Hydration-Rind Dating of Basaltic Glass: A New Method for Archaeological Chronologies

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ABSTRACT

A REVIEW of the historical development of hydration-rind dating is presented. Basaltic glass has been found to hydrate at a linear rate. During glass hydration an immobile product layer is formed at the interface between reactants. The immobile product layer develops from a microfracture chemical-channel zone. This layer converts to a band of palagonite. The rate of palagonite banding is directly related to the chemistry of the glass, the availability of water, and the temperature during hydration. Rate formulas are presented. Archaeological sites in the Hawaiian Islands provide a test of the validity of this new dating tool. Sites from two islands are discussed in relation to the correspondence of hydration-rind with C-14 dates. The immediate prospects for the use of the method and tentative conclusions are offered.

INTRODUCTION

Much of the literature concerning the structure, chronology, and technology of glass begins by emphasizing that these processes are poorly understood. Little has changed since the past, and we also begin with the same declaration. Glassmaking is probably one of the oldest manufacturing arts, dating back to about 3000 B.C. (Greene 1961). Glass is not solely a manufactured substance; it is available in perhaps greatest volume as a natural product of vulcanism. Glass has been defined by Morey (in Greene 1961) as "an inorganic substance in a condition which is

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continuous with, and analogous to, the liquid state of that substance, but which, as a result of a reversible change in viscosity during cooling, has attained so high a degree of viscosity as to be for all practical purposes rigid." Bonatti (1965) suggests that glass viscosity can approximate 10^{14} poise. Thus, glass is essentially a super-cooled liquid which for the most part is not in equilibrium with its environment. As a consequence, glass favors a change in state toward a more stable substance or a series of more stable substances.

This paper will examine the process by which volcanic glass changes state and the implications of this process for the archaeologist, geologist, and historian. The theory and method of hydration-rind dating of naturally occurring glass is specifically examined, and tests of its utility in substantiating chronologies in the Hawaiian Islands are presented. Specific reference is made to archaeological sites in Halawa Valley on the island of Molokai and to Anaehoomalu sites on the island of Hawaii.

Historical Development of Hydration-Rind Dating

On the basis of chemical content, there are two major categories of natural glass: obsidian, an acid glass (high silica content) predominantly produced in continental areas, and sideromelane, a mafic glass (low silica content) commonly found in oceanic as well as continental areas. These glasses hydrate to intermediate products called perlite and palagonite, respectively. The basaltic glass-palagonite system was first studied in 1846 when Von Waltershausen introduced the term palagonite to distinguish a brown glassy material associated with pyroclastics in eastern Sicily and Iceland. Peacock (1926), in a study of the petrology of Iceland, defined palagonite to be a hydrated volcanic glass with a refraction index ranging from 1.46 to 1.49. He found the water content of these palagonites to be between 18 and 25 percent. Fuller (1932), Hoppe (1941), Hentschel (1951), Denaeyer (1963), and Morgenstein (1967) concluded that palagonite is an alteration product of mafic volcanic glass. Bonatti (1965) believes that most palagonite is formed at high temperatures (during syngenesis) and that low-temperature palagonites (diagenetic) are rare. He based most of his conclusions on the work done by Marshall (1961). The latter estimated the diffusion coefficient of glass by using Fick's Law and found that, at 20°C, the coefficient for all natural glasses is about the same. He calculated that at temperatures less than 50°C it would take on the order of 100 million years to form 2 to 5 microns of perlite rind; but at temperatures greater than 300°C, less than a year's time would be required to form perlite rinds to a depth of 100 microns. Sholze and Mulfinger (1959), Marshall (1961), and Hawkins and Roy (1963) calculated the activation energy E ($D=D_oe^{-E/RT}$ equation for the diffusion coefficient as a function of temperatures) for the diffusive process, and obtained values ranging between 19 and 31 K cal/mole. (Marshall [1961], E=30 K cal/mole; Hawkins and Roy [1963], E=25 K cal/mole; Sholze and Mulfinger [1959], E=19–31 K cal/mole.) In 1966 Friedman et al. published their most extensive work on the thermodynamics of glass hydration. They found that in the obsidian-perlite system the activation energy E was 20 K cal/mole and the diffusion coefficient was 5×10^{-5} cm^2/10^6 years at 20°C. This diffusion coefficient is greatly different from the 10^{-10} cm^2/10^6 years published by Marshall (1961), and as a consequence those authors concluded that hydration of natural glass takes place during low-temperature diagenesis

(20 microns per 40,000 years at 20°C). Friedman et al. (1966) explain their larger diffusion coefficient thusly: "Marshall assumed that the diffusion coefficient is independent of the concentration of water in a glass. Our observations on the optical properties of perlite rims and obsidian cores appear to contradict this assumption."

Today the problem of hydration-rind dating is no longer centered about the earlier question of syngenetic versus diagenetic formation of hydration rinds, but rather in the rate formula which is used for diagenetic hydration. Meighan et al. (1968) have established C-14 dates and hydration analyses on obsidian tools from the Morret archaeological site in Colima, Mexico. They assumed a linear rate of hydration (years/micron). Friedman and Evans (1968), in a discussion of a paper by Meighan et al. (1968), pointed out that hydration appears to proceed at a quadratic rather than a linear rate, and recalculated the linear rate using the formula:

$$\text{Thickness}^2 = K \text{ time (microns}^2/\text{year)}$$

The basis for Friedman and Evans' (1968) argument is the belief that water diffuses into the glass structure at an increasingly slower rate as the thickness of the alteration layer increases. Friedman et al. (1966) believe that this rate of diffusion is repeated every 20 microns in the perlite structure. This 20-micron banding was suggested by Friedman et al. (1966) to account for the increases in volume brought about through the addition of water to the glass. Therefore, in their opinion hydration proceeds in 20-micron steps which are produced in response to glass fracturing. The present work, however, does not support the concept of 20-micron fracturing, nor does it support the concept of decreasing rates of hydration with increasing time. We fully support the work done by Meighan et al. (1968). Our basis is a theoretical development of glass hydration which does not rely on thermodynamic calculations derived from crystalline solids applied to amorphous glasses (Morgenstein 1969), but does rely on petrographic evidence.

Two other publications are important when considering the historical development of hydration-rind dating. Michels (1967), in a discussion of the historical development of hydration studies on glasses, mentioned several problems which have occurred with this new technique. Among these are the problems of artifact reuse and the dependence of the rate formulas on local temperatures. Finally, Newton (1971) has given a chronological account of the investigations of hydration-rind dating on manufactured glasses. His paper points up the fact that there have been few applied scientific investigations undertaken on the manufactured glasses over a substantial period of time. Newton (1971) has, however, handled the historic survey with a careful presentation.

THEORY

Hydration-Rind Dating of Basaltic Glass

Glass hydration is an intermediate process between solid state and fluid reactions. In solid state reactions an immobile product layer is built at the interface of the reactants. In fluid reactions, molecules are available to one another because of kinetic effects such as Brownian movement. In liquid to solid diffusion, as in the case of

glass hydration, an immobile product layer builds up between the basaltic glass and the atmospheric interface (either as a water body such as in the oceans, lakes, or ground water; or as water vapor in the air and soil). The immobile product layer contains a higher concentration of water than does fresh glass. This concentration varies depending on the duration and degree of hydration. The hydrated immobile product layer reacts in a manner similar to a sponge in that it easily transports fluid to the fresh glass surface. In this way the reaction does not slow down with increasing depth of hydration, but rather remains constant (Morgenstein 1969). This concept is fundamental in the development of the theory of glass hydration. The rate of reaction is controlled at the interface of the fresh glass and the water-bearing agent. The fresh glass surface is an area of reaction which contains the least concentration of water. The water-bearing environment (the supplier) can be either the ocean or, as in a later stage of hydration, the immobile product layer and the hydrated perlite or palagonite glass itself (the transporter).

The immobile product layer is composed of two genetically interrelated zones. The first to develop is a microfracture-chemical channel zone which may be considered the mist zone of the glass. This zone represents the path taken by water during its entrance into the glass structure. The second zone, which develops from the first, is the true immobile product layer. It has a high density of water conduits and shows initial remobilization of iron and manganese ions. These begin to combine and crystallize out of the palagonite to form both iron and manganese oxide hydrates. Smectites (clay minerals) also begin to organize at this stage of hydration (Morgenstein 1967, 1969).

The geometry of the immobile product layer is directly related to the design of the palagonite bands. The mist zone grows to a maximum length of 50 microns in basaltic glass (sideromelane) in the ocean system (with temperatures between 0° and 5°C). At this stage of growth the quantity of water and density of channels are now sufficient to consider this zone the true immobile product layer. The new immobile product layer develops to a maximum length of 50 microns for similar basaltic glass in the ocean system. During the transfer of the mist zone to the immobile product layer, a new continuing mist zone develops at the interface of the immobile product layer and the fresh glass. Hydration is not interrupted during this process. The resulting palagonite banding is 50 microns in thickness. These bands are distinguishable by their differing degrees of ionic remobilization and resulting crystallization. The palagonite bands develop from the 50-micron immobile product layer at the time this layer contains a sufficient quantity of water for major crystallization.

In similar glasses not in the ocean system and situated in environments of higher temperatures, the widths of the mist zone, immobile product layer, and palagonite bands remain equal but are thinner than in the ocean system. In addition, if glass composition changes to a more silica-rich state (i.e., toward obsidian) and temperatures remain constant, the banding width becomes smaller. Friedman et al. (1966) report 20-micron banding widths for perlite. These are 30 microns smaller than the low temperature oceanic palagonites. Thus, in effect, an increase in temperature and/or an increase in the silica-aluminum concentration of the glass results in smaller banding widths. In order to extend this concept to syngenesis, the very high-temperature palagonites (at the time of glass formation) do not have any

banding width whatsoever. Their rinds are an unstructured continuous zone of equal hydration. In most cases of syngenesis, fresh glass does not occur along with the palagonite. These samples are solid chunks of highly fractured hydrated glass. They are easily distinguished from the diagenetic-produced palagonites by the absence of banding and therefore are not applicable to hydration-rind dating.

Pure silica-aluminum-oxygen glasses are relatively rare, even in manufactured artifacts. They hydrate at very slow rates so that at normal diagenetic temperatures they remain relatively fresh over geologically long periods of time. Philpotts and Miller (1953) report on unaltered Precambrian glass (nonmarine) which was dated (K/Ar) at 975 million years. It is very doubtful that this Precambrian glass is composed of a pure silica-aluminum-oxygen composition. However, it is probably closer to that composition than to a glass of basaltic composition. The very acid glasses also eventually hydrate, but usually during metamorphic and hydrothermal disturbances (i.e., at high temperatures and pressures).

In summary, water enters the glass structure through channel pores at the mist zone. This zone enlarges through a diffusive process into the glass until a specific concentration of water has been reached. This concentration is dependent upon glass chemistry (i.e., the silica, aluminum, oxygen concentration). The mist zone converts to the immobile product layer which grows to the same thickness as the original mist zone. The mist zone continues to grow into the glass structure. At a point where there is an increased and sufficient quantity of water in the immobile product layer it converts to a band of palagonite. The process continues until all the fresh glass is used up. The resulting geometry is a sequence of palagonite bands, each of equal thickness and each paralleling one another (Plate I*a*).

In Plate I*a*, 50-micron palagonite bands can be seen growing around a calcic-feldspar phenocryst. The feldspar is unaltered during this process. The palagonite bands are of equal width and vary only slightly around corners. In all cases the bands parallel one another and only when the section has been cut obliquely do the bands appear to converge. The lower photograph (Plate I*b*) is taken in the mist zone of the glass. The microfracture-channels are growing into the fresh glass at the top of the photograph. There is a higher density of these channels at the bottom of the photograph. This is the interface between the mist zone and the immobile product layer. Plate II*a* shows the mist zone along an internal glass fracture. The channels are equidimensional on either side of the fracture. An immobile product layer is beginning to form at the center of the fracture. Plate II*b* shows the entire sequence of the features discussed in the text. The portion of the photograph labeled *S* is sideromelane (fresh glass); *P1* through *P4* are individual palagonite bands. The mist zone and immobile product layer are between the sideromelane and the first band of palagonite.

Plate II*c* is the most comprehensive photograph of the palagonite formation process. Once again *S* represents fresh sideromelane glass, and *P* represents palagonite. The mist zone and immobile product layer separate these two glasses. The fossilized mist zone and immobile product layer are visible in the palagonite bands. Both left and right of the *P* in the photograph, linear palagonite fossil-channels of the mist zone appear. These relationships indicate continual growth of the palagonite during hydration. They appear to confirm the theoretical development of palagonite bands from the mist zone and immobile product layer.

Let us now consider the development of a palagonite band through time as well as the derivation of the rate formula. It has been previously stated that the mist zone is the first to form and it does so through a diffusive process of hydration. Consider an imaginary banding width of 1 micron for the mist zone under any set of specific environmental parameters. During the first period of time (T1) when a newly chipped glass artifact undergoes hydration it forms this 1-micron-thick mist zone structure. During an equal imaginary period of time (T2) the mist zone is replaced by a 1-micron-thick immobile product layer, and a new mist zone forms at the fresh glass surface. During T1 and T2 no palagonite is formed; there has been only the development of the intermediate morphologies. However, during these periods of time there has been hydration, and the rate of hydration (R_h) is equal to 2 microns of development during a total time period equaling two time units. At T3 the immobile product layer is replaced by a 1-micron-thick band of measurable palagonite. The mist zone is replaced by the immobile product layer and a new 1-micron-thick mist zone has grown into the fresh glass. The rate of hydration (R_h) is equal to:

$$R_h = (N + 2) \, Q/T \qquad\qquad (1)$$

where N equals the number of palagonite bands, Q equals the thickness of each band, and T equals time. Let us give a value of one year to T; since 3 years have elapsed, T=3. The rate of hydration is therefore:

$$R_h = (1 + 2) \, (1 \text{ micron}) \, / \, 3 \text{ years}$$
$$= 1 \text{ micron} \, / \text{ year}$$

The rate of palagonitization is different, however, because in a 3-year period of time only 1 micron of palagonite was formed. The rate formula for palagonitization (R_p) is:

$$R_p = N \, Q \, / \, 3 \, T \qquad\qquad (2)$$

This formula only applies to the first stage of palagonite formation (i.e., one band of palagonite). The rate formula for the second and consecutive stages of palagonite formation is:

$$R_p = N \, Q \, / \, T \qquad\qquad (3)$$

Neither formula (2) nor formula (3) will apply to the overall rate of palagonite formation for an unknown aged artifact or volcanic glass. The rate formula which must be used to determine the actual age of a sample, based upon the knowledge of the rate of reaction, is:
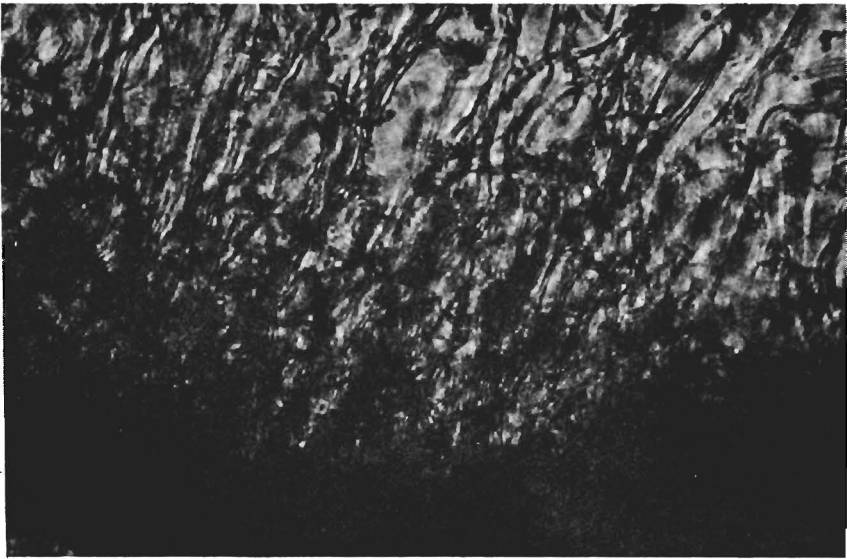
$$R_p = (N - 2) \, Q \, / \, T \qquad\qquad (4)$$

This states that the rate of palagonitization is equal to the number of bands of palagonite counted, minus two bands (for the immobile product layer and mist zone which is not counted), multiplied by the thickness of each band and divided by time. Formulas (1) and (4) are directly applicable to hydration-rind dating. If the
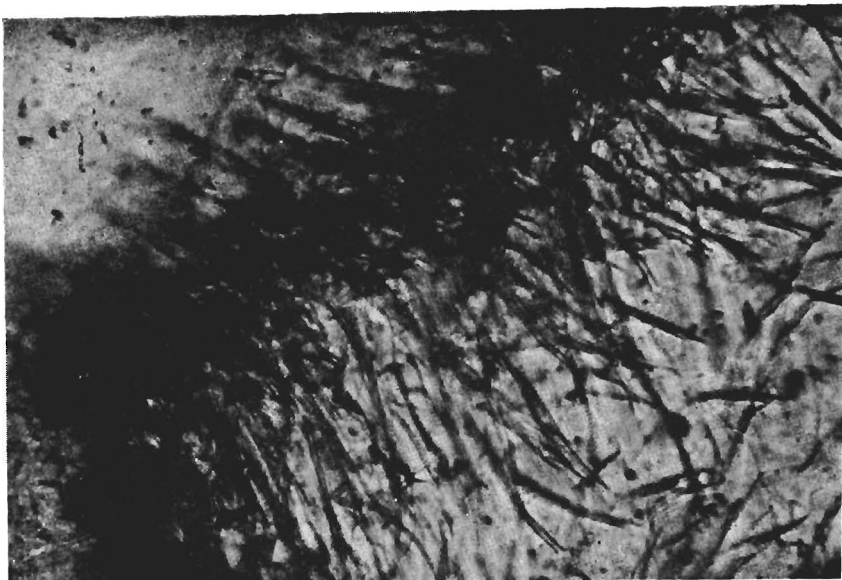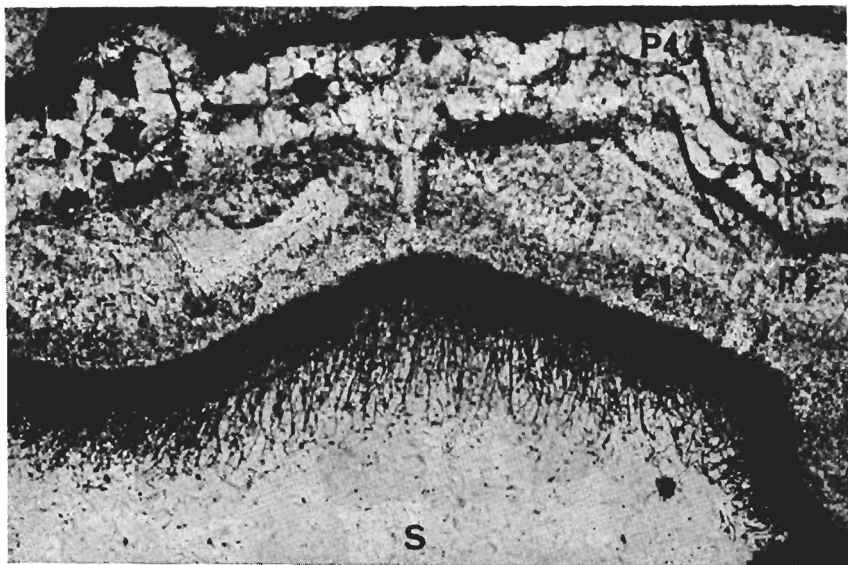
A

200μ

B

25μ
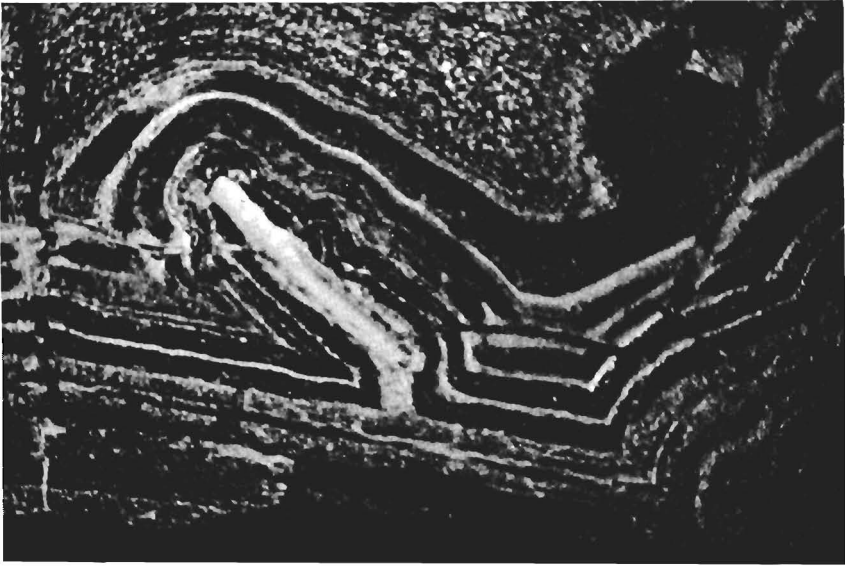
Plate I   The palagonite bands and the details of the mist zone. *a*, palagonite bands
         are shown growing around a feldspar phenocryst. Plane polarized light.
         Scale as shown. *b*, the mist zone with its micro-fracture chemical channels
         which transport water into the glass. Plane polarized light. Scale as shown.

A

50 μ

B

100 μ

Plate II The relationship between the mist zone and the immobile product layer. *a*, the mist zone along a fracture is shown in sideromelane glass. Plane polarized light. Scale as shown. *b*, the mist zone, immobile product layer, fresh sideromelane glass *(S)* and palagonite bands *(P1* through *P4)* are shown. Plane polarized light. Scale as shown.
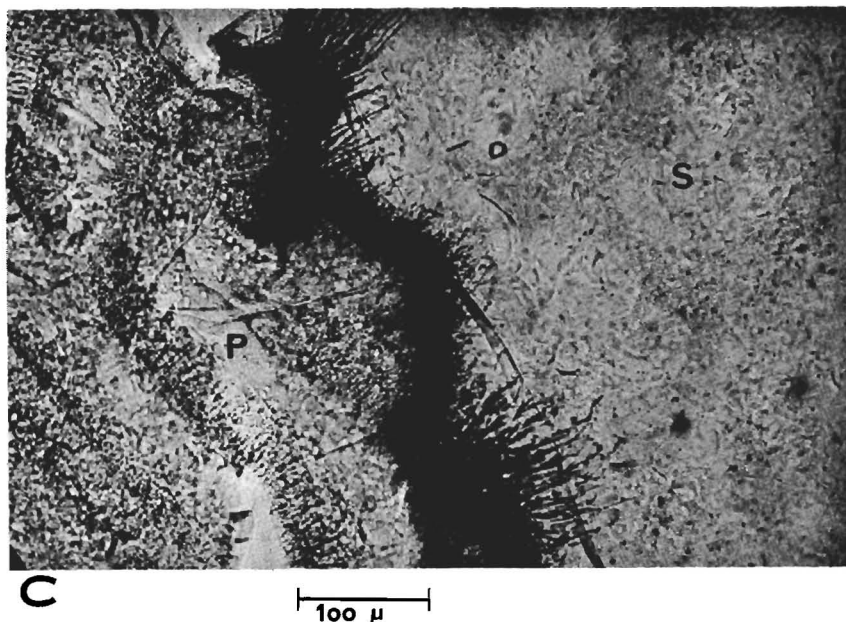
Plate II c, the relationship between the immobile product layer and the palagonite bands. S represents fresh sideromelane glass. P represents palagonite. Plane polarized light. Scale as shown.

immobile product layer and mist zone can be measured along with the palagonite bands, then a linear formula of:

$$R_h = N Q / T \qquad (5)$$

will apply. If the intermittent morphologies cannot be measured, then either formula (1) or formula (4) will apply.

A comprehensive study of the theoretical development of hydration-rind dating is the subject of a forthcoming paper (Morgenstein, in preparation). Both physical and chemical aspects of natural and artifact glasses will be reviewed. There are, however, several points in this study which are relevant here. In brief, Figure 1
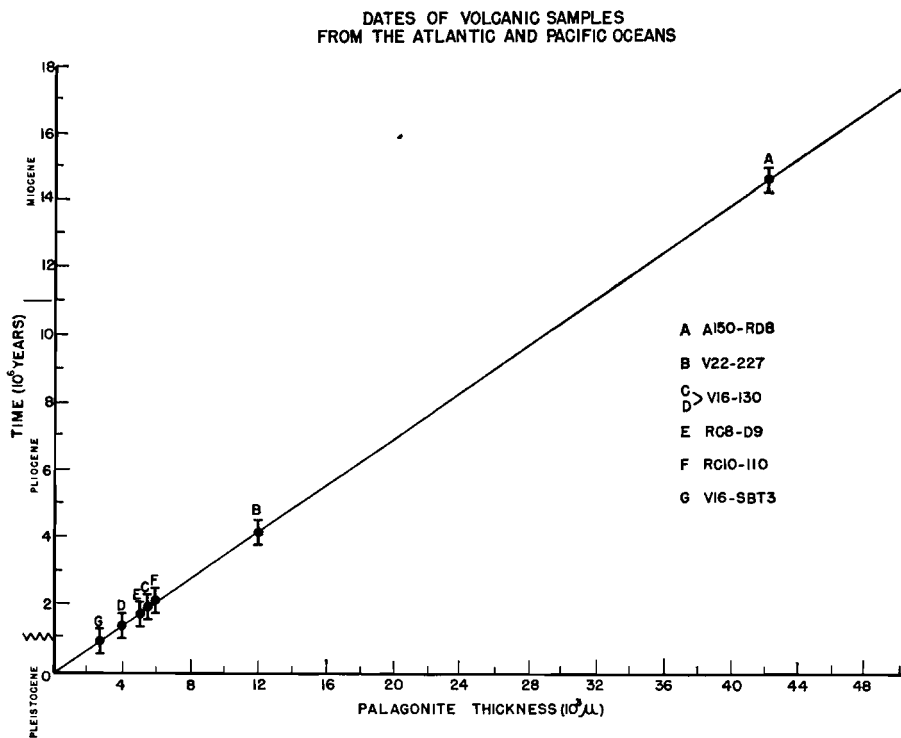

Fig. 1   Dates of volcanic samples from the Atlantic and Pacific oceans.

depicts the rate curve for basaltic glass in the marine environment. Seven Miocene to Pleistocene glasses were dated using the hydration-rind method. Sample A is a dredge (A150–RD8) acquired by Lamont-Doherty Geological Observatory at lat. 31°49′N and long. 42°25′W on the Atlantic Ocean floor. It has been dated as Miocene by paleontological methods (Saito et al. 1966). The corresponding hydration-rind date of approximately 14 million years fits the paleontological data very well.

During 1970 seven lava flows were sampled on the island of Hawaii for volcanic glass. These are listed in Table 1 along with the corresponding hydration-rind measurements obtained. A least-squares analysis program was used to find the slope

TABLE 1. HYDRATION-RIND THICKNESSES OF HAWAII LAVA FLOWS

LAVA FLOW	RANGE OF RIND (MICRONS)
1843 Flow, Mauna Loa, Saddle Road	1.50 to 1.51
1859 Flow, Kona Coast	1.21 to 1.24
1926 Flow, Hoopuloa Flow, Kona Coast	0.49 to 0.55
1935 Flow, Mauna Loa, Saddle Road	0.38 to 0.41
1950 Flow, Honokaa Branch, Kona Coast	0.22 to 0.25
1950 Flow, Kaapuna Branch, Kona Coast	0.23 to 0.25
1950 Flow, Kaohe Flow, Kona Coast	0.21 to 0.27

of the line drawn from the mean thickness and known data reported in Table 1. The rate of hydration was obtained by use of the formula: $Y = mX + b$. The calculated value for X was 11.7668 microns and the rate of hydration rounded to 11.77 microns / 10^3 years. Using the theoretical temperature curve obtained by Friedman et al. (1966) and redrawing the basaltic hydration curve as a function of temperature while applying the slope of the Friedman et al. (1966) curve, a hydration rate for 24°C was determined to be 11.11 ± 0.90 microns / 10^3 years. The actual observed rate of hydration as derived through sampling the lava flows correlates with the theoretical data. Figure 2 shows the effect of temperature on the rates of hydration of basaltic glasses for three different environments.
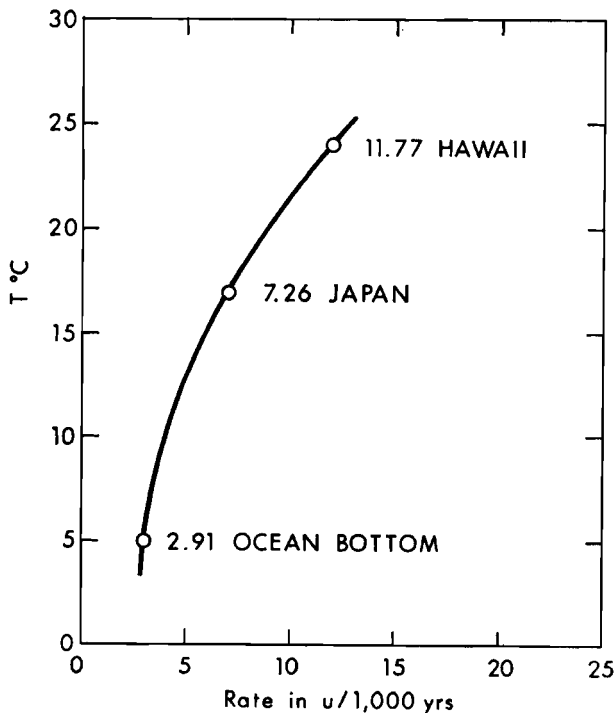

Fig. 2   The effect of temperature on the rate of hydration
of basaltic glass.

Systematic archaeological investigation in the Hawaiian Islands has been under way for only the last two decades. During this short time a number of archaeological sites yielding basaltic glass flakes have been excavated (Emory and Sinoto 1961; Newman 1970; Pearson et al. 1970). In most instances these flakes have been catalogued and then hidden away in storerooms. Only within the last two years has the significance of these flake assemblages become apparent, first, in terms of the informal flake-tool industry that they represent, and second, in terms of support for radiogenic dating in constructing adequate chronologies for the Hawaiian Islands.

Studies by Kirch (1971a) and Guiala (1971) have demonstrated that the basaltic glass materials found in the context of archaeological sites on the islands of Molokai and Oahu represent flake assemblages with well-defined positive bulbar scars, some step flaking, and edge wear from use. The corollary of this is that flaked and utilized surfaces of the artifacts can be dated by the hydration-rind method previously outlined. The dates should, in most cases, directly relate to the archaeological contexts from which the artifacts were drawn.

Recent excavations in Halawa Valley, Molokai (Kirch 1970, 1971a; 1971b; Riley 1970a, 1970b) and at Anaehoomalu on the island of Hawaii (Barrera 1971) provide a test for the hydration-rind dating method and its accuracy in relation to radiogenic dating of archaeological contexts in which the basaltic-glass flake tools occur. These dates largely correlate with C-14 dates available from the same sites, which indicates a fairly high level of correspondence between the two methods.

At Halawa Valley on the eastern tip of Molokai, excavations by the Bernice P. Bishop Museum and the University of Hawaii yielded a basaltic-glass flake tool assemblage related to more sophisticated aboriginal artifacts and features, including some round-ended or ovate houses (Kirch 1971a, b). The features and artifacts from this site, 50 Mo Al 3, suggested an initial occupation early in the Hawaiian sequence. Sixty to 70 cm of occupation deposition in layer IV apparently represented a fairly continuous occupation for nearly 600 years. Radiocarbon dating of features from this site supports the antiquity of the artifact content and places the time range of the occupation between A.D. 570 ± 90 and A.D. 1130 ± 90 (Kirch 1971a, b).

Flakes of basaltic glass from this site were dated by the hydration-rind method using the rate of 11.77 microns/10^3 years previously outlined. Samples were selected for dating from each of six 10-cm levels within layer IV. Only five of these samples were determined to be usable for the dating method (Morgenstein 1970). Between two and ten traverses were made on each sectioned specimen, and its range of thickness in microns was averaged. The average micron thickness was then translated into a true date with the range in thickness representing ± years. The results of these dates and comparisons with the radiocarbon dates from the same site are presented in Table 2. In general, there is a good correspondence between the results of the two methods. However, one problem arose in correlating the contexts of the hydration dates and the radiocarbon dates. The charcoal and ash samples selected for radiogenic dating were related to specific features on different living floors at the site. The flake tools, on the other hand, were selected from the quantitative sample that had been collected and recorded by arbitrary 10-cm levels within the site. Thus, the correspondence of the two methods was skewed to some degree in the process of collection. For this reason the centimeter depths below the

TABLE 2.   CARBON-14 AND HYDRATION-RIND DATES FROM SITE 50 MO AL 3,
HALAWA VALLEY, MOLOKAI ISLAND

LAYER IV	C-14 DATE A.D. (UNCORRECTED)	AVERAGE THICKNESS (IN MICRONS)	HYDRATION DATE A.D.
25–30 cm	1130 ± 80 (HRC-179)		
30–40 cm		11.20	1018 ± 34
		11.17	1021 ± 54
		10.97	1038 ± 45
40–50 cm		13.01	865 ± 69
		12.30	925 ± 60
55–60 cm	570 ± 90 (HRC-181)		

interface of layers III and IV are noted for radiocarbon dates as well as for hydration dates in Table 2.

Excavations at Anaehoomalu on the west coast of the island of Hawaii provide a second archaeological test for the method. There, the Bernice P. Bishop Museum excavated and tested a large number of sites that were in danger of destruction owing to a proposed resort development. A total of 102 hydration-rind determinations were made from 25 sites yielding basaltic-glass flake tools. In addition, 8 radiocarbon age determinations were made from 5 of the sites excavated there. In three instances radiocarbon dates and hydration-rind age determinations were made using materials with the same archaeological provenance. Only the dates that were directly associated were considered here as tests of the method.

A single site, 50 Ha El 148, yielded nearly 25% of the entire artifact assemblage from Anaehoomalu (Barrera 1971). Site 148 was a lava-bubble habitation shelter with unstratified midden varying in depth from 15 to 50 cm. A single, slab-lined hearth in the site yielded charcoal giving a radiocarbon date of 235 ± 90 B.P. (HRC-204). The hearth also yielded basaltic glass flakes, four of which were dated by the hydration-rind method. Here both the charcoal sample and the basaltic glass flakes were directly associated within the same archaeological feature. Table 3 shows the correlation between results of the two dating methods. As at Halawa, the dates for each specimen from the Anaehoomalu sample were determined from a number of traverses across the hydration rind of the sample. In most cases the number of traverses was 10, but in some cases with poorly readable rinds the number was as low as 2.

TABLE 3.   CARBON-14 AND HYDRATION-RIND DATES FROM SITE 50 HA EL 148,
ANAEHOOMALU, HAWAII ISLAND

HEARTH SQ 8	C-14 DATE A.D. (UNCORRECTED)	AVERAGE THICKNESS (IN MICRONS)	HYDRATION DATE A.D.
	1715 ± 90		
		2.68	1742 ± 36
		2.75	1736 ± 47
		2.75	1736 ± 30
		2.49	1759 ± 27

The second site at Anaehoomalu where a good archaeological correspondence between basaltic-glass flake tools and a radiocarbon sample could be demonstrated was site 50 Ha El 133, which consisted of a cave shelter and an apparently associated rock-overhang shelter. Here again a direct relationship was noted between the stratigraphic position of a charcoal sample taken for radiocarbon dating and basaltic glass flakes suitable for hydration-rind readings (Barrera 1971). The samples were in adjacent squares in layer III (10–15 cm) of the excavation. The radiocarbon age determination arrived at for layer III at this site was 185 ± 90 B.P. (HRC-194). Basaltic glass flakes from the adjacent square 6 yielded the dates noted in Table 4.

TABLE 4. CARBON-14 AND HYDRATION-RIND DATES FROM SITE 50 HA EL 133, ANAEHOOMALU, HAWAII ISLAND

LAYER III	C-14 DATE A.D. (UNCORRECTED)	AVERAGE THICKNESS (IN MICRONS)	HYDRATION DATE A.D.
square 1	1765 ± 90 (HRC-194)		
square 6		1.96	1804 ± 23
		2.16	1786 ± 23
		2.15	1787 ± 22
		2.00	1800 ± 18

A third set of dates utilizing the two methods was noted for site 50 Ha El 103 at Anaehoomalu. At this site there were three radiocarbon dates that could be correlated with basaltic glass flakes within the excavation. Two corresponding dates were noted from square 3 in the excavation, where charcoal samples in layer 3 and layer 6 yielded dates of 505 ± 95 years B.P. (HRC-201) and 875 ± 95 years B.P. (HRC-197), respectively. Table 5 presents the radiocarbon dates and the corresponding hydration age determinations from these squares and levels.

TABLE 5. CARBON-14 AND HYDRATION-RIND DATES FROM SITE 50 HA EL 103, ANAEHOOMALU, HAWAII ISLAND

SQUARE 3	C-14 DATE A.D. (UNCORRECTED)	AVERAGE THICKNESS (IN MICRONS)	HYDRATION DATE A.D.
level 3	1445 ± 95 (HRC-201)		
level 3		5.98	1462 ± 28
		5.94	1460 ± 35
		5.81	1476 ± 36
		5.78	1479 ± 33
level 6	1075 ± 95 (HRC-197)		
level 6		9.81	1136 ± 44
		9.28	1180 ± 58
		9.85	1126 ± 32
		9.97	1122 ± 37

In square 1 from the same site, however, a set of dates corresponding to archaeological stratigraphy did not correlate chronologically. In this square the radiocarbon

dates for level 1 and level 2 were inconsistent, with a 305 ± 120 years B.P. date for
level 2 and a 580 ± 105 years B.P. date for level 1. In contrast, the hydration age
determinations for level 2 at this site are consistently clustered in the first half of
the twelfth century A.D. Table 6 compares the hydration readings from level 2 with
the radiocarbon date from the same level.

TABLE 6.   CARBON-14 AND HYDRATION-RIND DATES FROM SITE 50 HA EL 103,
ANAEHOOMALU, HAWAII ISLAND

SQUARE 1	C-14 DATE A.D. (UNCORRECTED)	AVERAGE THICKNESS (IN MICRONS)	HYDRATION DATE A.D.
level 1	1370 ± 105 (HRC-195)		
level 2	1600 ± 120 (HRC-202)		
		9.65	1150 ± 22
		9.97	1123 ± 37
		9.92	1127 ± 41
		10.05	1116 ± 30

This is the only square at the Anaehoomalu sites in which a serious discrepancy
between the two dating methods was noted, and the reversal of the radiocarbon
dates in this square suggests that the problem might rest with these dates rather
than with the hydration dates from the same level. However, this discrepancy
cannot be resolved with the present data.

IMMEDIATE PROSPECTS

The application of hydration-rind dating to geological problems has been shown
by Morgenstein and Felsher (1971) in a publication on the origin of manganese
nodules. Here volcanic glass centers of manganese nodules were dated by the
hydration-rind method and the rate of manganese accretion was determined. Other
applications of hydration-rind dating to geological problems, such as dating
paleomagnetic reversals, deriving the ages of the guyots in the Pacific and deter-
mining their tectonic history, and checking Hamilton's hypothesis of guyot forma-
tion will serve as topics for future investigations.

In addition, the hydration-rind method is proving useful in archaeological
contexts as a supplement to the standard radiogenic methods of dating. The method
is at present being used in the Hawaiian Islands with positive results. But its
application is not restricted to the Pacific area. Friedman et al. (1963) have noted
Egyptian basaltic glass of a nature similar to that of material from the Hawaiian
Islands. This material as well as basaltic glass from other parts of the world may
be dated by the processes outlined in the paper.

There remain some problems with the method, most of them related to the
archaeological context of the basaltic glass artifacts, the time of their manufacture,
and the relationship of their time of manufacture to the time of the archaeological
context. These difficulties have been discussed elsewhere by Friedman et al. (1963)
and Green (1964), among others. While these problems exist the method should not
be accepted as a universally valid absolute-dating technique. But with the use of

careful controls, such as the backing of a reliable archaeological context, and with the support of C-14 dating and other recognized absolute dating techniques, the method is reliable and extremely useful for the archaeologist.

There has been much discussion of the feasibility of the hydration-rind dating tool as an absolute method. The state of the method of Friedman and colleagues (1963, 1966) is not absolute but relative because of its dependence on micro-environmental temperatures. We are now beginning to approach absolute dating by making the method independent of temperatures, pressures, and even glass chemical composition. The hydration rind itself is a function of these parameters, and the rate of hydration is depicted in the rind thickness. More raw data must first accumulate before an accurate demonstration of these preliminary data is upheld. We sincerely hope that other investigators of hydration-rind dating will try these methods and thus help further the techniques that were initially developed by Friedman and others (1963, 1966). In theory, the quadratic approach differs from the method reported here. Each side of the argument has supporting data, but independent and accurate checks of both methods would be fruitful in helping to solve the problem of which method to use.

CONCLUSIONS

1. During glass hydration an immobile product layer forms at the interface of the reactants. This develops into a band of altered glass. For mafic glass this band is palagonite, and for acid glass, it is perlite.

2. Water enters the glass structure via a microfracture chemical channel zone which is designated the mist zone.

3. The immobile product layer develops from the mist zone.

4. Palagonite banding thickness corresponds to the thickness of the immobile product layer and the mist zone for specific environmental parameters and glass chemistry.

5. Rates of hydration of glass are linear. The rate is determined at the least hydrated sector of the outer surface of the fresh glass. The rate of hydration does not decrease with increasing depths of alteration.

6. Glass flake assemblages from archaeological sites in the Hawaiian Islands have been dated by hydration-rind and C-14 methods. The resulting corresponding chronologies demonstrate the utility of the hydration-rind method. Hydration-rind datings of archaeological flakes from specific site levels are also consistent with archaeological configuration and stratigraphic position. The numerous dated flakes from each level or feature in these sites are reasonably well clustered.

7. The dating range of this linear hydration-rind method is from approximately Cretaceous time to within ± 10 years of the present. One reason for the inability to date before the Tertiary-Cretaceous boundary is the lack of glass samples from earlier temporal contexts. The major limitation for archaeological use of this method rests in the limitation of distribution and utilization of glass for tools. The upper temporal limitation rests in the accuracy of reading a rind

through a conventional petrographic microscope. This problem may be eliminated by the use of the scanning electron microscope.

8. Finally, the linear hydration method as described in this paper is not qualitatively better than that used by Friedman and others. Neither rate equation has yet to be demonstrated absolutely valid by an independent investigation.

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