

## RE-EXAMINING COSO OBSIDIAN HYDRATION RATES

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*Obsidian hydration data on Coso obsidian artifacts from upland Pinyon Zone and lowland Volcanic Field localities in Inyo County show differences attributable to difference in effective temperature between the two areas. Data presented here shows that the magnitude of the difference becomes greater with increasing age. I address this problem by generating a new temperature correction factor and employing new hydration/radiocarbon pairings from recent research in Owens Valley to arrive at new calendric rate equations for both areas. The results underscore the importance of effective temperature as an overriding variable controlling the hydration process.*

Since its proposal ten years ago, Basgall's (1990) hydration rate equation for Coso obsidian has been successfully applied in a number of settings throughout the southwestern Great Basin. This rate equation was a great improvement over its many predecessors, as it explicitly addressed temperature as the primary variable controlling local hydration rates. Since that time some problems applying the rate have become apparent, particularly at the early end of the chronology, where it appears that the rate equation overestimates true age (Basgall 1993; Delacorte 1999). Also, problems have arisen in applying the rate in temperature settings markedly different from the Owens Valley floor.

For example, Hildebrandt and Ruby (1999) compared samples of hydration measurements for various projectile point types from recent projects in two adjacent, but climatically very different, areas: the Coso Volcanic Field, at about 4,000-ft elevation (Gilreath and Hildebrandt 1997), and the adjacent pinyon zone of the Coso Range, at elevations between 7,000 and 8,000 ft (Hildebrandt and Ruby 1999). Both data sets show reasonably well-distributed hydration values (Figure 1; Table 1), underscoring the general utility of both obsidian hydration and projectile point typologies as chronometric tools. However, large differences between the means for each type are apparent. All other things presumably being equal, these effects are due to the difference in effective temperature between the two areas. While temperature data are not available for the higher pinyon zone, Hildebrandt and Ruby suggest that effective hydration temperature (EHT) ought to be on the order of 7° C cooler there than in the lower zone. However, differences in EHT as great as 13° would be

required by the Coso rate equation in order to bring each type's age estimates into the same approximate range. Further, the magnitude of the required correction becomes greater with increasing age, suggesting to Hildebrandt and Ruby that a fundamentally different approach to temperature correction needed to be developed.

This paper attempts to address these problems by proposing yet another rate equation and temperature correction for Coso obsidian, employing new hydration/radiocarbon pairings from recent research in Owens Valley, as well as some theoretical considerations drawn from the literature on experimental obsidian hydration rate development. I would like to turn first to the theoretical issues.

### THEORETICAL CONCERNS

Researchers studying hydration rate development have taken both experimental and empirical approaches, often producing results that are markedly at odds. While experimental rates have met with little acceptance from many archaeologists attempting to reconcile real archaeological problems, they do have the advantage of incorporating a theoretical understanding of the chemistry behind the process. This could profitably be considered when formulating empirical rates. Specifically, two issues are relevant to empirical rate derivation: the shape of the rate curve, and approaches to temperature correction.

The first experimental hydration rate derivations (Friedman and Long 1976; Friedman and Smith 1960) found that the process of obsidian hydration is similar

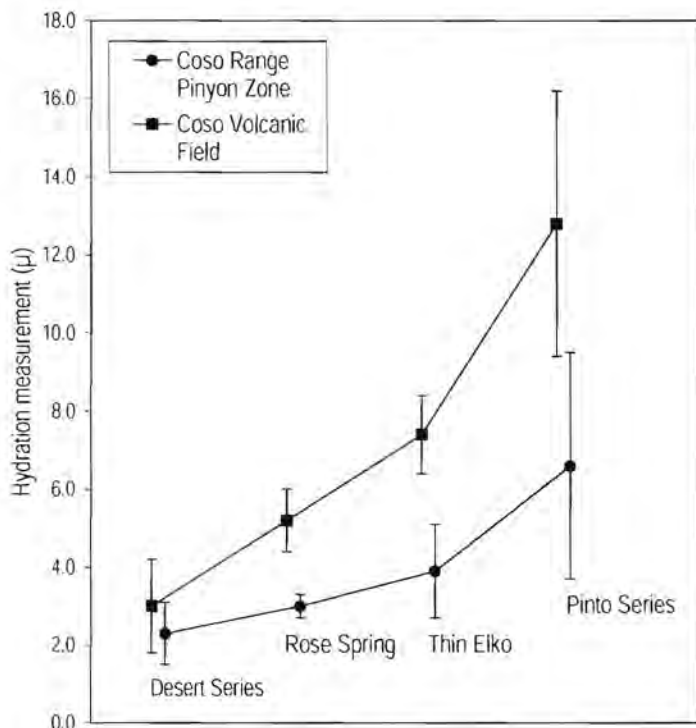


Figure 1, Table 1: Obsidian Hydration Values from Coso Volcanic Field and Coso Range Pinyon Zone.

note: all means recalculated excluding outliers via Chauvenet's criterion.

Pinyon Zone	x	n
Desert Series	2.3 ± 0.8	49
Rose Spring	3.0 ± 0.3	105
Thin Elko	3.9 ± 1.2	39
Little Lake/Pinto	6.6 ± 2.9	11
Volcanic Field	x	n
Desert Series	3.0 ± 1.2	12
Rose Spring	5.2 ± 0.8	20
Thin Elko	7.4 ± 1.0	12
Little Lake/Pinto	12.8 ± 3.4	12

to most diffusion processes in that it falls off with the square root of time:

$$t = x^2 / k$$

where t equals time in years, x is the obsidian hydration measurement in microns, and k is a source- and temperature-specific rate constant.

They found that this is common to all obsidians regardless of their trace-element chemistry. A number of experimental and empirical studies since then have confirmed that the exponent in the equation ought to be two (Bouey 1995; Onken 1991; Tremaine 1987), but researchers working with real archaeological assemblages have generally ignored this constraint when trying to fit hydration results with other chronological data, proposing instead exponents from as low as one (i.e., a purely linear formulation) to more than three. Like many empirically-derived rates, Basgall's Coso rate equation simply finds the best fit to the data, resulting in an exponent of 2.32:

$$t = 31.62x^{2.32}$$

or, expressing the equation in the form given above,

$$t = x^{2.32} / 0.03162$$

I suggest instead that the experimental data are strong enough that empirical rate formulations should be bound by the simple square-root falloff rate. I also

argue that using the same rate exponent for all obsidian sources is a parsimonious approach, because it acknowledges that despite trace-element variability, the basic chemical composition of all obsidians is similar. In any case, many empirically-derived rate equations, such as the present Coso rate, approach the square-root falloff model and could be recalculated to fit it with only marginal loss of fit to the data points.

Another area where theory could better inform empirically-developed rates is that of temperature correction. Basgall's (1990) Coso rate equation specifies that for each degree difference in EHT between the base Lone Pine locality and the locality being corrected, a 6 percent correction should be applied to the micron reading:

$$x' = x(1 - 0.06[T' - T])$$

where x is the original micron reading, x' is the corrected micron reading, T is the base EHT at Lone Pine (16.85 °C), and T' is the EHT value for which the correction is applied.

While this correction is easy to apply and works well within a certain temperature range, both experimental data and general theory indicate that the relationship between temperature and hydration rate does not behave this way, and is instead logarithmic in nature (Friedman and Trembour 1984; Hull n.d.; Hull et al. 1995; Tremaine 1987). The rate of chemical

reactions in relationship to temperature is expressed via the Arrhenius equation:

$$k = Ae^{-E/RT}$$

where  $k$  is the rate constant in the equations above,  $A$  is an empirically determined coefficient of reaction,  $e$  is the base of natural logarithms (2.71828),  $E$  is the reaction's activation energy in joules per mole,  $R$  is the universal gas constant (8.31 j/mol K), and  $T$  is the reaction temperature in Kelvins.

To adjust a hydration rate equation for temperature effects, one calculates a new value not for the micron value, but for the rate constant  $k$  (Hatch *et al.* 1990):

$$k' = ke^{E(1/T - 1/T')/R}$$

where  $k$  is the rate constant at the base EHT,  $k'$  is an EHT-corrected rate constant,  $T$  is the base EHT in Kelvins, and  $T'$  is the EHT to which the rate is being corrected, also in Kelvins.

While different from the arithmetic correction specified in Basgall's rate equation, this method of correction still leaves one with the task of empirically determining the overall magnitude of change in rate in relation to temperature, which is expressed by the activation energy  $E$ .

To illustrate the differences between the two methods, Figure 2 shows the age estimates produced by the existing Coso rate equation with a 6 percent per-degree correction vs. a logarithmic correction with an activation energy of 110,000 j/mol, for a hypothetical specimen with a hydration measurement of 5.0 microns. This value for  $E$  is similar to the 13 percent-per-degree logarithmic correction that Onken (1991) calculated for Mono Craters tephra, and I would suggest that something in the neighborhood of this value applies to all natural glasses. (Note, however, that the magnitude of the per-degree correction is not constant using this method; see Tremaine 1987). The logarithmic correction approximates the arithmetic correction within a few degrees of the base EHT, but diverges significantly at lower temperatures.

## DATA POINTS

Having specified these theoretical concerns, I would now like to turn to some empirical data. While a number of good hydration/radiocarbon pairs is

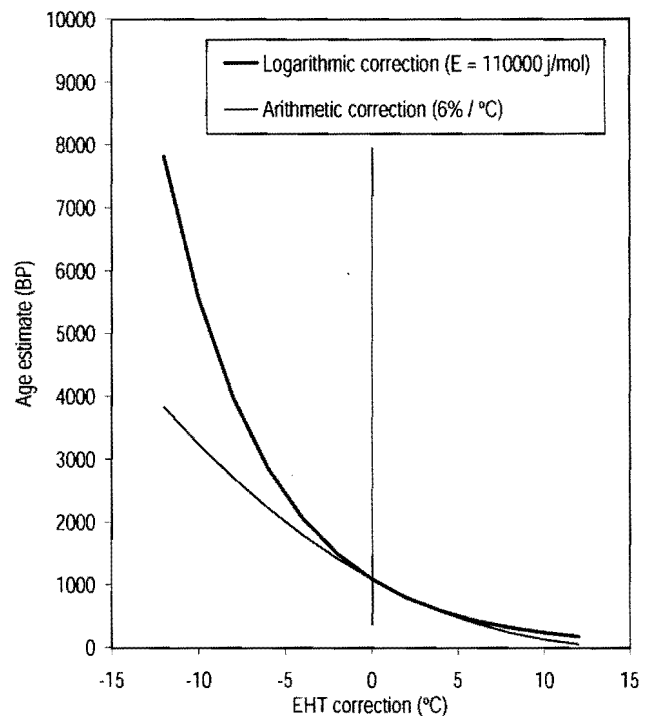


Figure 2: Age estimates produced by the existing Coso rate equation with a 6% per-degree correction vs. a logarithmic correction with an activation energy of 110,000 j/mol.

available from sites further afield, this sample is limited to southern Owens Valley, so that effective temperature can be treated as more or less constant.

Five new data points are included here (Figure 3; Table 2). For all five points, outlying hydration values have been excluded via Chauvenet's criterion and multiple radiocarbon dates averaged using Calib 4.2. Only one of the points (from CA-INY-2750; see Delacorte 1999) is a discrete feature context similar to the original pairs from site CA-INY-30. The others are based on single-component sites from which the entire hydration assemblage serves as a data point. These include two Haiwee-period sites (CA-INY-1428 [Gilreath 2000] and INY-3806/H [Delacorte and McGuire 1993]), as well as two early and middle Holocene data points from soil organic carbon dates at sites INY-4554 (Gilreath 2000) and INY-328/H (Delacorte 1999). While soil dates record geological rather than cultural events, in both cases the dates are on well-defined buried soil horizons with clearly associated cultural assemblages. While the use of soil dates is less than an ideal solution to the lack of other early data points, they at least provide a maximum acceptable age for the associated hydration means. Note, however, that I have judgmentally excluded one of the three soil carbon dates from INY-4554 as probably less representative of the site's period of occupation.

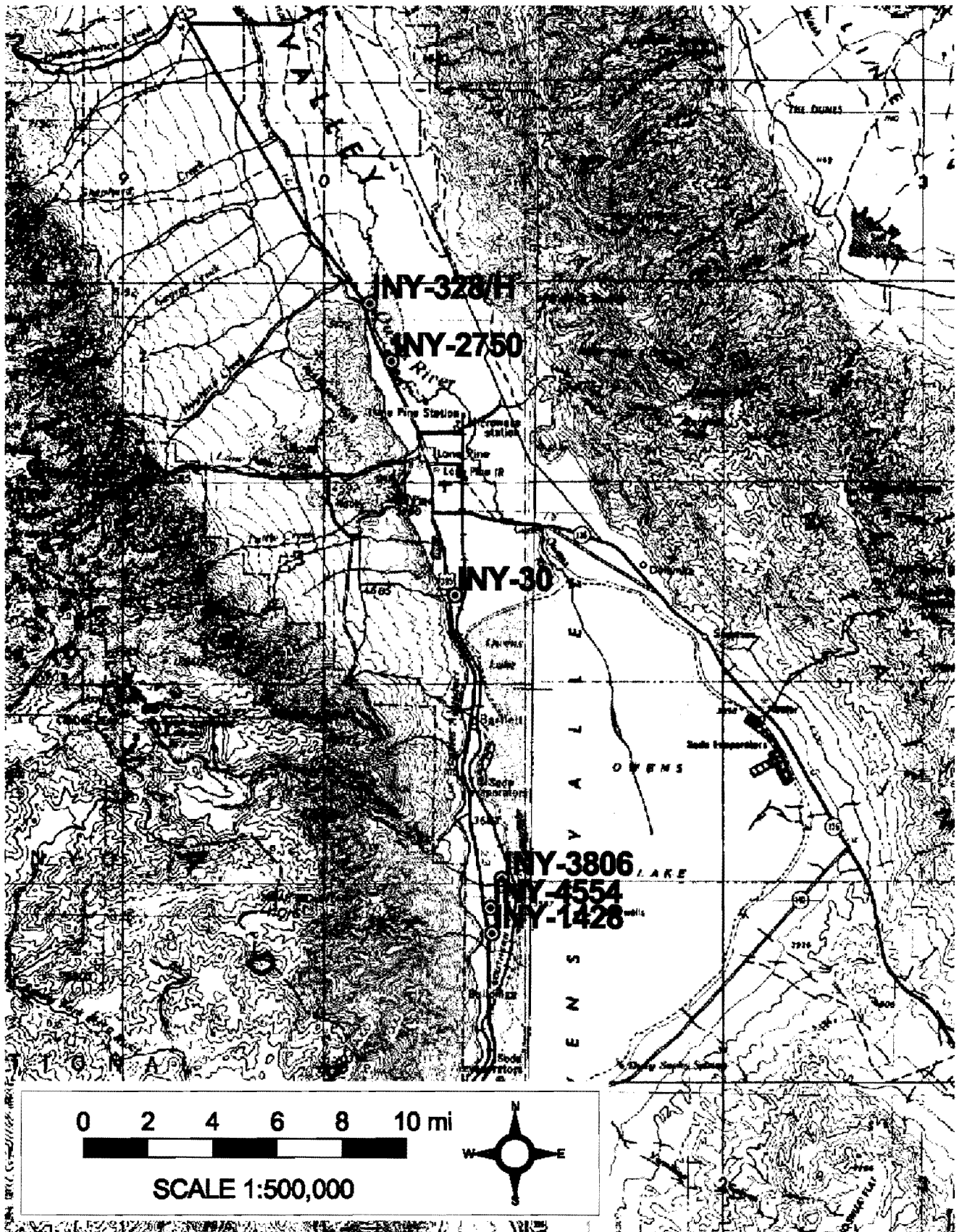


Figure 3: Location of INY-30 and the five new Owens Valley data points Included in this study.

Site	Feature	OH count	OH mean	14C dates used (not used)	14C mean	Source
INY-30	Feature 5	18	4.44 ± 1.18	960 ± 100 760 ± 100	860	Basgall and McGuire 1988
INY-30	Structure 11	30	5.35 ± 1.62	1220 ± 70 1600 ± 70	1410	Basgall and McGuire 1988
INY-30	Structure 12	12	5.28 ± 0.49	1530 ± 80 1860 ± 70	1715	Basgall and McGuire 1988
INY-30	Structure 14	11	5.19 ± 0.86	1650 ± 100 1840 ± 80	1765	Basgall and McGuire 1988
INY-4554	-	93	10.05 ± 1.35	6740 ± 90 7010 ± 100 (7780 ± 90)	6860	Gilreath 2000
INY-1428	-	58	4.44 ± 0.54	1270 ± 70 990 ± 80	1150	Gilreath 2000
INY-2750	Feature 6a	12	4.03 ± 0.23	1330 ± 70	1330	Delacorte 1999
INY-3806/H	-	34	4.40 ± 1.00	1160 ± 90 1600 ± 100	1355	Delacorte and McGuire 1993
INY-328/H	-	44	11.22 ± 2.19	9440 ± 100	9440	Delacorte 1999

Table 2: Hydration/radiocarbon pairs used in calculating rate equation.

Basgall's original set of ten hydration-radiocarbon pairs from site INY-30 (see Basgall and McGuire 1988) was also reexamined; two changes were made to these data points. First, outlying hydration values within each feature context were excluded from each sample statistically (via Chauvenet's criterion), rather than judgmentally. Second, the five post-650 B.P. pairs are excluded entirely. Hydration samples from these features are very small, with most obsidian apparently deriving from earlier occupations; this problem was originally addressed by excluding the majority of each feature sample as outliers. In any case, these pairs have very little overall effect on the result relative to that of the earlier data points.

Like the existing rate equation, this rate is calculated relative to the radiocarbon time scale, in recognition of the fact that most researchers still prefer not to calibrate their dates. It should be recognized that there are potential problems with this approach, since the relationship between radiocarbon and calendar years is not strictly linear, and depending on where they fall on the calibration curve, some

radiocarbon dates have greater temporal resolution than others. In addition, the radiocarbon chronology ends at A.D. 1950, and the difference between then and the year the hydration measurements were taken needs to be considered. To approximate this, the y-intercept for the rate curve is set at -50 B.P..

## RESULTS

The best fit to the nine data points using the constraints described above is as follows:

$$\tau = x^2 / 0.1600 - 50$$

with an r-squared value of .988. Figure 4 shows the regression graphically (note the use of the squared micron value on the x axis).

For temperature corrections to this equation I am proposing a value for activation energy  $E$  of 110,000 j/mol, because it best approximates the arithmetic correction within an effective temperature range going

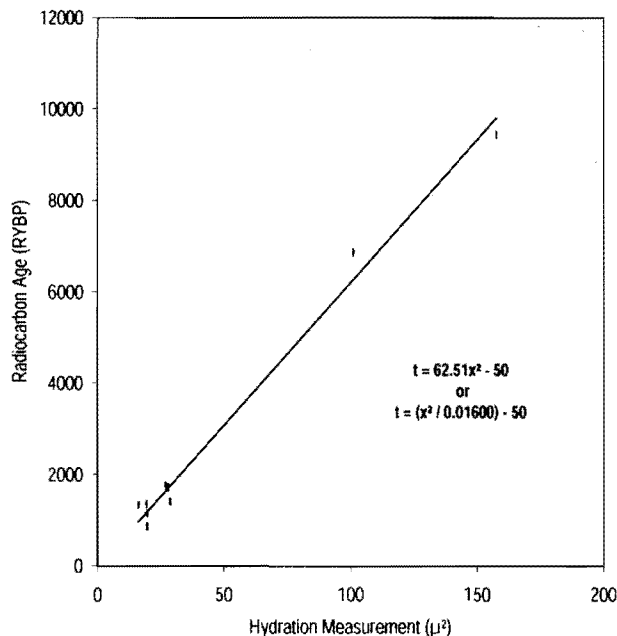


Figure 4: Linear best fit for the regression  $t = 2/0.1600 - 50$ . Note the use of the squared micron value on the x axis.

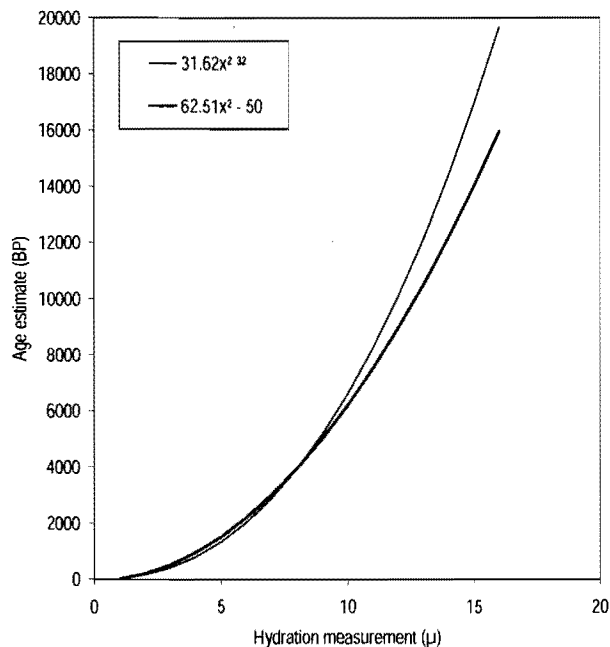


Figure 5: Regression curves for the Coso Range Pinyon Zone and Coso Volcanic Field samples, showing significant divergence after 7000 B.P.

from about two degrees below to about five degrees above the base EHT, and this is the range within which the existing rate equation has been most successfully applied. It also fits reasonably well with other empirical and experimental estimates of temperature effects on hydration (Friedman and Trembour 1984; Hatch *et al.* 1990; Onken 1991; also see Hull *et al.* 1995). However, this value should be treated as a rough estimate, and could be refined with better temperature data from dated Coso obsidian assemblages in a range of temperature settings. Indeed it may be considered an open question whether the air temperature data used to calculate EHT values are even appropriate for archaeological assemblages. This is beyond the scope of this paper, but it should be recognized that this is a continuing problem in hydration dating generally.

## DISCUSSION

So, having reformulated the rate equation for Coso obsidian and its accompanying temperature correction, the next question is whether the new rate equation produces plausible results, and whether it solves any problems or simply creates new ones. Perhaps the most important result of this exercise is that for much of the prehistoric sequence, both rate equations produce similar results, lending support to the numerous site component age estimates based on the

existing rate. Significant differences between these rate equations emerge in two main areas: at the early end of the chronology, and in temperature settings substantially cooler than the base EHT.

Figure 5 shows that beyond 7000 B.P. the two rates diverge significantly, this formulation giving substantially younger dates. This is in line with the opinion of many researchers that the existing rate overestimates age at the early end of the chronology, and helps to bring a number of seemingly anomalous age estimates for large hydration measurements into the realm of the plausible.

Returning to the Coso Range example, Figure 6 shows age estimates for the Pinyon Zone and Volcanic Field projectile point samples as produced by both rate equations and their accompanying temperature corrections, using the seven-degree difference in EHT suggested by Hildebrandt and Ruby (1999). Again, all other things being equal, the age estimates ought to come out approximately the same for each type. This rate, while not without its own discrepancies, offers generally better correspondence between age estimates than does the existing rate. For example, this rate equation narrows the disparity in age estimates for Rose Spring points from 310 years to 10 years, and the disparity for Elko series points from 1,030 years to 380 years. While an even more dramatic effect on the Pinto samples is apparent, I hesitate to



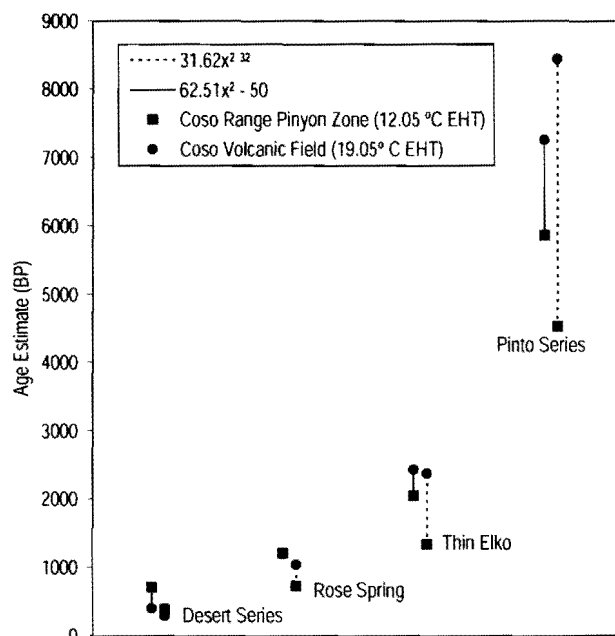


Figure 6: Corrected age estimates for Pinyon Zone and Volcanic Field projectile point samples, using the seven-degree difference in EHT.

read too much into these results, because samples are small.

To conclude, I think these results clearly underscore the importance of effective temperature as an overriding variable controlling the hydration process. I would argue, as have many others, that progress in refining obsidian hydration as a chronometric tool is going to rely mostly on better understanding of microclimatic variation within and between sites. Until such progress is made, rate equations such as these should continue to be treated as rough approximations.

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