Unreliability of the induced obsidian hydration method with abbreviated hot-soak protocols

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ABSTRACT

The induced hydration method is based on temperature scaling; obsidian samples are hydrated in the laboratory at elevated temperatures, and hydration rims are then measured. The activation energy and diffusion constant are determined analytically, and the hydration rate computed for temperatures of archaeological interest. It is desirable to minimize the hot-soak times in the interest of efficient use of laboratory equipment; however, the technique yields poor results for some obsidians when used with such experimental protocols. We applied the induced hydration method to obsidian specimens from seven sources in southeastern Nevada, using a frequently-used protocol which minimizes the hot-soak times. We then measured the hydration rims using optical microscopy. When plotted graphically, the resulting rates are not linear as would be expected, but instead consistently form shallow sigmoid curves. They are also found to be unrealistically high. Further, we find that hydration rate varies with time at a constant temperature, contrary to expectations. We conclude that this protocol does not adequately model long-term hydration and discuss the implications of this finding. We recommend the development of experimental designs that adequately model long-term hydration.

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1. Introduction

Obsidian hydration as a technique for constructing archaeological chronologies dates from the 1960 article by Friedman and Smith (1960). Since that time, the technique of obsidian hydration dating (OHD) has gone through periods of great enthusiasm (e.g., Friedman and Long, 1976; Hull, 2001; Rogers, 2007, 2012) and periods of rejection and disillusionment (e.g., Ridings, 1995). Nevertheless, it is a widely used technique in the archaeology of the American desert west, where frequently no other data exist for constructing a chronology.

Quantitative measurement of hydration rate by induced hydration is part of this equivocal history for OHD in archaeology. The temperature dependence of hydration rate is well known, and attempts have been made in the past to measure hydration rate in the laboratory (e.g., Friedman and Long, 1976; Michels et al., 1983a,1984; Stevenson and Scheetz, 1989; Stevenson et al., 1998). However, rates measured in the laboratory often do not agree well with archaeological data (see, for example, the pointed observations in Hall and Jackson, 1989:32) and are generally not trusted by practicing archaeologists today. The method has, however, recently been demonstrated to yield results which are consistent with archaeological data in the case of Topaz Mountain obsidian from Utah (Rogers and Duke, 2011) and obsidians on Rapa Nui, Chile (Stevenson et al., 2013).

This paper describes an analysis in which the induced hydration technique, with hydration measured by optical microscopy, was employed with obsidian specimens from seven sources in southeastern Nevada; the research was carried out under the Lincoln County Archaeological Initiative (LCAI), a Bureau of Land Management (BLM)-administered program to support archaeological research in Lincoln County, Nevada. The experimental protocol was developed in consonance with Origer's Obsidian Laboratory, to yield readable hydration rims and still minimize the hot-soak times. Minimizing hot-soak times is desirable because longer hot-soak times tend to tie up laboratory assets and reduce throughput. However, the computed rates do not conform to theoretical expectations: they are found to form a shallow sigmoid curve instead of a straight line when plotted in the form of the logarithmic Arrhenius equation, and to be unrealistically high. Since the sigmoid is consistent across specimens and sources, it is unlikely to be due to random errors.

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A further experiment was thus conducted with the obsidians by measuring the hydration rate over extended hot-soak times, which indicated a variation in hydration rates with time at a constant temperature, which is also contrary to the Arrhenius model. Other researchers have observed a similar effect when measured by Secondary Ion Mass Spectrometry (Anovitz et al., 2004; Stevenson and Novak, 2011) or by water mass uptake (Stevenson and Novak, 2011), but this seems to be the first time it has been observed with optical microscopy.

We conclude that, in order for the induced hydration process to yield valid hydration rates at archaeological temperatures, the measurements must be made after sufficient time for the process to be past the transient phase and reach equilibrium. We recommend that any researcher using induced hydration review the rate development procedure, and determine that near equilibrium conditions were reached.

2. Hydration measurement techniques

Obsidian is an alumino-silicate, or rhyolitic, glass that is formed by rapid cooling of magma under the proper geologic conditions. Like any other glass, it is not a crystal, and thus it lacks the lattice structure typical of crystals at the atomic level. Glasses do, however, possess a matrix-like structure exhibiting some degree of spatial order (Doremus, 1994:27, Fig. 2; 2002:59–73). Obsidians are typically about 75% SiO_2 and about 20% Al_2O_3 by weight, the remainder being source-specific trace elements (Doremus, 2002:109, Table 8.1; Stevenson et al., 1998). The minute interstices within the glass matrix, on the order of 0.1–0.2 nm in diameter, are where water diffusion takes place. All obsidians also contain small amounts of water, known as intrinsic water or structural water, resulting from the magma formation process; the amount is generally <2% by weight, although cases of somewhat higher concentration are occasionally encountered.

Glass is often viewed as an inert material, easy to clean and not subject to corrosion, but this is not true at the molecular level. Glass, including obsidian, is readily eroded by water, especially deionized water at high temperature and pressure (Stevenson et al., 1998).

Three methodologies have been reported in the literature for measuring obsidian hydration. The first is measurement of water mass increase or loss vs. time (Ebert et al., 1991; Newman et al., 1986; Stevenson and Novak, 2011). This is based on the knowledge that the process of water mass increase is a function of temperature, pressure, and openness of the glass matrix as measured by intrinsic water concentration. Water mass gain or loss proceeds proportional to t^n where t is time and n is an exponent lying between approximately 0.5 and 0.6 (Stevenson and Novak, 2011).

A second method is direct measurement of water profiles vs. depth (Anovitz et al., 1999, 2004, 2008; Riciputi et al., 2002; Stevenson et al., 2004). The water concentration profile measurement is generally performed by Secondary Ion Mass Spectrometry (SIMS) or the electron microprobe, using H+ ions as a proxy for water. The principle is to measure the concentration of H+ ions as a function of depth into the obsidian. The depth of the half-amplitude point is found to be proportional to t^n, where t is time and n is an exponent lying between approximately 0.6 and 0.7 (Anovitz et al., 1999, 2004; Stevenson and Novak, 2011).

The third method is to measure the width of the hydration rim by observation of the leading edge of the hydrated zone, or the stress region, from the artifact edge by polarized optical microscopy (many papers, e.g., Friedman and Smith, 1960; Friedman and Long, 1976). The stress arises because the volume hydrated volume has enlarged due to penetration of the glass matrix by water molecules, while the matrix of the unhydrated glass has not. Measurement in classic OHD is by optical microscopy, using a polarized microscope at a magnification of at least 500X. This is the most widely used obsidian hydration dating technique in archaeology today due to its low cost and apparent simplicity. All experimental evidence, and correlation with archaeological data, indicate that the position of this stress zone, or hydration front, progresses into the obsidian proportional to t^n, where n is approximately 0.5 within limits of experimental error (Rogers and Duke, 2011; Stevenson and Scheetz, 1989; Stevenson et al., 1998). The agreement with classic diffusion theory, in particular Fick's formulations and the Boltzmann transformation (Crank, 1975:105ff.; Rogers, 2007, 2012), may be a coincidence or may be due to an as-yet-undiscovered property of the diffusion process itself. Because of the popularity of this technique, it is the basis of the analysis reported here.

3. Principles of induced hydration

The induced hydration method (Anovitz et al., 2004; Michels et al., 1983, 1984; Rogers and Duke, 2011; Stevenson and Scheetz, 1989; Stevenson et al., 1998, 2004) is based on temperature scaling, with the key assumption that the functional form of the temperature dependence is known (the so-called Arrhenius model, discussed below). Obsidian samples are hydrated in the laboratory at five elevated temperatures between 110 °C and 150 °C, using silicon-buffered distilled water to eliminate the possibility of surface erosion of the specimens. The protocol typically terminates the hot-soak times once a clearly measureable hydration rim has developed, and hydration rims are then measured. The activation energy and diffusion constant are determined analytically, and hydration rate is computed from the Arrhenius model for a temperature of archaeological interest (20 °C in this case). The mathematical technique for computing activation energy and pre-exponential factor (or diffusion constant) is based on methods developed in physical chemistry for computing reaction kinetics (Cvetanovic et al., 1979). Table 1 summarizes five previously-employed laboratory protocols, with the protocol employed in this paper.

Obsidian hydration is by definition a time-dependent phenomenon, as the amount of water absorbed by the glass increases with time. Regardless of measurement method, an implicit assumption is that the hydration rate is constant with time at any

Table 1
Typical experimental protocols employed in induced hydration studies.

Obsidian	Temperature range, °C	Hot-soak time range, days	Number of temperature-time combinations per specimen	Reference
East Africa	150–200	0.5–4	9	Michels et al., 1983b
Camels Back Cave, UT	150–200	0.5–4	9	Michels 1984
Coso volcanic field CA	160–190	3–12	4	Stevenson and Scheetz 1989
Camels Back Cave, UT	110–150	29–58	3	Rogers and Duke 2011
Seven various	150–190	40–60	4–6	Stevenson and Novak 2011
Lincoln County, NV	110–150	10–30	4–6	This paper