Journal of Archaeological Science: Reports 6 (2016) 109–114

Contents lists available at ScienceDirect

Journal of Archaeological Science: Reports

journal homepage: www.elsevier.com/locate/jasrep

Calibrations for the determination of water species in bulk and hydrated obsidian by infrared photoacoustic spectroscopy

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ARTICLE INFO

Article history:
Received 20 November 2015
Received in revised form 8 January 2016
Accepted 26 January 2016
Available online xxxx

Keywords:
Archeology
Dating
FTIR
Obsidian
Photoacoustic

ABSTRACT

The obsidian hydration dating method requires a measurement of the amount of diffused water (%H_2O_D) within the surface hydration layer and an assessment of the structural water (%OH) contained within the underlying glass matrix. Infrared photoacoustic spectroscopy (IR-PAS) has the ability to sample deeply within the glass and capture both regions simultaneously. The calibrated infrared water band at 3570 cm^{-1} may be used to measure total water (%$H_2O_t = H_2O_m + OH$) content and the concentration of diffused molecular water (%H_2O_D) is assessed with the band at 1630 cm^{-1}. Subtraction of the band specific concentrations provides an estimate of the obsidian structural hydroxyl (%OH) content. Calibrations of the IR-PAS water bands, to permit inferring water concentrations from IR-PAS measurements, were developed using obsidians of known water content established by standard infrared transmission. Three calibration equations are presented, for H_2O_t, H_2O_m, and OH, along with computed estimates of accuracy.

1. Introduction

The concentration of water species — hydroxyl (OH) and molecular water (H_2O_m) — in natural rhyolitic glasses (obsidian) is an important variable in multiple disciplines. The geologic study of volcanic processes has shown that water plays an important role in the explosive energy of volcanic eruptions (Gonnerman and Magna, 2007; Giachetti et al., 2015). The glassy products of those eruptions, modified by prehistoric humans to make tools, constitute part of an archeological record that may be dated from the measurement of diffused ambient water into the glass surface (Friedman and Long, 1976; Stevenson and Novak, 2011; Stevenson et al., 2013). Similarly, diffused molecular water into geological surfaces has been proposed as a method to date volcanic eruptions from the Holocene and earlier (Friedman and Obradovich, 1981).

The obsidian hydration dating method is based upon the diffusion of water into the surface of volcanic glass over time. It begins with a human induced fracture event that creates a new and previously unexposed surface. Environmental water (H_2O_D) is immediately adsorbed onto the surface and diffuses into the glass matrix to create a hydration layer that progressively becomes thicker over time. The rate of hydration layer formation, with other factors such as temperature and humidity held constant, has historically been attributed to the chemical composition of the geological deposit, or the composition of individual flows with in a larger volcanic field (Beck and Jones, 2000). The reasons behind this assumption have largely been unspecified but a uniformity of hydration rate has been inferred for individual flows from a similarity in concentration of the anhydrous components or trace element values. In their early experimental work on accelerated hydration, Friedman and Long (1976) identified structural water content as a contributing variable and incorporated it into their rate prediction equation, or "Chemical Index" ($CI = SiO_2–45(CaO + MgO) − 20H_2O^+$). However, the technical demands of water determinations using wet chemical methods such as the Penfield Technique deterred the routine measurement of this variable and obsidian structural water content became subsumed under the assumption of flow-specific uniformity.

The analysis of obsidian structural water by infrared spectroscopy within the context of laboratory hydration experiments has changed these historically long-held assumptions. Volcanic flows can exhibit considerable variation in structural water within and between flows as a result of variation in their cooling and degassing histories (Stevenson et al., 1993). In addition, it has been shown by laboratory accelerated hydration that diffusion coefficients progressively increase with additions to the structural water content [0.1–1.6%] and this observation has led to the hypothesis that obsidian structural water is the primary determinant of hydration rate velocity (Stevenson et al., 1998; Stevenson and Novak, 2011). The measurement of structural water content has now become a necessary requirement for the application of obsidian hydration dating.

A variety of analytical methods may be used to measure the concentration of water species in glass. Some of the techniques applied include confocal Raman micro-spectroscopy (Di Muro et al., 2006), ^{15}N nuclear resonance depth profiling (Lanford et al., 1979), secondary ion mass

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http://dx.doi.org/10.1016/j.jasrep.2016.01.033

spectrometry (Hauri et al., 2002), hydrogen manometry (Yamashita et al., 1997), specific gravity determined by the Archimedes method (Ambrose and Stevenson, 2004), and Fourier Transform infrared spectroscopy (FTIR). FTIR is often preferred because of its ability to assess the concentration of individual water species (OH, H_2O) at multiple positions along the infrared and near-infrared spectrum (400–6000 cm^{-1}). The availability of well-developed calibrations (Newman et al., 1986) have resulted in the method being widely applied.

Archeological and geological obsidian hydration dating requires that the species of water be measured on the glass surface (diffused water [H_2O_D]) and in the bulk glass (structural [OH and H_2O_m]). FTIR reflectance spectroscopy has been calibrated to determine the near surface concentrations of CO_2 and H_2O on unweathered samples (Lowenstern and Pitcher, 2013; Moore et al., 2000), but naturally hydrated volcanic glasses have thick (1–10 μm) water rich layers that cannot be adequately sampled by reflectance or attenuated total reflectance because of their low penetration depth (<3 μm). A further shortcoming of transmission FTIR is the requirement that bulk rhyolitic glasses be transparent to infrared light. In many cases, the limitation can be eliminated by the preparation of very thin parallel sided wafers (50 μm). However, because the sensitivity of FTIR is path length dependent the thinner sample results in a loss of detection for species specific overtone bands (4500 cm^{-1} and 5200 cm^{-1}) in the near infrared (NIR).

To address both of these problematic issues, we have applied infrared photoacoustic spectrometry (IR-PAS) to the measurement of water species in rhyolitic glasses. Because of its ability to sample at depths of 20 μm or more, IR-PAS has the capacity to adequately sample both the near surface and bulk glass, and does not require transparency. In this application, an incident infrared beam is trained upon a rhyolitic glass sample contained within a helium purged sample compartment and an oscillatory heating causes the water species to swell more than the anhydrous glass structure. This establishes a pressure wave that rises to the surface of the glass. The release of this pressure at the glass-helium interface causes a minute noise that is monitored by a highly sensitive microphone attached to the sample compartment (McClelland et al., 1992). The concentration of the water species is related to the intensity of the audio response.

2. Calibration method

The use of IR-PAS to measure intrinsic water content requires a calibration equation relating IR-PAS response to water concentration. The method employed was to use FTIR to measure intrinsic water content of a set of specimens, and plot these data against IR-PAS measurements on the same specimens. The intrinsic water content can be computed from the FTIR absorbance by application of Beer's law:

$$W = M_w * A/(\rho * p * e) \tag{1}$$

(Levine, 2002:774). Here w is the water species concentration in weight percent, M_w is the corresponding molecular weight, A is the measured infrared absorbance of a specimen at a particular wavenumber (dimensionless), p is the optical path length (specimen thickness) in millimeters, ρ is the specimen density in grams/cm^3, and e is the extinction coefficient (L/mol ∗ cm), or proportionality constant, of a particular water species or combination band at a specific wavenumber (cm^{-1}). Parameters A, ρ and p were measured for each analyzed sample and the values for the extinction coefficients (e) were obtained from Newman et al. (1986:1537). The extinction coefficients (e) for two water bands were applied: OH (4500 cm^{-1}) = 1.73 ± 0.02 (L/mol ∗ cm) and H_2O_m + OH (5200 cm^{-1}) = 1.61 ± 0.05 (L/mol ∗ cm).

Although H_2O_m and OH have slightly different molecular weights, the extinction coefficient values reported by Newman et al. (1986) are corrected to a standard molecular weight of 18.02 for both species. The concentrations are then:

$$w_{H2Om} = 18.02 * A_{5200}/(\rho * p * e_{5200}) \tag{2}$$

$$w_{OH} = 18.02 * A_{4500}/(\rho * p * e_{4500}) \tag{3}$$

The total molecular water $_{WH2Ot}$ is then the sum of these two results.

Sample thickness was measured by a digital micrometer and obsidian densities were measured by the Archimedes method. Density values were computed for each obsidian coupon using the formula from Torrence and Victor (1995):

$$\rho_{ob} = W_{air} * \rho_{liq}/(W_{air} - W_{liq}) \tag{4}$$

where: ρ = density (grams/cm^3) of the gravimetric liquid (liq) or the obsidian (ob), W = weight of the sample in grams in air or heavy liquid (liq).

The calibration curve was developed by measuring the IR-PAS response of two water absorption bands (1630 cm^{-1} for H_2O_m (or H_2O_D)and 3570 cm^{-1} for OH/H_2O_m) and then plotting the response against the values of water concentration from Eqs. (2) and (3).

3. Sample preparation and infrared analysis

A total of 18 obsidian samples from different rhyolitic obsidian flows were obtained (Table 1). These sources contain H_2O_t structural water values between 0.08 and 1.52%, a range that is inclusive of many global obsidian sources. These geological hand samples came from Truman/Queen, Nevada/California (BARD); the Coso volcanic field, California (CVO); Rio Hondo, Colombia (RHCO); Red Hill, New Mexico (RHNM); Superior, Arizona (SUAZ); Takayama, Japan (TAK); and Tolicha Wash, Nevada (TWO); obsidian sources that were heavily exploited in prehistory. Each sample was cut with a Buehler slow-speed saw to produce a parallel-sided coupon that was polished to an 800 grit finish on a vertical four inch disk sander. Each coupon was transparent to visible light and free of phenocrysts or banding. Measurements of sample thickness (optical path length p) in millimeters were made with a Mitutoyo IP65 coolant proof micrometer with a precision of 0.001 mm. Obsidian density values (ρ) were computed by the Archimedes method on an Ohaus analytical balance with a precision of ±0.0001 g. The immersion fluid was Unigrav with a specific gravity of 1.6 g/mL at 20°C.

Infrared transmission analysis was conducted using a Thermo Nicolet Avatar 360 FTIR. Each sample analysis consisted of 64 scans

Table 1
Beer's Law parameters and percent water content values for obsidians determined by transmission FTIR.

Lab No.	Thickness (mm)	Density (g/cm^3)	ABS 4500cm^{-1}	%OH	ABS 5200cm^{-1}	%H_2O_m	%H_2O_t
MAULE 42B	1.00	2.4025	0.019	0.08	0	0	0.08
MAULE 18	0.97	2.3984	0.018	0.08	0	0	0.08
HUENUL 2	0.79	2.3838	0.017	0.09	0	0	0.09
LAS CARGAS 39A	0.87	2.3811	0.018	0.09	0	0	0.09
BARD10D	0.957	2.3273	0.024	0.11	0.003	0.02	0.13
TAK048D	1.058	2.3383	0.030	0.13	0.002	0.01	0.14
TWO09C	1.081	2.3619	0.040	0.16	0.000	0.00	0.16
SUAZ08B	0.984	2.3453	0.045	0.20	0.004	0.02	0.22
RHCO1D	1.031	2.3353	0.059	0.26	0.008	0.04	0.29
RHCO3D	1.067	2.3355	0.089	0.37	0.023	0.10	0.48
RHCO8D	0.817	2.3316	0.077	0.42	0.018	0.11	0.53
RHCO2F	1.047	2.3326	0.106	0.45	0.032	0.15	0.60
CVO713C	0.927	2.3496	0.081	0.39	0.059	0.30	0.69
CVO707C	0.900	2.3386	0.128	0.63	0.045	0.24	0.87
RHNM25B	0.924	2.3291	0.143	0.69	0.084	0.44	1.13
RHNM26C	0.891	2.3253	0.149	0.75	0.097	0.52	1.27
RHNM25A	0.944	2.3293	0.162	0.77	0.100	0.51	1.28
RHNM22D	0.742	2.3217	0.139	0.86	0.101	0.66	1.52