Reports

Glass Hydration: A Method of Dating Glass Objects

Abstract. *A new nondestructive method for dating or authenticating man-made glass is proposed, and the initial results of an exploration of the potential of this method are presented. The method is based on a relation between the age of a glass object and the thickness of the layer of hydrated glass on its surface, with the thickness of this hydrated surface layer being measured by means of the* ^{15}N *nuclear resonance depth profiling technique. A qualitative age scale is established for some common 19th- and 20th-century American glass.*

Because glass has been commonly used for thousands of years (*1*), a scientific method for dating or authenticating objects made of glass can make key contributions to the study of cultural history. I propose here a method for dating glass based on the depth profile of the layer of hydrated glass on the surface of the object; the preliminary results of an exploration of the method are presented.

The proposed method is based on the fact that, on exposure to atmospheric water, the surface of glass begins to hydrate and the thickness of the hydrated surface layer increases with the age of the object. In many ways the dating method proposed here is similar to the method of hydration dating of obsidian introduced by Friedman and Smith (*2, 3*). Obsidian is a natural volcanic glass that was commonly used by ancient man to make arrowheads, knives, and other tools. When these objects were made, fresh (unhydrated) fracture surfaces of obsidian were exposed to air and hence to atmospheric moisture. The surface of obsidian, like that of man-made glass, has a strong affinity for water, and the obsidian slowly combines with it chemically to form a hydrated surface layer. One can optically measure the thickness of this hydration layer by cutting, mounting, and polishing a thin cross section of the surface (*3*). Since hydrated obsidian has a specific volume different from unhydrated obsidian, there is a stress line between the hydrated and unhydrated regions, and this appears as a dark line when polarized light is used to illuminate the sample. The age of the artifact is then calculated from the thickness of this hydration layer.

In general, one cannot use the same optical method for measuring the thickness of hydration layers on man-made glass as is used for obsidian. This is so principally because the hydration process in glass is different from that in obsidian, with the result that there is not always a well-defined stress line between the hydrated and unhydrated regions. Moreover, glass that is less than a few hundred years old would generally have hydration layers thinner than the wavelength of visible light, and consequently these layers would be unobservable microscopically. Finally, the optical method is destructive in that it requires the removal of a slice of glass from the object to be dated; art historians are understandably reluctant to subject objects in their care to such procedures.

By using a newly developed analytical method based on a resonant nuclear reaction between ^{15}N and ^{1}H for measuring the distribution of hydrogen in solids (*4*), one can measure complete depth profiles of this surface hydration layer nondestructively and can thus date the object. This technique is based on the fact that at a precise energy (the resonance energy) a nuclear reaction takes place between ^{15}N and ^{1}H yielding a characteristic gamma ray. At energies above or below this resonance energy the yield from this reaction is negligible. To use this reaction as a probe for hydrogen, the sample is bombarded in a ^{15}N beam from an accelerator. If the sample has hydrogen on its surface and if the ^{15}N is at the resonance energy, the yield of characteristic gamma rays is proportional to the hydrogen concentration on the surface. If the energy of ^{15}N is raised, there are no longer reactions with hydrogen on the surface, but, as the ^{15}N loses energy passing through the sample, it reaches the resonance energy at some depth. The yield of characteristic gamma rays is proportional to the concentration of hydrogen at this depth. Hence by measuring the yield of characteristic gamma rays versus ^{15}N energy, one determines the concentration of hydrogen as a function of depth. This new technique avoids the difficulties encountered by the optical method as outlined above and allows the development of a nondestructive dating procedure based on hydration to be applied to man-made glass and possibly to other materials. A similar method has recently been applied to obsidian dating (*5*).

The proposed dating method depends upon the fact that glasses are unstable with respect to reactions with water. Common experience indicates that this reaction must be very slow, and indeed it is. Common window glass reacts so slowly that in 1000 years of exposure to atmospheric moisture, only the first few micrometers of the surface glass would have reacted with water to form a hydrated glass. Glass is primarily a three-dimensional matrix of silicon and oxygen atoms, and it is the Si–O–Si chain which reacts with water (*6*). This reaction can be summarized as

$$\mathrm{Si{-}O{-}Si} + H_2O \rightarrow 2\mathrm{Si(OH)}$$

The rate of this reaction is controlled by the diffusion of water into the glass, and it is this diffusion which is so slow. Because the hydration is controlled by diffusion, it is expected that the thickness of the hydration layer, X, is related to the age of the sample, T, by $X^2 = KT$, where K is a constant. This relationship has been verified in laboratory experiments both for obsidian (*7*) and for common glass (*8*).

In order to date a sample of glass, one measures X and then calculates $T = X^2/K$. There is no doubt that this method would work if all glasses were carefully made from the same material and by the same manufacturing methods and if the glass samples were always kept in a controlled environment. These conditions, however, are almost never satisfied for samples of interest. As a consequence, the reliability and utility of the dating procedure depends (i) on how sensitive K is to changes in glass composition (or, alternatively, on how well one can determine K by measuring the composition of a sample) and perhaps to changes in manufacturing methods; and (ii) on the validity of the assumption that, for objects tens or hundreds of years old, the environment, averaged over several years, can be considered constant. As will be seen below, the initial results of measurements with glasses of known ages indicate that, even without considering the composition dependence of K, one can construct a qualitative dating scale. Although even a qualitative date assignment can be decisive when one is trying to authenticate an object, a detailed study of the composition dependence of K may make it possible to develop a quantitative dating procedure.

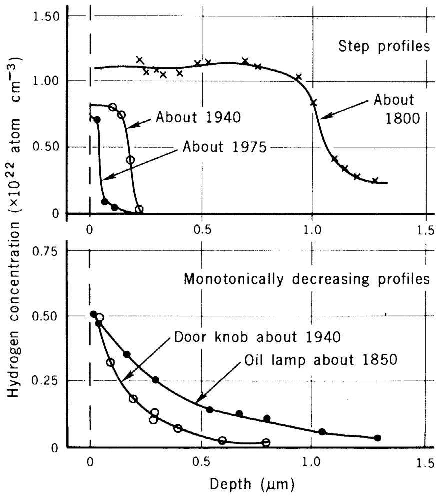

Fig. 1. Hydration profiles of American glasses of known ages. These profiles demonstrate that the thickness of the hydration layer is greater for older glass than for newer glass. The step profiles are characterized by a region of fully hydrated glass and a rapid change in hydration versus depth at the hydration front; the monotonically decreasing profiles show a continuous decrease in hydrogen content with depth.

It might be expected a priori that the hydration observed in a sample would be very sensitive to the average relative humidity of its lifetime environment. This appears not to be the case (*3*). A fresh surface of a glass reacts readily with atmospheric water to produce a continual surface coverage of water (or OH groups). Even in the driest climate, there is enough atmospheric water to maintain this hydrogen-bearing film. This surface layer acts as a buffer between the atmosphere with its varying humidity and the glass interior that is being hydrated. The results of obsidian-dating studies confirm this expectation. Michels and Bebrich reported that the hydration rates of obsidian in dry Egyptian tombs are similar to those in humid tropical Ecuador (*3*). It is to be expected that the hydration rate will depend on temperature, with hydration occurring more rapidly at higher temperatures. The dating methods for both glass and obsidian are based on the assumption that, because the objects of interest are many years old, one can average over the cyclical annual temperature variations and consider only the resultant average K value when calculating dates.

Hydration profiles of a number of glass objects of known ages are shown in Fig. 1. Two distinct types of profiles are observed. The so-called step profiles (shown in the upper half of Fig. 1) show a clearly evident layer of hydrogen on the surface with a rapid decrease in hydrogen content at the interface between the regions of hydrated and unhydrated glass. Older glasses have thicker layers of hydrogen. The so-called monotonically decreasing profiles (shown in the lower half of Fig. 1) show a continuous decrease in hydrogen content with depth. As with the step profiles, the older glass has a thicker layer of hydrogen. The reason for these two types of profiles is not completely understood, but both are characteristic of diffusion processes. Step profiles result when the diffusion coefficient is strongly dependent upon the concentration of the diffusing material (*9*), whereas monotonically decreasing profiles result when the diffusion coefficient is independent of the concentration. Although, as yet, there are too few data to permit a quantitative statement, the monotonically decreasing profiles seem more common on decorative glasses. It seems likely that these differences in the hydration process reflect differences in the compositions of the glasses involved.

I have investigated whether there is any obvious relationship between the measured thickness of hydration and the age of the sample for these two types of profiles. For the step profiles, the thickness was defined by the depth at which the hydrogen concentration was reduced to one-half its value near the surface. For the monotonically decreasing profiles, the depth at which the concentration is one-third of its value at the surface was arbitrarily chosen. These definitions of hydration thickness make it possible for one to compare age versus thickness for both profiles on the same scale.

Figure 2 is a plot of the thickness of the hydrated layer versus the square root of the known age. The closed circles are for the step profiles, and the open circles are for monotonically decreasing ones. The straight line indicates what the correlation would be, assuming $X^2 = KT$, for an arbitrary value of K. Although there is considerable scatter in the data, there is a clear correlation of thickness with age. On the basis of a study of the mechanisms for hydration and, in particular, the effects of composition on hydration, I believe that it will be possible to greatly reduce the scatter.

I have demonstrated a relation between age and hydration depth. For this method to be quantitative, it is essential to know the dependence of the hydration process (rate) on composition. However, even with the small data sample presently available, it is clear that the method can help to authenticate or properly attribute glass objects, and perhaps it is in authentication that this method will prove most useful. I have reported here on profiles of only rather recently produced glass. There is no intrinsic reason to limit the method to such modern pro-

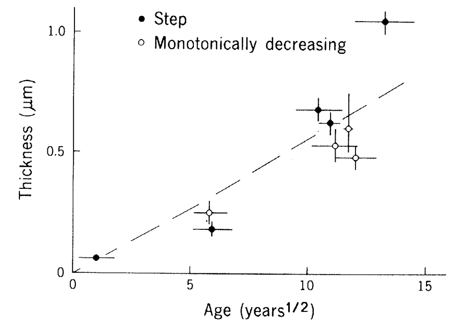

Fig. 2. Summary of the hydration thickness plotted versus the square root of the age of the glass test object, showing a qualitative correlation between age and hydration thickness. The straight line is the correlation expected for $X^2 = KT$ on the assumption that $K = 3.3$ μm^2 per 1000 years.

ductions, and, since glasses with compositions similar to modern soda-lime glass have been made for thousands of years (*10*), it would seem that this method could be applied to ancient glasses. However, the preliminary results of a study of ancient glasses which had been excavated indicates that the surface corrosion present on excavated glasses may make reliable hydration dating difficult (*11*).

The method of hydration dating need not be limited to glass. Since most silicates are unstable against slow reactions with atmospheric water, many may develop surface hydration layers suitable for dating or authenticating. The glazes on pottery are chemically similar to glass, and it may be possible that a dating method for glazed pottery based on the same procedures as outlined above for glasses can be developed.

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References and Notes

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12. I thank Prof. C. F. Montgomery for his encouragement and for supplying some of the samples. I thank Prof. D. A. Bromley for advice and encouragement.

16 August 1976; revised 26 October 1976