this in the existing computer program by adding a branching statement that redefined the mean annual temperature as 5°±2.5°C between about 3000 and 6000 B.P. This corresponds to the deposition of Loess 6, Sand 2, and part of Loess 5 which are found between 45 and 75 cm below surface in the Dry Creek stratigraphic profile (Figure 4). The results of this change were as follows:

	Group I	16,613	+ 8,183 - 5,640
	Group II	11,827	+13,603 - 6,030
Component 2 (radiocarbon age: 10,690 ±250)	Group IV	9,052	+15,833 - 5,397
∼140 cm	Group V	9,799	+15,359 - 5,624
Grou (weig	ps I,II,IV,V hted average)	12,487	+12,536 - 5,666
Component 3 (radiocarbon age: 3,430 ±75 3,655 ±60 4,670 ±95)	Group III	8,651	+ 2,533 - 2,053

~ 50 cm

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This is a considerable improvement, but Group III is still 3500 years too old and its hydration age overlaps almost completely with Component 2 as shown in Figure 11.

If the climatic optimum is made 2°±2.5°C warmer and shifted to 2000-4000 B.P. (40-60 cm) where it most strongly affects Group III, the calculated ages are as follows:

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	Group I	15,923	- 5,288
	Group II	11,388	+12,647 - 5,718
Component 2 (radiocarbon age: 10,690 ±250)	Group IV	8,704	+14,764 - 5,133
∼140 cm	Group V	9,417	+14,286 - 5,337
Group (weigh	s I,II,IV,V ted average)	11,992	+11,585 - 5,356
Component 3 (radiocarbon age: 3,430 ±75	Group III	6,755	+ 1,984 - 1,599

~50 cm

3,655 ±60

4,670 ±95)

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Component 2 is now in acceptable agreement with the radiocarbon age. However, Group III is still too old, but less so, and there is still overlap in the Component 2 and Component 3 hydration ages, as seen in Figure 12. The Group III hydration age could be lowered by making the climatic optimum still warmer and later, but to do so would do violence to what is known about the hypsithermal as reviewed by Péwé (1975:111). Further, Péwé cites no evidence for a hypsithermal in the



Figure 11. Summary of results with simulated climatic optimum (hypsithermal). Inset: Simulated air temperature increase from 75 to 45 cm, roughly equivalent to a hypsithermal between 6000 and 3000 B.P. Note the improved agreement between hydration and radiocarbon ages.





Healy area and there seems to be little in the stratigraphic profile between 75 and 40 cm.

From Figure 3, it is clear that obsidian with a chemical index around 20, <u>e.g.</u>, Group III, is relatively insensitive to temperature change from 0° to 8°C. Additional temperature changes required to lower the hydration age of Group III would be unrealistically large. Therefore, the author is forced to conclude that all of the variance between hydration ages and radiocarbon ages cannot be explained by inaccuracies in the temperature model alone.

The predicted average hydration rate for Group III with a warm, late climatic optimum is $0.38 \mu^2/1000$ yrs. The actual rate is about $0.6 \mu^2/1000$ yrs as computed from

 $k = R^2/t$ or $k = (1.60\mu)^2/~4000$ yrs = $0.6\mu^2/1000$ yrs To arrive at a rate this high, since it is dangerous to raise temperatures any further, the chemical index must be raised from 21.3 to about 30. That is far beyond the limits of error for determination of the chemical index. From this, we must conclude that Friedman and Long's (1976) method of relating chemical composition to hydration rates (see page 22) is not universally applicable. The two groups (I and III) with the lowest chemical indices (27.4 and 21.3) produce the most anomolous hydration dates. The other groups with chemical indices above 37 yield acceptable ages with either climatic optimum simulation, so it would seem that Friedman and Long's chemical index formula

 $CI = SiO_2 - 45(MgO + CaO) - 20(H_2O^+)$

holds for some obsidians but not for those relatively high in MgO, CaO, and perhaps H_20^+ . Group I has the highest H_20^+ value (0.98%) and Group III has the highest MgO and CaO values (0.23% and 0.81%); apparently, the relationship between these and perhaps other constituents and the hydration rate is more complex. The obsidian from Hokkaido analyzed by Katsui and Kondo (1976:133) is also high in MgO and CaO (0.43% and 1.90%). Friedman and Long's formula gives a chemical index of -35.0 for this obsidian. Using -35.0 yields a predicted hydration rate about one hundredth of that observed by Katsui and Kondo.

Summary.

This experiment with obsidian hydration dating as an independent dating technique gave results that begin to agree with the radiocarbon dates only when the temperature model approaches fantasy. This can be summarized as follows: ¹⁴C ages

		initial temp. model	with hypsithermal	warm, late hypsithermal	
Component	3	11,200	8,650	6,760	3,355-4,765
Component	2	17,050	12,500	12,000	10,690 ±250

Hydration Ages

Error that could not easily be attributed to poor temperature modeling was attributed to weaknesses in the chemical compositionhydration rate relationship used here.

B. SUGGESTIONS FOR FUTURE RESEARCH

Before obsidian hydration can be used with confidence as an independent, absolute dating technique, more work needs to be done in the areas of chemical composition-hydration rate relationships and subarctic soil temperature modeling. The former involves straightforward laboratory techniques but little has been done in this area because it takes years for measurable hydration rinds to form even at elevated temperatures. There may be danger in extrapolating back to lower temperatures but there is no evidence on this yet. What is needed is a repetition of Friedman and Long's work (see pages 21 -23) involving a more inclusive sample of obsidians. When we can relate chemical composition to hydration rates with more precision, error factors can be reduced by 50% or more.

Soil temperature modeling may be a problem for some time to come. While it may soon be possible to model present-day soil temperature regimes, it does not seem likely that accurate models will be developed for paleo-soil temperatures. As mentioned earlier, there are numerous variables involved that will be difficult to assess diachronically. Until we can, obsidian hydration dates are doomed to be bounded by large error factors and, consequently, of little use to the prehistorian interested in absolute dates.

After more work is done on chemical composition, obsidian hydration could be useful as a relative dating technique. In shallow sites, temperature could be arbitrarly set at a constant. Adjusted hydration rates based on chemical composition could then be used to find relative ages within or between sites.

Another interesting possibility is that obsidian hydration could be used to generate quantitative information on paleoclimates. This project has produced evidence of a sort for a climatic optimum in the Healy area where none was reported before. However, it would be necessary to have some obsidian temporally between Components 2 and 3 to arrive at more definite conclusions.

In retrospect, this work, if nothing else, points out what variables have to be considered in using obsidian hydration as a chronological indicator. Before archaeologists can begin to realize its promise, answers must come from laboratory work, not field work. The problem need not be passed to geochemists; we, as archaeologists, stand to gain the most from the solution.

APPENDIX I

KNOWN AND POSSIBLE ALASKAN OBSIDIAN SOURCES

Because the number of obsidian sources within a region is often small and because these sources differ in amounts of sodium, manganese, iron, rubidium, scandium, zirconium, titanium, the rare earths, and other minor elements that they contain, archaeological obsidians that are chemically characterized in terms of these elements ("fingerprinted") can be traced to their geologic source and trade routes can be hypothesized. This has been sucessful in Southwestern Asia and the Mediterranean (Dixon, Cann, and Renfrew 1968; Dixon 1976), New Zealand (Reeves and Ward 1976), Mesoamerica (Stross et al. 1976) and California (Ericson, Hagan, and Chesterman 1976) where the obsidian sources are relatively well known.

Presently, eight geological sources are known for Alaska. These are as follows:

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- <u>Batza Tena</u> (Patton and Miller 1970; Clark 1972). This source is near the village of Hughes on the Koyukuk River. Archaeological obsidian from as far away as Dry Creek and Lake Minchumina is from this source (written communication from Erle Nelson to Charles Holmes of April 8, 1976). The sodium-manganese ratios for Healy Lake (Cook 1969) are within the range reported for Batza Tena (Wheeler and Clark 1977).
- <u>Gold Creek</u> (John P. Cook, personal communication). This source lies between Gold Creek and Linda Creek in the Chandalar (C-6) quadrangle at approximately N67°31'/W149°10'.
- 3. <u>Nowitna River</u> (Griffin, Wright, and Gordus 1969). The Nowitna flows northward into the Yukon near the village of Ruby. The specimen reported is "from a beach near the Norwitikata River" (<u>ibid</u>., p.155). It is designated here

as Nowitna since Orth (1967:705) gives "Norwitikata" as a variant of Nowitna. This source is partially confirmed by the presence of large rhyolitic and andesitic flows near the Nowitna's headwaters (Eakin 1918:Plate II).

4. Wrangells Group.

a. <u>Nizina Mountain</u> (Moffit 1938:93). This source is located near the village of Kennicott in the central Wrangells. Moffit reports obsidian in the "morainal debris" immediately west of Fredrika Glacier.

b. <u>Mount Drum</u> (Griffin, Wright, and Gordus 1969). This source may not be separate from Nizina Mountain. It is reported (<u>ibid.</u>, p.155) as being from "Mount Drum, Nizina District" although Mount Drum is about 160 km from Nizina. For now, I presume it is a separate source since Mendenhall (1905:62) reports acidic lavas from the southwest slope of Mount Drum.

c. <u>Jacksina River</u> (Moffit 1943:153, 158). This source is near the village of Chisana in the north central Wrangells. Obsidian is said to occur in the Wrangell lavas around Nutzotin Mountain and near the Jacksina Canyon south of Wait Creek.

5. Aleutian Islands Group.

a. <u>Cape Chagak</u> (Byers 1959:312). Dense black and vesicular gray obsidian occurs about 5 km inland from Cape Chagak on the northern tip of Umnak Island. Laughlin (1967:436) says that artifacts made of this obsidian are found at Anangula.

b. <u>Semisopochnoi</u> <u>Island</u> (Coates 1959:489). Dacitic obsidian can be found associated with pumice from the eruption of the central caldera of the island.

It is likely that other obsidian sources can be found on the Aleutians and the Alaska Peninsula. My literature search on this area was not exhaustive.

Some of the obsidian from Lake Minchumina (Holmes 1975:106) and Gulkana (Workman 1976) comes from the "same unknown source" (written communication from Erle Nelson to Charles Holmes of April 8, 1976). To my knowledge, the obsidians from Nizina Mountain and Jacksina River have not been fingerprinted, so it is possible that the "unknown source" is one of these. On the other hand, there could be a number of undescribed sources. Obsidian is most likely to form from felsic (acidic) lavas. Generally, obsidian older than than the late Tertiary is devitrified or perliticized so the most likely places to look would be around Tertiary and Quaternary felsic lava flows. Such flows are shown on Map I along with the known obsidian sources. Until all of the known geologic sources as well as a great many more of the archaeological obsidians have been fingerprinted, we do not known if more sources exist, nor can we say much about prehistoric obsidian procurement patterns.

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Map I. Location of known and possible obsidian sources. The numbers indicate known sources and correspond to those in the text. The shaded areas are Tertiary and Quaternary en lo felsic volcanic flows and are possible obsidian sources. Data on the volcanics are from Beikman (1974a, 1974b, and - 8 , 217h. 1975) and Seikman and Lathram (1976). 5.P • 0 a 00. 2000 D 0'

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APPENDIX II

RADIOCARBON DATING AT DRY CREEK

Below is a list of the accepted dates from the Dry Creek site. There are several others but these are from small samples, have high counting errors, and as such, are unreliable. When the dates shown here are plotted versus depth as shown in Figure 13, it shows that deposition has been relatively constant over the last 11,000 years.

Laboratory Number	Age, Years B.P.	P. Provenience			
SI-2880	11,120 ±85	Comp. 1, Loess 2			
SI-1561	10,690 ±250	Comp. 2, Paleosol 1			
SI-2329	9,340 ±195	Paleosol 2			
SI-1935B	8,355 ±190	Paleosol 3			
SI-2331	6,270 ±110	Paleosol 3			
SI-1937	4;670 ±95	Comp. 3, Paleosol 4a			
SI-1934	3,655 ±60	Comp. 3, Paleosol 4a			
SI-2332	3,430 ±75	Comp. 3, Paleosol 4a			
SI-2333	1,145 ±60	Paleosol 4b			
SI-1933B	375 ±40	Paleosol 4b*			

* On peat and roots; all others are on charcoal

SI = Smithsonian Institution

Laboratory numbers are from Thorson and Hamilton (1977:166).





APPENDIX III

TEXT OF COMPUTER PROGRAM

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OBSIDIAN HYDRATION DATING
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WRITE (6,2)

2 FORMAT (1H1, T7, 'CATALOG NO.', T20, 'GROUP', T30, 'CI', T37, 2'RIND', T44, 'DEPTH, CM', T57, 'AGE') 7 AMP = 13.98 PI = 3.1416 3Z = 0.05 SUMRAT = 0.0SUMKMX = 0.0SUMKMN = 0.010 READ (5,11) ICATNO, IGROUP, CI, RIND, IDEPTH, DEPTH 11 FORMAT (1X, I4, 1X, I1, 2X, 2F10.2, I7, F10.2) 12 IF (CI .GT. 100.) GO TO 120 IF (CI .LE. 35.0) GO TO 13 IF (CI .GE. 37.0) GO TO 14 13 A = (2.085E14)*CI + 1.186E16AMAX = A + 1.400*(0.671E30*(.25 + (CI - 14.875)**2/470.499))**.5AMIN = A - 1.400*(0.671E30*(.25 + (CI - 14.875)**2/470.499))**.5 EOR = -11.613*CI + 10890.24 EORMAX = EOR + 1.400*(615.57*(0.25 + (CI - 14.875)**2/470.449))2**0.5 EORMIN = EOR - 1.400*(615.57*(0.25 + (CI - 14.875)**2/470.499))2**0.5 GO TO 16

14 A = (-4.667E14)*CI + 2.666E16 AMAX = A + 1.250*(3.868E30*(0.2 + (CI - 44.54)**2/38.814))**.5 AMIN = A - 1.250*(3.868E30*(0.2 + (CI - 44.54)**2/38.814))**.5 EOR = -54.028*CI + 12340.604 EORMAX = EOR + 1.250*(4009.558*(0.2 + (CI - 44.54)**2/38.814)) 2**0.5 EORMIN = EOR - 1.250*(4009.558*(0.2 + (CI - 44.54)**2/38.814)) 2**0.5 16 DO 75 J = 1, IDEPTH, 1 4 YEARK = 0.0YERKMX = 0.0YERKMN = 0.017 X = 0.018 D0 55 I = 1,50,120 ALPHA = 1.050*Z + 0.236 ALMAX = (ALPHA + 1.150*(0.01040*(1./7. + ((Z - 0.796)**2)/ 21.0837))**D.5 ALMIN = (ALPHA + 1.150*(0.01040*(1./7. + ((Z - 0.796)**2)/ 21.0837))**0.5 IF (DEPTH .LT. 40.) GO TO 21 IF (DEPTH .LT. 65.) GO TO 22 ANTEMP = -4.6GO TO 25 21 ANTEMP = -1.1GO TO 25 22 ANTEMP = 7.0

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25 TEMP = ANTEMP + AMP*(EXP(-Z*(PI/ALPHA)**0.5))*SIN(2.*PI*X/50. 2-Z*(PI/ALPHA)**0.5

TEMPMX = ANTEMP + AMP*(EXP(-Z*(PI/ALMAX)**0.5))*SIN(2.*PI*X/50. 2-Z*(PI/ALMAX)**0.5)

TEMPMN = ANTEMP + AMP*(EXP(-Z*(PI/ALMIN)**0.5))*SIN(2.*PI*X/50. 2-Z*(PI/ALMIN)**0.5)

IF (DEPTH - 45.) 30,40,40

30 GO TO 45

40 TEMPMX = TEMPMX + 2.5

TEMPMN = TEMPMN - 2.5

45 DAYK = A*EXP(-EOR*(1./(TEMP + 273.18)))

DAYKMX = AMAX*EXP(-EORMIN*(1./(TEMPMX + 273.18)))

DAYKMN = AMIN*EXP(-EORMAX*(1./(TEMPMN + 273.18)))

50 YEARK = YEARK + DAYK

YERKMX = YERKMX + DAYKMX

YERKMN = YERKMN + DAYKMN

- 53 X = X + 1.0
- 55 CONTINUE
- 60 YEARK = YEARK/50.

YERKMX = YERKMX/50.

YERKMN = YERKMN/50.

65 Z = Z + 0.01

DEPTH = DEPTH - 1.0

70 SUMRAT = SUMRAT + YEARK

SUMKMX = SIJMKMX + YERKMX

SUMKMN = SUMKMN + YERKMN

75 CONTINUE

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AVERAT = SUMRAT/(100.*Z)

AVRTMX = SUMKMX/(100.*Z)

AVRTMN = SUMKMN/(100.*Z)

80 AGE = (RIND**2./AVERAT)*1000.

AGEMAX = (RIND**2./AVRTMN)*1000.

AGEMIN = (RIND**2./AVRTMX)*1000.

PLUS = AGEMAX - AGE

SMINUS = AGE - AGEMIN

WRITE(6,100) ICATNO, IGROUP, CI, RIND, IDEPTH, AGE, PLUS, SMINUS

100 FORMAT (1H0, T9, 15, T22, 11, T29, F4.1, T37, F5.2, T47, 13, T56, 2F7.0, T67, '+', T68, F7.0, T79, '-', T80, F7.0)

GO TO 7

120 STOP

END

SAMPLE PRINTOUT

CATALOG NO.	GROUP	CI	RIND	DEPTH,CM.	AGE		
1000	1	27.4	2.20	138	15,923	+ 7,377	- 5,228
2000	2	40.4	2.61	141	11,388	+12,647	- 5,718
3000	3	21.3	1.60	53	6,755	+ 1,984	- 1,599
4000	4	37.3	1.82	145	8,704	+14,764	- 5,133
5000	5	38.1	2.05	134	9,417	+14,286	- 5,337

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