Dating of the Devils Hole Calcite Vein

I. J. Winograd *et al.* (*1*) and K. R. Ludwig *et al.* (*2*) present a long, continuous, high-resolution climate record extracted from a calcite vein in Devils Hole, Nevada. If their dating is accurate, the record appears to contradict the Milankovitch hypothesis (*3*).

Dating of subsamples of the vein was done with the use of well-established principles of ^{230}Th dating (*4*) and with recently developed techniques for precise measurement of ^{230}Th and ^{234}U by thermal ionization mass spectroscopy (*5*). Careful analytical work has produced a precise ^{230}Th chronology (*2*).

The accuracy of the chronology (*1*) depends on the assumption that the calcite behaved as a closed system and that no ^{230}Th was incorporated during calcite growth. The first assumption appears to hold because initial $^{234}U/^{238}U$ ratios of subsamples are generally the same, even for the oldest subsamples. The second assumption also appears to hold on the basis of the following argument. The $^{230}Th/^{232}Th$ value of thorium initially incorporated in the calcite was estimated; by multiplying this value by the measured ^{232}Th content of the calcite, the initial ^{230}Th content was calculated. Thus, the initial ^{230}Th in each sample from Devils Hole was found to be negligible (*2*), which apparently confirmed the second assumption.

Although conventional wisdom argues that the calculated ages are accurate, there is a question with regard to the fate of ^{230}Th produced by the radioactive decay of ^{234}U dissolved in the water in Devils Hole. While the detailed chemical behavior of ^{230}Th in groundwater is not well understood, it has low solubility in most natural waters and it is likely that ^{230}Th produced in Devils Hole water was adsorbed onto the walls of the hole. We offer a simple model with an idealized reservoir geometry and assume that ^{230}Th is instantaneously adsorbed onto the walls. This mechanism would invalidate the assumption of no ^{230}Th incorporation and offset ^{230}Th ages to artificially high values. Such an offset would be insignificant in most cases; however, at Devils Hole it may be important because of extremely slow calcite growth rates.

In our model, a "hole" is bounded by two parallel infinite half-planes and filled with water containing dissolved ^{234}U. Calcite precipitates on both walls and incorporates ^{234}U from the water as it precipitates. ^{234}U in the water decays to ^{230}Th, which is adsorbed instantaneously onto the walls. At the surface of each wall, the ratio of adsorbed ^{230}Th atoms to ^{234}U atoms incorporated in the calcite is

$$(^{230}Th/^{234}U)_{surface} = \{C^{H_2O}\, W_{1/2}\lambda_{234}\}/\{C^{CaCO_3}G\} \quad (1)$$

where C^{H_2O} is the number of ^{234}U atoms per unit volume of water, $W_{1/2}$ is the half-width of the hole, λ_{234} is the ^{234}U decay constant, C^{CaCO_3} is the number of ^{234}U atoms per unit volume of calcite, and G is the linear growth rate of calcite on each wall. The numerator is the rate of radioactive production of ^{230}Th in the water and has units of ^{230}Th atoms per area per time. The denominator is the rate of ^{234}U addition to the wall in units of ^{234}U atoms per area per time.

Equation 1 is easily combined with the ^{230}Th age equation (*6*) if the age equation is first linearized by taking the zero and first-order terms of a Taylor expansion of ^{230}Th age about 0. This version of the age equation

$$^{230}\text{Th age} \sim (^{230}Th/^{234}U)/(1/\lambda_{234}) \quad (2)$$

is valid for ^{230}Th age $<< 1/\lambda_{234}$. Combining equations 1 and 2 gives the equation for the ^{230}Th age of newly formed calcite on the surface of each wall:

$$^{230}\text{Th age}_{surface} \sim \{C^{H_2O}W_{1/2}\}/\{C^{CaCO_3}G\} \quad (3)$$

Inserting values for Devils Hole, where C^{H_2O} is 1.2×10^9 ^{234}U atoms/cm^3 (*7*), $W_{1/2}$ is 150 cm (*8*), C^{CaCO_3} is 4.8×10^{11} ^{234}U atoms/cm^3 (*2*), and G is 0.07 cm per thousand years (*2*), we arrive at a value for the ^{230}Th age of the surface of 5.3 ka (thousand years ago).

An offset of this magnitude is larger than analytical error for Devils Hole subsamples that are younger than 270 ka. If 5000 years is subtracted from the ^{230}Th age of Devils Hole Termination II, the age of the termination is 135 ± 3 ka, synchronous with the rise in Northern Hemisphere summer insolation (*9*) and consistent with the Milankovitch hypothesis. Consideration of the offset would appear to invalidate one of the key observations (*1*) that contradicts Milankovitch—that climatic warming preceded insolation rise at Termination II. However, one must add an unknown amount of time [less than 10,000 years (*1*)] to the Devils Hole ages to obtain the true age of rain or snowfall. The added interval corresponds to the ground-water transit time and, if large enough, could resurrect the original contradictory Termination II observation. Finally, our model is simple. The adsorption of ^{230}Th on the walls may not be uniform because of varying advection rates and the complex geometry of the hole. The residence time of ^{230}Th may be significant and may change with changing chemical conditions in the ground water. The added complexity might well introduce errors in the magnitude of the ^{230}Th age offset of half an order of magnitude in either direction. Given these uncertainties, the weight of evidence still supports the Milankovitch mechanism as a major factor in Quaternary climate change.

It is now possbile to measure ^{230}Th concentrations in relatively small volumes of ground water (*10*) and in newly formed carbonate (*11*). Measurements of this sort, as well as ^{234}Th measurements (for constraining thorium residence time), in ground-water systems will be important to our understanding of the process that we have attempted to model. Such studies are critical for establishing high-resolution chronologies in continental carbonate deposits. In the Devils Hole case, measurements of ^{230}Th, ^{232}Th, and ^{234}Th in modern water, and ^{230}Th age determinations of newly formed surfaces (if such surfaces can be found and identified), would constrain the magnitude of initial ^{230}Th in the carbonate and shed light on the accuracy of the chronology of an important climate record.

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Response: Edwards and Gallup present a plausible mechanism that could lead to a small but significant bias in the ^{230}Th dates

Table 1. Isotopic analyses of two vein calcite surfaces from Devils Hole. Dates and 2σ errors were calculated as in (*1*), which corrects for detrital Th and U by assuming a ^{232}Th-bearing component with ^{232}Th/^{238}U = 1.21, (^{230}Th/^{234}U/^{238}U) = 1; all ratios are activity ratios. The DH-11 dates in (*1*) are not as sensitive to this assumption (because their ^{230}Th/^{232}Th ratios are higher), but the surface-sample dates will vary by as much as −5000 to +2000 years for initial ratios that are geochemically reasonable.

Sample	U (ppm)	^{230}Th/^{232}Th	^{230}Th/U date (ka)	Initial ^{234}U/^{238}U
DH-11	0.50	27.3	68 ± 6	3.18 ± 0.20
DH-2	0.48	27.1	64 ± 7	3.08 ± 0.14

of the DH-11 sample core of vein calcite from Devils Hole. However, considerations of the aqueous environment and petrology of the vein calcite argue against the hypothesized mechanism, and a test shows that its effects on the DH-11 dates would be orders of magnitude less than that calculated by Edwards and Gallup.

We have calculated the possible maximum effect on the DH-11 dates assuming that all of the water-generated ^{230}Th was transferred to the wall, using an iterative solution for both ages and growth rates, together with the complete DH-11 data set of U-Th isotopic concentrations (*1*).

Our results show that the potential bias ranges from about 1500 to 3500 years, with the higher figure applying to the samples taken from a depth of 44.5 to 48.5 mm (crucial because of their relatively slow growth rate). Such biases would apply only if all or most of the newly created ^{230}Th atoms in the water came into contact with the walls of the cavern before these atoms were adsorbed onto suspended particulates that then were removed by gravitational settling. Turbulent mixing would be the most efficient mechanism for transferring ^{230}Th atoms from the water to the cavern walls. But, except during earthquakes, turbulence is not observed in Devils Hole. As a result, adsorption of ^{230}Th on the cavern walls would have been governed by diffusion, in competition with gravitational settling.

There is a sensitive and direct test of the hypothesis of Edwards and Gallup. Calcite stopped precipitating onto the walls of the Devils Hole cavern at about 60 ka (*1–3*), so that the proposed mechanism, if significant, should have resulted in a large excess of ^{230}Th built up since then (and only partially diminished by radioactive decay) on the cavern wall surfaces. Even if the proposed process operated at only 5% efficiency, apparent ages of more than 200,000 years would be predicted (if we take into account the competing processes of influx and radioactive decay) for a 50-μm-thick sample of the vein surface, compared with the expected date of approximately 60,000 years (*1, 3*).

We performed this test on two samples (Table 1), one milled from the free surface of the DH-11 core (*1, 2*) (44 μm thick) and another from the free surface of the DH-2 sample (56 μm thick) (*3*).

Taking the surface sample dates at their nominal values of 68 and 64 ka and assuming that the true surface age of the vein should be about 60 ka (*1–3*), we calculated that the transfer efficiency for the water-generated ^{230}Th was 0.6% for sample DH-11 and 0.4% for sample DH-2. Apparently, gravitational settling of adsorbed ^{230}Th is a more efficient mechanism for the removal of water-generated ^{230}Th than is adsorption onto vertical or overhanging walls. Even if the small degree of ^{230}Th excess suggested by the nominal ^{230}Th dates of the surface samples is real (which is not clear, given the uncertainties in the dates), calculations with the complete DH-11 data set show that the resulting effect on the DH-11 dates (*1*) is less than 20 *years* for all samples.

It seems unlikely that the process that resulted in cessation of calcite precipitation in DH-11 and DH-2 about 60 ka coincidentally also inhibited the plating out of ^{230}Th on the walls of Devils Hole only since that time. That a rain of suspended particulates has occurred in Devils Hole for hundreds of thousands of years is indicated by a comparison of vein calcite samples collected from the hanging wall and foot wall of this fault-controlled cavern. For example, samples DH-11 and DH-2, obtained from the hanging wall, are white to yellowish-white and have little or no banding. In contrast, samples from the foot wall or from upward-facing surfaces are prominently and finely banded. One such sample, DH-7, has bands that vary from light to dark gray and from orange to dark brown and yielded alpha-spectrometic ^{234}U/^{238}U ages progressing (lower surface toward upper surface) from 520 to 100 ka (*4*). Thus, DH-7 records a rain of dust likely to have scavenged the bulk of the water-generated ^{230}Th during the time of DH-11 growth.

The character of the aqueous environment and the petrology of the vein calcite at Devils Hole argue against the likelihood of significant transfer of water-generated ^{230}Th to the environment of the DH-11 core. Direct measurements of the magnitude of the ^{230}Th-excess mechanism proposed by Edwards and Gallup demonstrate that this mechanism has not been effective during the past 60,000 years. Therefore, the implications of the DH-11 dates (*2*) remain.

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5. The analysis in Table 1 was first prompted by another comment by N. J. Shackelton (*Nature*, in press).

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Social Learning in Invertebrates

G. Fiorito and P. Scotto (*1*) find evidence of observational learning in *Octopus vulgaris*: octopuses that observed a conspecific attacking a stimulus learned faster than did those directly conditioned to the task. Although this study may show some evidence for imitation by observers (a conclusion complicated by the observers' preference for attacking a red as opposed to a white ball), it gives no unequivocal evidence for observational learning.

In the experiment, demonstrators were trained through direct conditioning [(*1*), p. 545] to attack one of two colored balls (*2*). Observers then watched demonstrators attack that stimulus with no contingent reward or punishment given to the demonstrator; when observers were exposed to the