

# Obsidian hydration dating: accuracy and resolution limitations imposed by intrinsic water variability

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Received 19 November 2007; received in revised form 15 January 2008; accepted 17 January 2008

## Abstract

Obsidian hydration dating typically yields a range of ages for a single chronometric measurement, even after controlling for source chemistry and effective hydration temperature. Previously published data suggest that this range is due to hydration rate variations caused by variability in the concentration of intrinsic water, and specifically hydroxyl ions, in the obsidian. Such variability exists within any given obsidian source, and even within any particular specimen. This paper analyzes the effect on age estimates of intrinsic water variability and concludes that if a controlled sample of obsidian yields a range of ages, there is no way to tell whether the range is due to long site use or to variations in hydroxyl concentration. At present there is no robust and cost-effective protocol for measuring hydroxyl concentration. Suggested guidelines for obsidian hydration dating are developed using a case study. These findings do not invalidate obsidian hydration as a chronometric technique, but they do suggest limits to the temporal resolution achievable.

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*Keywords:* Obsidian; Obsidian hydration dating; Intrinsic water

## 1. Introduction

Obsidian hydration dating (OHD) is a very useful and cost-effective technique for chronological analyses, particularly in regions where radiocarbon and dendrochronology cannot be applied. It is well known, however, that OHD typically reveals a range of rim thicknesses or ages corresponding to a single chronometric measurement, even after controlling for source chemistry and effective hydration temperature (e.g., Hull, 2001, p. 1033; Ridings, 1996, p. 138; Yohe, 1992, p. 150).

This analysis explicitly draws hydration rate data from two disparate lines of research, laboratory (induced) hydration, and rates developed from correlations with radiocarbon. Most practical archaeology depends on the latter technique, since laboratory methods have generally failed to provide reliable measurements of hydration rate. However, laboratory methods have provided insight into some of the apparent causes of hydration *variability*, which are the subject of this analysis.

It is explicitly postulated, following Ambrose and Stevenson (2004), Stevenson et al. (1998, 2000), and Mazer et al. (1992), that the rate variations are caused by variability in the concentration of hydroxyl ions within any obsidian source. Data are presented showing the correlation between hydration rate and hydroxyl ion concentration in obsidian, and, further, that the hydroxyl ion concentration can be related to total intrinsic water content. As an example, data are presented showing variability of Coso obsidian. Limitations of current protocols for measuring hydroxyl concentration are discussed in terms of archaeological application. Guidelines for OHD analysis are suggested from a case study.

## 2. Hydration theory

### 2.1. Background

The use of obsidian hydration measurements for archaeological chronometry was first proposed by Friedman and Smith (1960). It is based on the principle that, when a freshly exposed surface of obsidian is exposed to water, either liquid

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or vapor, water molecules diffuse into the glass at a predictable rate (Doremus, 2002; Stevenson et al., 1998). As the water diffuses into the glass it causes a change in refractive index in the hydrated layer; if a small cross-sectional sample is cut from the obsidian, mounted on a microscope slide and polished to transparency, the interface between hydrated and unhydrated volumes can be observed under a polarizing microscope (Anovitz et al., 1999; Scheetz and Stevenson, 1988). The hydrated volume is referred to as the hydration rim, and its thickness in most archaeological cases is of the order of micrometers. If the rate of hydration is known or can be inferred, the time since the surface was exposed can be estimated. Alternative methods for measuring the rim are secondary ion mass spectrometry (e.g. Stevenson et al., 2004) and tritium-exchange (Lowe et al., 1984).

The rate of hydration is dependent on the obsidian chemistry (Friedman and Smith, 1960; Friedman and Trembour, 1983), the intrinsic water content of the glass (Mazer et al., 1992; Stevenson et al., 1993, 2000), and temperature and relative humidity (Ebert et al., 1991; Friedman and Long, 1976; Friedman et al., 1994; Mazer et al., 1991; Stevenson et al., 1993, 2000). The chemistry of the diffusing water also affects the surface structure of the glass and the nature and rate of the hydration process (Morgenstein et al., 1999). The most comprehensive treatment of water diffusion and chemical reaction in silica and aluminosilicate glasses are those of Doremus (1968, 1994, 1995, 2000, 2002), who characterized the hydration process as a “diffusion-reaction” process.

The physics of the diffusion process suggests the relationship between age and rim thickness should be quadratic,

$$x^2 = kt \quad (1)$$

where  $t$  is age in years,  $x$  is rim thickness in micrometers, and  $k$  is a constant, the hydration rate (e.g. Ebert et al., 1991; Doremus, 2000, 2002; Stevenson et al., 1989, 1998; Zhang et al., 1991). Further discussion of the physics of diffusion may be found in Crank (1975), Doremus (2002), and Rogers (2007a).

The hydration rate is temperature-dependent, described by the Arrhenius equation (Friedman and Long, 1976)

$$k = A \exp(-E/RT) \quad (2)$$

where  $E$  is the activation energy associated with diffusion,  $R$  is the universal gas constant per mole,  $T$  is absolute temperature, and  $A$  is a pre-exponential proportionality constant. Stevenson et al. (1989, 2004) showed this equation to be approximately applicable to obsidian, and Doremus (1994) showed its validity across a range of glasses. However, Eq. (2) is based on an idealized model of the hydration process, so its validity is only approximate.

Because the rate of hydration is temperature dependent, and temperature at an archaeological site varies both diurnally and annually, the hydration rate varies over time. The effect of this varying temperature is summarized by the concept of effective hydration temperature (EHT), defined as a constant temperature which yields the same hydration results as the actual time-varying temperature over the same period of time. Due

to the mathematical form of the dependence of hydration rate on temperature, EHT is always higher than the mean temperature (Hull, 2001; Onken, 2006; Ridings, 1996; Rogers, 2007a; Stevenson et al., 1989, 1998, 2004).

Hydration rate has also been suggested to vary with relative humidity (Ebert et al., 1991; Friedman et al., 1994; Mazer et al., 1991; Onken, 2006). Although the data show the effect to be real, the results are difficult to reconcile with theory. Rogers (2007c) suggested the apparent divergence may be due to an unexamined assumption in the models, particularly regarding the definition of the “hydration front”. The effect is not addressed further here, but humidity must be borne in mind as a further source of variability in obsidian dating results.

## 2.2. Analysis of rate variation

Any variation in hydration rate will affect the outcome of the hydration process. Eq. (1) can be rewritten as

$$x = (kt)^{1/2} \quad (3)$$

Taking the derivative of  $x$  with respect to  $k$  in Eq. (3),

$$\frac{\partial x}{\partial k} = \frac{t}{2}(kt)^{-1/2} \quad (4)$$

Rearranging terms,

$$\frac{\partial x}{x} = \frac{1}{2} \frac{\partial k}{k} \quad (5)$$

Thus, if the rate  $k$  varies in a random manner about a mean, such that its statistics can be described by a coefficient of variation (CV, defined as the ratio of standard deviation to mean), the CV of  $x$  ( $CV_x$ ) is related to the CV of  $k$  ( $CV_k$ ) by

$$CV_x = CV_k/2 \quad (6)$$

Thus, variations in  $k$ , due to any source that cannot be controlled for, will reflect directly into variations in rim thickness and hence in estimated age. Specifically, if  $CV_k$  can be estimated from other measurements, the  $CV_x$  will be given by Eq. (6), and  $CV_t$ , the CV of the age estimate, is equal to  $CV_k$ .

## 3. Source of variation

### 3.1. Hydration rate and hydroxyl content

Intrinsic water is always present in obsidian, due to geologic processes when the obsidian was formed. It has been shown that the water in glass can exist in several forms, or species, notably molecular water ( $H_2O$ ) and hydroxyl ion ( $OH^-$ ) (Bartholomew, 1982; Silver et al., 1990; Zhang et al., 1991). It has also been shown that molecular  $H_2O$  is the mobile species which participates in diffusion, while the  $OH^-$  is less mobile and is presumably chemically bound to the glass matrix (Zhang et al., 1991).

Obsidian chemistry has long been known to affect hydration rate, and empirical formulas relating hydration rate to the relative proportions of the obsidian constituents have been proposed (e.g. Friedman and Long, 1976). More recently,

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