AN IMPROVED EQUATION FOR COSO OBSIDIAN HYDRATION DATING, BASED ON OBSIDIAN-RADIOCARBON ASSOCIATION

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It has been 20 years since Basgall's pioneering development of a dating equation for Coso obsidian, and considerable progress has been made since then in the understanding of hydration. This paper reports an improved equation, based on a similar data set but with the advantage of rigorous corrections for effective hydration temperature (EHT). The equation itself is based on the physics of the hydration process, and gives reasonable ages even for large hydration rims. The equation is $t = 42.69\ r^2$*, where t is age in calibrated years before 2000 (cyb2k) and r is hydration rim thickness in microns (*μ*), corrected to an EHT of 20.4°C. The range of validity for the equation is* $0 < r < 16\ \mu$ *at 20.4°C, or* $0 < t < 11{,}000$ *cyb2k. The accuracy of age estimates from this equation is* ~ 20 *percent. The equation represents a composite for the Coso volcanic field; research to define flow-specific rates is in progress.*

Previous estimates of Coso hydration rate (e.g. Basgall 1990; Basgall and Hall 2000; Pearson 1995) represented the state of the art at the time, but the researchers did not have access to newer theoretical developments or numerical techniques. This paper reexamines the problem of developing a hydration rate from obsidian-radiocarbon association data, using a database from the Mojave Desert and Owens Valley, California, similar to the database of previous researchers (Basgall 1990; Gilreath and Hildebrandt 1997). The intent is not to criticize the work of earlier researchers, but to build on it with newer techniques and insights which were not available to them. We also point out some land mines which await the unwary person who attempts a hydration rate analysis without a familiarity with numerical analysis.

The present analysis applies the well-accepted diffusion-reaction model (Doremus 1994, 2000, 2002) as the description of the obsidian hydration process, and uses the archaeological data to compute the necessary model parameters. The form of the equation is a linear dependence of hydration rim thickness on the square root of time, which is well-accepted in materials science and geochemistry (e.g. Ebert et al. 1991; Zhang and Behrens 2000) and has been demonstrated in the laboratory (Stevenson et al. 1989, 1998, 2004). The analysis employs a rigorous correction for effective hydration temperature (EHT), which includes a correction for burial depth (Rogers 2007a). Temperature parameters for the sites are computed by means of regional temperature scaling (Rogers 2008a). The rate is computed by a linear least-squares best-fit technique, with variables chosen to minimize propagation of error (Cvetanovic et al. 1979). The resulting rate is based on current conditions, so any adjustments for paleotemperature changes must be taken into account when age computations are made (see Rogers 2010a).

We emphasize that determining a hydration rate is *not* a regression problem, but a problem of parameter optimization. Regression is a technique to estimate to what extent one variable depends on another, and is frequently encountered in the social sciences; for example, a regression might be used to investigate to what extent final examination scores depend on completion of homework. In the present case, however, the degree of dependence is fully known *a priori* from physics, so the problem is of optimizing a parameter (the rate) which defines the fit between data and the physical model. Mathematically, the formalism used to compute the linear best fit, described below, is the same as that used in a regression analyses for a quadratic fit with no linear term and the best-fit line constrained to pass through the origin; the difference is that here the physical model, and hence the degree of dependence, is known.

It follows that, since the form of the hydration equation is known from physics, other forms must be explicitly avoided, such as inclusion of higher-order terms or other exponent values. With virtually any archaeological data set it is possible to obtain a better fit (measured by residuals) by other forms of the equation; however, the apparent accuracy thus achieved is spurious. Each data point is a combination of valid data and experimental error, and the higher degree polynomial or exponent is simply a better fit to the experimental error. Good practice in numerical analysis is to select the model equation based on the nature of the problem (Hanning 1973; Matthews 1992); for obsidian hydration, this means the physical or chemical model, which is a linear dependence of hydration rim thickness on the square root of time.

It is important to state explicitly the range of validity of the age equation, which is the range of rim values and ages spanned by the original data set (including zero rim at zero time, by definition). Use of the resulting equation to compute ages within the original range of values is a process of interpolation, which suppresses errors; use outside the range of the original data is extrapolation, which may amplify errors. Thus, the age equation is most trustworthy within this range of validity, and any analyst who uses the age equation needs to know what the range of values for the original data was.

Finally, since this problem is an optimization rather than a regression, use of Pearson's R as a sole criterion of goodness of fit is inappropriate. A better measure is the standard deviation of hydration rate, which affects the predictive accuracy of the best-fit rate (Rogers 2010b). These topics are discussed further below.

HYDRATION THEORY

Hydration of obsidian has both a physical and a chemical aspect, and is known as a diffusion-reaction process (Doremus 1994, 2000, 2002). The physics and chemistry of the process suggest that the relationship between age and rim thickness should be approximately quadratic, i.e., of the form

$$r^2 = m\,t \qquad (1)$$

where t is age in calendar years, r is rim thickness in microns, and m is the hydration rate (see e.g., Doremus 2000, 2002; Ebert et al. 1991; Rogers 2010b; Stevenson et al. 1989, 1998, 2004; Zhang et al. 1991). Equation 1 indicates that the rim growth should proceed as $t^{0.5}$, and Crank (1975:37-38) showed that mass uptake of water varies by the same relationship as the hydration rim.

The functional form of equation 1 has been questioned (Anovitz et al. 1999). Riciputi et al. (2002) found a good fit to a form of $t^{0.75}$, while a more recent study suggests that mass uptake varies as $t^{0.6}$ (Stevenson and Nowak 2011). Analyses of diffusion in polymers suggest the relationship should lie between $t^{0.5}$ and $t^{1.0}$, depending on whether the polymeric behavior is "rubbery" or "glassy" (Crank 1975:254-257). However, Haller argued, based on the physical chemistry of diffusion, that if any dependence other than quadratic is found, "it is more likely the fault of the experiment rather than any inherent feature of the diffusion process" (Haller 1963:217). Furthermore, the quadratic form has been demonstrated experimentally in the laboratory, both in terms of mass uptake (Ebert et al. 1991) and growth of the hydration rim (Rogers and Duke 2011; Stevenson et al. 1989, 1998, 2004). Since obsidian is a natural material, it is entirely possible that deviations from equation 1 occur, particularly at a fine-grained level; however, at the spatial level and accuracy involved in archaeological dating using optical microscopy, equation 1 appears to be valid for the time scales of interest. When obsidian data are expressed in radiocarbon years before the present (rcybp, by convention referenced to 1950), the quadratic form is still the best fit, giving the smallest overall error in age estimation, but with a different rate constant (Rogers 2006). Based on these data, equation 1 is the functional form employed here.

The hydration rate varies with EHT (see e.g. Hull 2001; Onken 2006; Ridings 1996; Rogers 2007a; Stevenson et al. 1989, 1998, 2004), with relative humidity (Friedman et al. 1994; Mazer et al. 1991; Onken 2006), and with intrinsic water concentration in the obsidian (Ambrose and Stevenson 2004; Friedman et al. 1966; Karsten and Delaney 1981; Karsten et al. 1982; Rogers 2008b; Stevenson et al. 1998, 2000; Zhang and Behrens 2000; Zhang et al. 1991).

The analysis reported here controls for EHT by the time-dependent diffusion technique (Rogers 2007a), which specifically accounts for average annual temperature, annual variation, diurnal variation, and burial depth. The equation for EHT is

$$\mathrm{EHT} = T_a \times (1 - Y \times 3.8 \times 10^{-5}) + 0.0096 \times Y^{0.95} \qquad (2)$$

where T_a is annual average temperature, and the variation factor Y is defined by

$$Y = V_a^2 + V_d^2 , \qquad (3a)$$

in which V_a is annual temperature variation (July mean minus January mean) and V_d is mean diurnal temperature variation (Rogers 2007a). All temperatures are in degrees C.

The variation parameters V_a and V_d represent the temperature variations at the artifact burial depth; if the artifacts were buried, variations at the artifact depth are related to surface conditions by

$$V_a = V_{a0} \exp(-0.44\, z) \qquad (3b)$$

and

$$V_d = V_{d0} \exp(-8.5\, z) \qquad (3c)$$

where V_{a0} and V_{d0} represent nominal surface conditions and z is burial depth in meters (Carslaw and Jaeger 1959:81; Rogers 2007b). This dependence of temperature variation on depth is well attested in physics, geology, and soil science. The numerical parameters determining attenuation with depth were experimentally determined by the author in desert conditions, and the resulting thermal diffusivities agree well with the published values for sand (Carslaw and Jaeger 1959, Appendix 4; the depth attenuation values given in Rogers 2007a are incorrect).

Parenthetically, the Lee (1969) equation does not give correct values of EHT and should not be used in obsidian analyses (as in Fredrickson et al. 2006). The issues involved in use of the Lee equation are discussed at length by Rogers (2007a).

Effective hydration temperature summarizes the effects of temperature history in one parameter; furthermore, a change in EHT (ΔT_e) produces a change in rim value (Δr):

$$\Delta r / r = -\tfrac{1}{2} (E / R\, T_e^2)\, \Delta T_e \qquad (4)$$

(Rogers 2007a). Reported values of E/R lie in the range 9,500-11,000° K (Friedman and Long 1976:348, Table 1), with “faster” obsidians having lower values of E/R. Typical temperatures of archaeological interest are ~300° K. Thus, for nominal conditions, the parameter $\tfrac{1}{2} (E / R\, T_e^2) \approx 0.06$, leading to a change in rim of ~ 6 percent / ° K (or ° C). Finally, the EHT-corrected rim value r_c is

$$r_c = \mathrm{RCF} \times r \qquad (5)$$

where RCF is the rim correction factor, and is equal to the right-hand side of equation 4.

The value of EHT_r used for Coso obsidian is 20.4° C, corresponding to that of Lubkin Creek, or CA-INY-30. Since most Coso work uses INY-30 as a reference, correcting the rim to these conditions allows direct comparison of EHT-corrected rim data with other published data. However, if the rate is to be applied at a different EHT, the rate itself must be adjusted as discussed below.

Since climate has not been stable over the periods of archaeological interest, the effects of resulting temperature changes should be included when applying this rate to age computations. West et al.

Table 1. Radiocarbon-obsidian database and sources.

SITE	SAMPLE ID	RC AGE	RIM MEAN (μ), UNCORRECTED	DEPTH (m)	REFERENCES
INY-30	30.1	760	4.10	0.85	Basgall and McGuire 1988:116, Table 12, Appendix B
INY-30	30.2	960	4.73	0.65	Basgall and McGuire 1988:116, Table 12, Appendix B
INY-30	30.3	1220	4.43	0.55	Basgall and McGuire 1988:116, Table 12, Appendix B
INY-30	30.4	1600	4.43	0.55	Basgall and McGuire 1988:116, Table 12, Appendix B
INY-30	30.5	1860	5.31	0.70	Basgall and McGuire 1988:116, Table 12, Appendix B
INY-30	30.6	1530	5.31	0.70	Basgall and McGuire 1988:116, Table 12, Appendix B
INY-30	30.7	1840	4.50	0.60	Basgall and McGuire 1988:116, Table 12, Appendix B
INY-30	30.8	1650	4.50	0.60	Basgall and McGuire 1988:116, Table 12, Appendix B
INY-372	372.1	2900	8.04	2.55	Lanning 1963; Jenkins and Warren 1984:57
INY-372	372.2	3520	8.20	2.89	Lanning 1963; Jenkins and Warren 1984:57
INY-372	372.3	3580	8.16	3.21	Lanning 1963; Jenkins and Warren 1984:57
INY-372	372.4	3900	8.16	3.74	Lanning 1963; Jenkins and Warren 1984:57
INY-372	372.5	3240	7.32	2.30	Yohe 1992:140, Table 5, Appendix
INY-372	372.6	4460	8.05	2.65	Yohe 1992:140, Table 5, Appendix
SBR-5250	5250.1	8410	15.19	0.60	Jenkins 1985:Appendix D, 1987; Haynes 2001:121, Table 1
SBR-5250	5250.1	8420	18.27	0.25	Jenkins 1985:Appendix D. 1987; Haynes 2001:121, Table 1
SBR-4562	4562.1	9470	13.50	0.85	Jenkins and Warren 1986:Appendix D, p. 8, Table 3; Haynes 2001:121, Table 1
SBR-4562	4562.2	9410	11.58	0.95	Jenkins and Warren 1986:Appendix D, p. 8, Table 3; Haynes 2001:121, Table 1
INY-3806/H	3806.1	1600	3.64	0.85	Delacorte and McGuire 1993:67, Appendix T
INY-3806/H	3806.2	1160	3.64	0.85	Delacorte and McGuire 1993:67, Appendix T
INY-3812	3812.1	1600	4.71	0.95	Delacorte and McGuire 1993:67, Appendix T
INY-3812	3812.2	1340	5.60	1.15	Delacorte and McGuire 1993:67, Appendix T
INY-4554	4554	6740	10.30	0.90	FWARG 1994:A17, 233
INY-1428	1428	990	4.30	0.35	Gilreath 1995:Appendix A
INY-328/H	328	9440	11.07	0.66	Delacorte 1999:39-40, 48
INY-2750	2750	1330	4.03	0.50	Delacorte 1999:41

(2007) presented a graph of mean temperature fluctuations over the past 18,000 years. Data from this graph have been used to model the effects of climate change on obsidian hydration, computed as a weighted average of effective diffusion rates over time, and a method of applying the correction has been developed (Rogers 2010a).

ANALYSIS

Archaeological and Temperature Data

The archaeological data set employed consists of 26 pairs of rim readings and associated radiocarbon data from 10 desert sites; all are on Coso obsidian with known excavation depths and corresponding radiocarbon dates. Subsource within Coso is not known, so the values refer to the volcanic field as a whole. Table 1 summarizes the site data and sources.

Temperature parameters were estimated from data for 13 sites in the southwestern Great Basin and northern Mojave Desert, reported by the Western Regional Climate Center, corrected for altitude. All represent 30 years of meteorological data, which is the standard length of time employed by meteorologists for establishing seasonal norms (Cole 1970). It has been shown (Rogers 2008a) that the annual average temperature in this region decreases by 1.8º C / 1,000 ft. altitude increase, and is predicted by the equation

$$T_a = 22.25 - 1.80\ x \qquad (6)$$

where x is altitude in thousands of feet. The error standard deviation of this model is 0.79º C. The annual temperature variation was found to decrease by 0.5º C / 1,000 ft. altitude increase, and to be predicted by

$$V_a = 23.14 - 0.5\ x \qquad (7)$$

with x defined as above. The error standard deviation is 0.90º C (Rogers 2008a).

The predictability of V_d with altitude is poor, so, in the absence of other data about a site, the most robust estimate is simply the mean ($V_d =$ 15.8º C). The accuracy of this estimate is 1.67º C, 1-sigma (Rogers 2008a).

These equations are for air temperatures. Obsidian on the surface is also affected by surface temperatures, which can be significantly higher than air temperatures in areas devoid of vegetation (Johnson et al. 2002; Rogers 2008a). However, for surfaces which have intermittent foliage coverage, the air temperatures are, on average, a good approximation to surface temperatures (Rogers 2008b)

Linear Best Fit Theory

Archaeologically useful rates for obsidian hydration are calculated by a best-fit procedure using hydration rim data and associated ages based on radiocarbon data. The best-fit slope is computed as (cf. Meyer 1975:71-75)

$$S = \sum x_i\, y_i / \sum x_i^{\,2} \qquad (8)$$

which is the standard best-fit equation for a line constrained to pass through the origin; $\{x_i, y_i\}$ are the data points being fit, each consisting of a single obsidian-radiocarbon pair. If each point is constructed of an aggregate of N_i individual data points, equation 8 becomes

$$S = \sum N_i\, x_i\, y_i / \sum N_i\, x_i^{\,2} \qquad (9)$$

Equations 8 and 9 yield exactly the same value of S.

The best fit is based on equation 1, which can be rearranged as

$$r = k_e\, t^{1/2} \qquad (10)$$

where r is the EHT-corrected rim measurement, t is age, and k_e is the square root of the parameter m in equation 1. The age is in calendar years before the hydration rim was measured, so the radiocarbon age must be converted to calendar age and some estimate of the offset since 1950 should be added (on the order of 50 years). The independent variable is chosen to be $t^{1/2}$ and the dependent variable is r; when a linear least-squares best fit is computed, the slope is k_e in microns/year $^{1/2}$. Setting $S = k_e$, equation 9 then becomes

$$k_e = \sum r_i\, t_i^{\,1/2} / \sum t_i \qquad (11)$$

The rationale for choosing to fit equation 10 instead of equation 1 is that simple linear best fit techniques (e.g. Cvetanovic et al. 1979; Meyer 1975:71-75) assume the independent variable is error-free, with all error confined to the dependent variable (Guest 1961; Taylor 1982). This is not the case for obsidian, since uncertainties may exist in both variables (Rogers 2008d, 2010b). It can be shown by propagation of error theory (Cvetanovic et al. 1979; Taylor 1982:173-178) that the coefficient of variation of errors in the independent variable in equation 9 is much less than it is for equation 1. Thus, equation 10 is preferable for analysis, since it more nearly meets the criterion of an error-free independent variable.

Using the same data set, the standard deviation of the rate estimate can be computed from

$$\sigma_{ke} = \sigma_r / \sum t_i \qquad (12)$$

where

$$\sigma_r^{2} = \sum (r_i^{\,2} - k_e\, t_i^{\,0.5})^{2} \qquad (13)$$

(equation 12 from Taylor 1982:173; equation 13 derived based on Taylor 1982:261, problem 8.8).

Techniques exist which avoid the errors-in-the-independent-variable problem by weighting the data points by the sum-squared deviation from the best-fit line, measured perpendicular to the line (Guest 1961:128-131; Meyer 1975:71-75; Rogers 2009; Van Huffel and Vandewalle 1991). However, the algorithms are much more complex and are dependent on more *a priori* knowledge about error sources than is usually available in obsidian hydration. Experience has shown that the total least squares algorithm does not give any practical improvement over equation 11, so the simpler formulation is employed here.

Linear Best Fit Process and Results

Effective hydration temperature was computed for each specimen based on equations 2 and 3 above, and the rim thickness for each sample was corrected for EHT by equations 4 and 5 above. Radiocarbon ages were converted to physical age (calendar years referenced to 2000) using Calib 5.01; no correction was made for δ^{13}C, since the data were not available for many of the data points. Table 2 presents the data set used in the analysis.

The linear least-squares best fit was computed by equation 11, using the EHT-corrected rim data of Table 1 and the calibrated age data of Table 2. The age coefficient K_0 is computed as $1/k_e$, and the resulting best-fit model for this data set is

$$t_{\text{cal yrs before 2000}} = (42.69 \pm 1.92)\, r^{2}, \quad 0 \le r \le 16\mu \text{ at } 20.4° \text{ C EHT} \qquad (14)$$

The equation is valid to an age of approximately 11,000 cyb2k; ages older than this represent an extrapolation and hence are less accurate. Equation 14 corresponds to a rate of $0.1530 \pm 0.0034\ \mu / \text{yr}^{1/2}$; thus, the coefficient of variation of the rate is approximately 2.2 percent. Figure 1 shows the fit graphically.

For the analyst who wishes to compute ages in terms of radiocarbon years before the present (rcybp, referenced to 1950) for direct comparison with radiocarbon dates, the appropriate equation is

$$t_{\text{rcybp}} = (39.03 \pm 1.78)\, r^{2}, \quad 0 \le r \le 16\mu \text{ at } 20.4°\text{C EHT} \qquad (15)$$

This equation is valid to an age of approximately 9500 rcybp.

If the age is to be computed at an EHT other than 20.4°C, the age coefficient in equations 14 and 15 must be adjusted, so that

$$K = K_0 \exp\,[C_t\,(20.4 - T_e)] \qquad (16)$$

where K is the age coefficient at an EHT of T_e, K_0 is the age coefficient in equation 14 or 15, and C_t is a temperature coefficient. The coefficient C_t is equal to $E / R\, T_e^{\,2}$, with E, R, and T_e as defined for equation 4. Laboratory measurements for Coso obsidian (Friedman and Long 1976; Stevenson and Scheetz 1989) yielded a value of $E/R \approx 10{,}000°$ K, which, for $T_e = 293°$ K, gives a value of C_t of 0.116 / ° K. On the other hand, the value of E / R computed from archaeological data by Stevens (2005) is 8813° K, which gives $C_t = 0.102$ / ° K. Until more definitive measurements can be made, a value of $C_t = 0.11$ is a reasonable compromise for archaeological analysis.

Table 2. Analysis database, arranged in order of increasing age.

Site	Site Altitude, kft. AMSL	RC Age, RCY before 1950	RC Age SD	Cal Age, Yrs. before 1950	Phys Age, Yrs. before 2000	Depth (m)	N	Rim mean (μ), uncorrected	Rim SD (μ), uncorrected	Rim mean (μ), EHT corrected	Rim SD (μ), EHT corrected
30.1	3.28	760	100	710	760	0.85	5	4.10	1.47	4.98	1.78
30.2	3.28	960	100	867	917	0.65	6	4.73	1.17	5.67	1.40
1428	3.71	990	80	893	943	0.35	6	4.30	0.25	5.33	0.31
3806.2	3.6	1160	90	1088	1138	0.85	5	3.64	0.97	4.61	1.23
30.3	3.28	1220	70	1146	1196	0.55	3	4.43	0.45	5.28	0.54
2750	3.66	1330	70	1247	1297	0.50	5	4.03	0.23	5.02	0.29
3812.2	4.21	1340	50	1268	1318	1.15	5	5.60	0.80	7.67	1.10
30.6	3.28	1530	70	1428	1478	0.70	11	5.31	0.50	6.39	0.60
3812.1	4.21	1600	60	1485	1535	0.95	5	4.71	0.44	6.39	0.60
30.4	3.28	1600	70	1488	1538	0.55	3	4.43	0.45	5.28	0.54
3806.1	3.6	1600	100	1497	1547	0.85	5	3.64	0.97	4.61	1.23
30.8	3.28	1650	100	1554	1604	0.60	7	4.50	1.08	5.38	1.29
30.7	3.28	1840	80	1771	1821	0.60	7	4.50	1.08	5.38	1.29
30.5	3.28	1860	70	1793	1843	0.70	11	5.31	0.50	6.39	0.60
372.1	3.58	2900	80	3051	3101	2.55	7	8.04	1.09	10.55	1.43
372.5	3.58	3240	60	3466	3516	2.30	6	7.32	1.40	9.63	1.84
372.2	3.58	3520	80	3798	3848	2.89	4	8.20	0.20	10.76	0.26
372.3	3.58	3580	80	3883	3933	3.21	9	8.16	0.22	10.73	0.29
372.4	3.58	3900	80	4324	4374	3.74	5	8.16	0.42	10.76	0.55
372.6	3.58	4460	110	5106	5156	2.65	2	8.05	0.35	10.57	0.46
4554	3.68	6740	90	7602	7652	0.90	14	10.30	1.34	12.78	1.66
5250.1	1.44	8410	140	9379	9429	0.60	9	15.19	1.00	14.17	0.93
5250.1	1.44	8420	140	9391	9441	0.25	10	18.27	4.03	16.79	3.70
4562.2	3.28	9410	115	10662	10712	0.95	4	11.58	3.09	13.71	3.66
328	3.73	9440	150	10722	10752	0.66	5	11.07	0.65	13.64	0.80
4562.1	3.28	9470	115	10767	10817	0.85	5	13.50	1.46	16.06	1.74

In applying equations 14 or 15, best results are obtained by including a correction for paleoclimatic temperature change (Rogers 2010a).

ACCURACY CONSIDERATIONS

The accuracy with which the best-fit model reproduces the age of the data set of Tables 1 and 2 is approximately 20 percent, which suggests that significant experimental errors exist in the data set. The error arises from six sources: hydration rim measurement; radiocarbon measurement and calibration; humidity history; estimation of EHT; intra-source variation in hydration rate; and site formation processes. The effects of the first three sources are negligible, while the remaining three are significant (Rogers 2010b).

Uncorrected variations in temperature history have a strong influence, since the hydration rate is strongly temperature-dependent. Techniques have been developed to compute EHT for various climatic regimes, for paleotemperature changes, and for the effects of burial depth (Hull 2001; Rogers 2007b, 2009). In either case, it is unlikely that EHT can be corrected much better than ~1.0° C (Rogers 2007a).

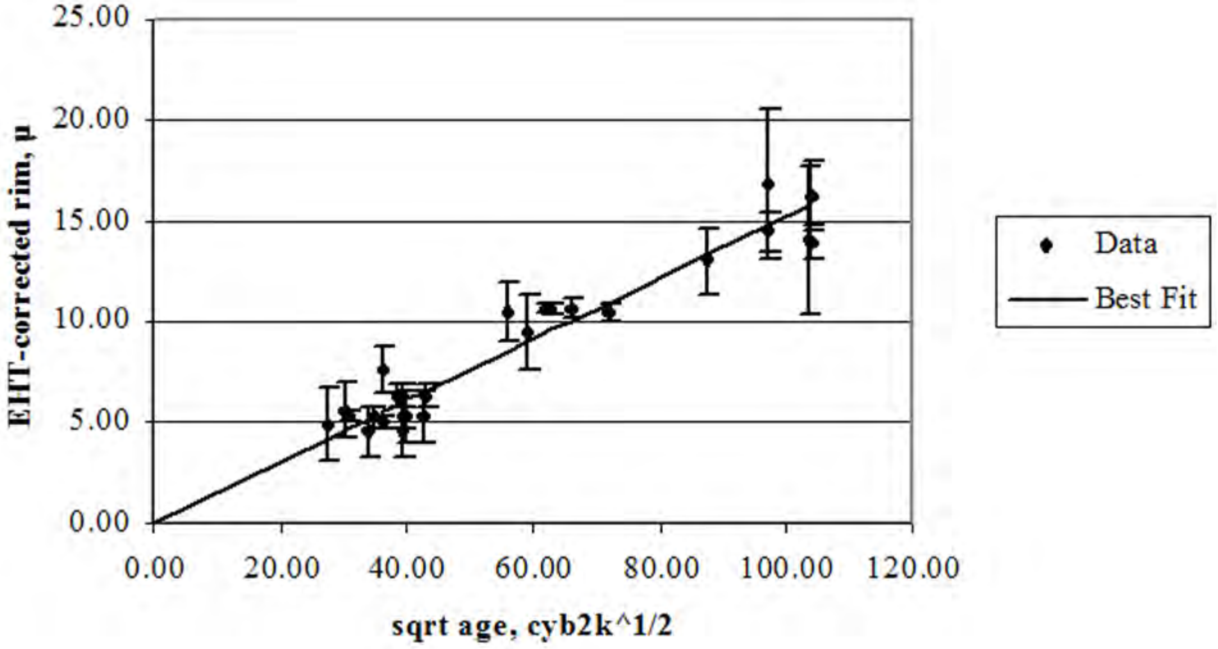

Figure 1. EHT-corrected hydration rims plotted against the square root of age in calibrated years before 2000. The slope is the hydration rate.

Variability of intrinsic water in obsidian arises from geologic processes when the obsidian was formed. Experiments have shown (Karsten and Delaney 1981; Karsten et al. 1982; Stevenson et al. 1998; Zhang and Behrens 2000; Zhang et al. 1991) that the hydration rate in obsidian at any given temperature is a function of the concentration of water in the glass (see equation 2). Intra-source variability in intrinsic water content has been measured in Coso obsidians (Stevenson et al. 1993) and is likely present in at least some others. Current methods of measuring intrinsic water in obsidian are micro-densitometry (Ambrose and Stevenson 2004; Stevenson et al. 2000), mass loss-on-ignition (Steffen 2005), and infrared spectrometry (Newman et al. 1986; Steffen 2005; Stevenson et al. 1993). All these techniques are costly and destroy the specimen; as a result, intrinsic water measurement is not conducted in most practical archaeological investigations in the United States today, and the resulting rate variations remain a source of uncertainty.

Site formation processes affect the association between obsidian and radiocarbon-based data sets, and primarily influence the age dimension. The principal phenomenon of concern is turbation, or vertical mixing, by biological, geological, hydrological, or cultural processes. Although good data are lacking, it is likely that stratigraphic perturbations caused by the first three processes are equally likely to be upward or downward. However, the principal cultural processes affecting site formation are reuse of materials and curation of artifacts, and the "old wood" problem (the use of recycled wood for fuel or structures, leading to radiocarbon ages which can be significantly too old; Schiffer 1987:309-312). Reuse and curation tend to bring older obsidian to younger ages and can cause a negative offset in mean age, while the old wood problem has the opposite effect.

Previous analyses have shown that rate accuracies of <4-6 percent are achievable (Rogers 2010b), which is the case here. This relatively small error CV is due to the least-squares best-fit process and avoidance of higher-order terms in equation 10. However, accuracy of chronometric estimates based on such a rate does not have the advantage of best-fit smoothing and hence is never as good as the rate accuracy. It has previously been shown that, for Coso obsidian, age standard deviations of the order of 20 percent of age can be expected (Rogers 2010b). This is for an estimate based on a single data point; if a sample size of N is employed, the probable error of the age point estimate is reduced by $N^{0.5}$.

A major caveat to equation 14, and one which potentially affects accuracy of age estimates, is that it is a composite value for the Coso volcanic field. Subsources for the obsidian data employed were generally not specified in the reports which provided the data set. Furthermore, the radiocarbon data generally did not have a $\delta^{13}C$ correction applied. Analyses to overcome these limitations are ongoing.

COMPARISON WITH PRIOR EQUATIONS

Equations 14 and 15 may be compared to a few of the previously available equations. The analysis below addresses five relatively well-known equations (Basgall 1990; Basgall and Hall 2000; King 2004; Pearson 1995; Stevens 2005).

Basgall (1990) proposed the equation

$$t = 31.62\ r^{2.32} \qquad (17)$$

based on a fit to a data set described in Gilreath and Hildebrandt (1997:15, Table 4). Pearson (1995) proposed

$$t = 125\ r + 25\ r^{2} \qquad (18)$$

based on analysis of obsidian at Little Lake and southern Owens Valley. Basgall and Hall (2000) more recently proposed the equation

$$t = 659.21 - 516.04\ r + 155.02\ r^{2} - 4.56\ r^{3} \qquad (19)$$

In none of these cases is a range of validity stated, although the age range for equation 17 can be inferred from Table 4 in Gilreath and Hildebrandt (1997).

King (2004) proposed the equation

$$t = r^{2} / 0.016 - 50 \qquad (20)$$

(Note: the equation as printed in King 2004:139 contains an apparent typographic error; it is correctly printed in King 2004:140, Figure 4). In equations 17-19, t is understood to be in rcybp; in equation 20, this is explicitly stated to be the case. Thus, they must be compared to equation 15 above.

Stevens (2005) conducted a very innovative analysis of obsidian hydration rates at high altitudes by an innovative application of the temperature dependence of the hydration rate. The temperature dependence, as defined by the Arrhenius equation, is generally used in laboratory hydration studies to compute the activation energy and diffusion constant, but Stevens (2005) took advantage of the natural temperature difference as a function of altitude to accomplish the same goal. From this he developed hydration equations for three sources (Casa Diablo, Fish Springs and Coso). Effective hydration temperatures were computed from meteorological data; however, the computation used the Lee equation, whose accuracy is suspect (Rogers 2007a). The equation he developed for Coso, adjusted to 20.4° C, is

$$t = 40.38\ r^{2} \qquad (21)$$

This is in remarkable agreement with equation 15 developed from the present analysis.

Figure 2 presents a comparison of the equations for rim values between 0 and 20 μ. The fit in equation 15 is quadratic (i.e., of the form of equation 1), based on the physics of obsidian hydration. Inclusion of higher-order terms (equation 19) leads to the anomalous behavior shown, in which the curve is turning down at rim thicknesses above about 15 μ; this occurs because the last term in equation 19 is negative, and it becomes the dominant term as values of r increase. In fact, the equation predicts decreasing rims at values above 20 μ, which clearly does not reflect physics; unfortunately no range of

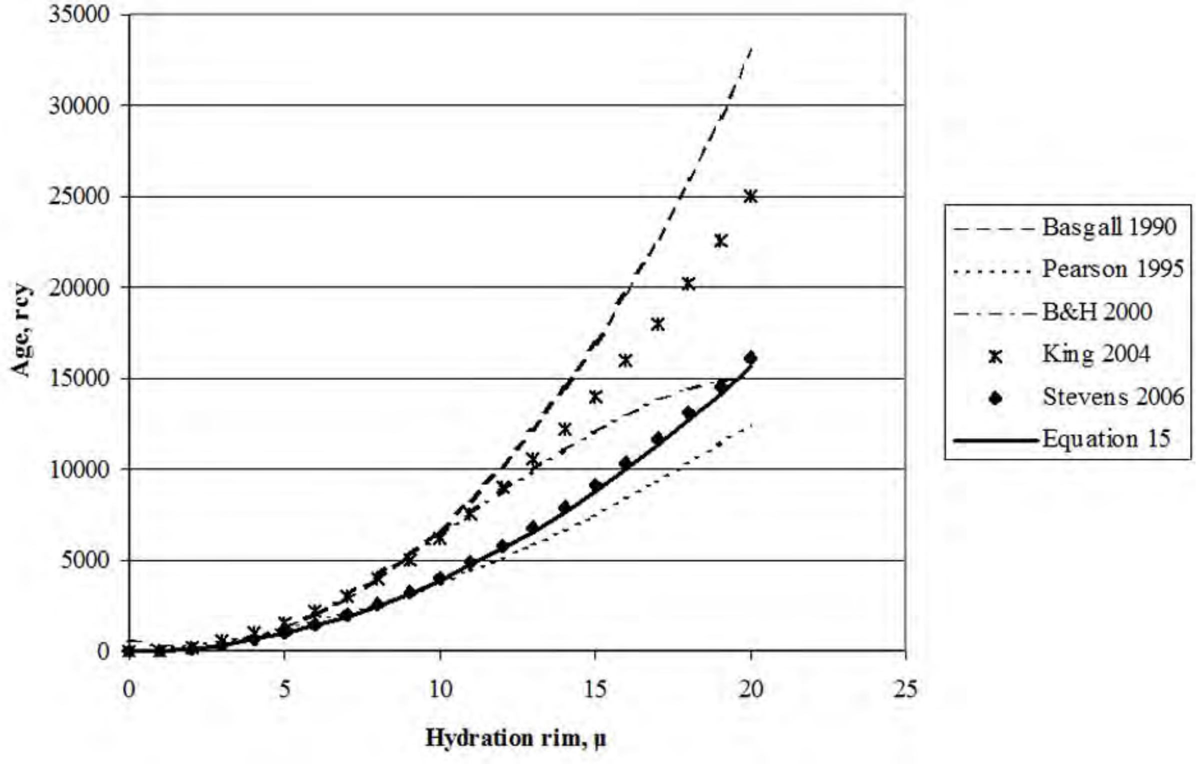

Figure 2. Comparison of ages predicted by the present analysis ("Equation 15"), Basgall 1990, Pearson 1995, Basgall and Hall 2000, King 2004, and Stevens 2006. Note that the B&H 2000 curve bends down as it approaches 20 μ; this physically unrealistic behavior is the result of including higher-order terms in the age equation. All calculations are based on an EHT of 20.4 °C.

validity was published. Use of forms with exponent other than 2 (equation 17) gives a good fit for $r \leq 5$ μ, but diverges significantly above 7 μ because of the exponent value.

Pearson's (1995) analysis was based on a large set of obsidian data from Little Lake Ranch in southern Inyo County, California. No radiocarbon dates were available at the time, so he estimated dates by temporally sensitive projectile points. His resulting equation, although not based on a physical model, gives remarkably good results for rim values r <~ 12 μ.

King (2004) explicitly took diffusion physics into account and based his computation leading to equation 20 on the diffusion-reaction model of equation 1. The age coefficient he determined is 62.51 yrs / μ^2 (King 2004:140, Figure 4), while the corresponding number for equation 20 is 39.03 yrs / μ^2. The obsidian-radiocarbon data sets employed for the two equations have many points in common. A careful analysis shows that the divergence arises because King did not have access to the more rigorous EHT correction techniques available now (Rogers 2007), which include the effects of burial depth. Making the necessary EHT corrections brings King's age coefficient into close agreement with equation 15. Incidentally, given the accuracy of the data set, making the correction between 1950 and 2000 (the term "-50" in equation 20) is unnecessary and has no practical benefit in terms of accuracy.

CONCLUSIONS

The analysis has led to a new equation for Coso obsidian hydration dating, equation 14. It is a best fit for calendar years before 2000, at an EHT of 20.4° C. For correct use, the hydration rim values to be dated must also be corrected to 20.4° C by equations 4 and 5. Equation 15 provides the same results in terms of rcybp, with the “present” being the “radiocarbon present” of 1950, and agrees closely with the results of Stevens (2005). The valid range of either equation 14 or 15 is $0 < r < 16\ \mu$, corrected to 20.4° C, and the accuracy of the rate is of the order of 2 percent. The rate is computed from a data set which probably included specimens from all the major flows in the Coso volcanic field, and hence must be regarded as a composite rate for the field; as a result, the CV of age estimates made with this rate is probably on the order of 20 percent / $N^{0.5}$, where N is the sample size.

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