Reports

Continental Pleistocene Climatic Variations from Speleothem Age and Isotopic Data

Abstract. *Speleothems from continental North American caves have been dated by means of the* ^{230}*Th/*^{234}*U method. Oxygen isotopic variations in the dated samples and phases of speleothem deposition can be interpreted in terms of climatic change. A glacial chronology constructed from the age and isotopic data lends support to the astronomical theory of climatic change.*

Speleothems (cave-deposited travertines) from some limestone caves in West Virginia, the southern Canadian Rockies, and the Northwest Territories have been dated by the ^{230}Th/^{234}U method (*1*). The West Virginia caves, Grapevine (GV) and Norman-Bone (NB), are 700 to 730 m above mean sea level and approximately 190 km southeast of the Wisconsin drift border (*2*). Caves in the Canadian Rockies were submerged by Wisconsin ice or stood above it within nunataks. The caves in the Northwest Territories, in the Nahanni plateau of the Mackenzie Mountains (*3*), escaped Wisconsin and probably Illinoian glaciation but experienced extremely cold, dry periglacial climate during glacial advances.

Pure calcite speleothems suitable for dating were recognized on the basis of the following considerations: (i) petrologic criteria for lack of diagenetic alteration, such as low porosity, coarsely crystalline primary calcite fabric, well-preserved internal stratigraphy, and absence of postdepositional erosion; and (ii) isotopic criteria including high ^{230}Th/^{232}Th activity ratios and internally consistent sequences of ^{230}Th/^{234}U ages. At each of the three sites the individual sample speleothems were found to have been deposited over relatively short time intervals so that only a fragmentary and incomplete record was obtained.

If $CaCO_3$ has been deposited on a speleothem in isotopic equilibrium with water of known isotopic composition, then the temperature of deposition can be found from the isotopic fractionation $\alpha_{c\text{-}H_2O}$. Two criteria for recognizing equilibrium deposits have been suggested by Hendy (*4*): (i) constant $\delta^{18}O_c$ (*5*) along a single growth layer and (ii) lack of correlation between $\delta^{13}C_c$ and $\delta^{18}O_c$ along a growth layer (a correlation between $\delta^{18}O_c$ and $\delta^{13}C_c$ probably indicates that kinetic isotope effects occurred during deposition, that is, that the layer did not form in oxygen isotopic equilibrium with the water from which it was deposited). Four of the dated speleothems from West Virginia were shown to be equilibrium deposits. The Canadian samples have not yet been investigated.

In order to estimate the isotopic composition of the water from which the speleothems were deposited, fluid inclusions were extracted from them. If the trapped water was initially identical to the depositing solutions, we can infer its initial oxygen isotopic composition from the relationship (*6*)

$$\delta D_i = 8\delta^{18}O_i + 10 \qquad (1)$$

where δD_i and $\delta^{18}O_i$ are, respectively, the hydrogen and initial oxygen isotopic compositions of the fluid inclusions. (Since the oxygen of the water can exchange with the host $CaCO_3$, $\delta^{18}O_i$ was not measured directly.) Drip waters collected from modern caves obey Eq. 1. Significant differences were observed between δD_i values for replicate speleothem samples; until the cause of these variations is determined, we consider that the method yields only approximate temperatures.

In West Virginia, the apparent temperatures of deposition vary over a range of 7° ± 2°C, whereas δD_i values were found to be relatively constant from layer to layer. Thus the $\delta^{18}O_c$ curves of Fig. 1B crudely represent paleotemperature variations, the ^{18}O-enriched carbonate having been deposited during periods of cooler climate. Duplessy *et al.* (*7*) and Geyh (*8*) have concluded that ^{18}O enrichment corresponded to warmer climate, although Emiliani (*9*), reevaluating the data of Duplessy *et al.*, concluded that the ^{18}O-enriched calcite was deposited at lower temperatures.

Additional paleoclimatic data may, in favorable circumstances, be obtained from the age data alone. The sample sites in the Canadian Rockies and Northwest Territories are situated in regions in which speleothem deposition probably ceased during periods of intense glacial or periglacial conditions. The interruption of deposition was due to a lack of seepage water or to a cessation of biotic activity necessary to produce HCO_3^- ions needed for speleothem growth. Although cessation of deposition at individual sites may occur at random intervals for a variety of causes, concurrent cessation at all sites within a cave system is indicative of climatically induced termination of deposition. In the area of study in West Virginia, true glacial conditions did not exist during the Wisconsin; periglacial features have been described from West Virginia at elevations of 910 to 1100 m (*10*). Nevertheless, biotic activity was probably suppressed during periods of coolest climate, resulting in slower or interrupted growth (*10*). Franke and Geyh (*11*) have shown by ^{14}C dating of about 80 speleothems from southern Germany that deposition ceased between 20,000 and 12,600 years before the present (B.P.), corresponding to the main Weichsel glaciation.

We have constructed a tentative glacial chronology for the Late Pleistocene by assigning periods of ^{18}O-rich speleothem deposition or multisite nondeposition to glacial intervals. These are shown as stippled areas in Fig. 1.

A modified form of the Milankovitch hypothesis has recently been used in attempts to explain the periodicity of Pleistocene climatic changes (*12*). Because of secular variations in the earth's orbital parameters, the seasonal amount of radiation incident upon the earth's surface changes throughout time, even though the annual radiation budget, or

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insolation, remains constant. During periods when the summer insolation is a minimum, the theory predicts glacial climate at high latitudes. Likewise, when the summer insolation is a maximum, interglacial climatic conditions are expected. It is interesting to test the theory against the speleothem data. Part of the insolation curve taken from (*13*) is plotted in Fig 1C. Although the speleothem record is incomplete at the present time, sufficient results are available to give some support to the astronomical theory of climatic change.

The insolation minima at 25,000 and 71,000 years B.P. may be correlated with the Classical and Early Wisconsin glacial periods, respectively. Support for a period of cooling between 60,000 and 75,000 years B.P. is provided by the GV2 stable isotopic record. Three speleothems from the West Virginia caves ceased to grow between 60,000 and 70,000 years B.P. (records NB1, NB13, and GV2). This interval agrees with other estimates for the onset of the Early Wisconsin glacial phase (*14*). The absence of speleothem deposition during the period between 30,000 and 6,000 years B.P. in the West Virginia caves suggests the occurrence of another glacial advance. The insolation theory also predicts a cold period at 115,000 years B.P. Deposition on record GV2 started again during a period of rapid warming 100,000 ± 4,000 years B.P., but deposition on record NB1 was apparently continuous from 135,000 to 65,000 years B.P. This suggests that a cool period did occur in West Virginia prior to 100,000 years B.P. but that conditions were not sufficiently cold for all deposition to stop. A 30-m glacial lowering of sea level dated at between 105,000 and 125,000 years B.P. has recently been recognized in Barbados (*15*).

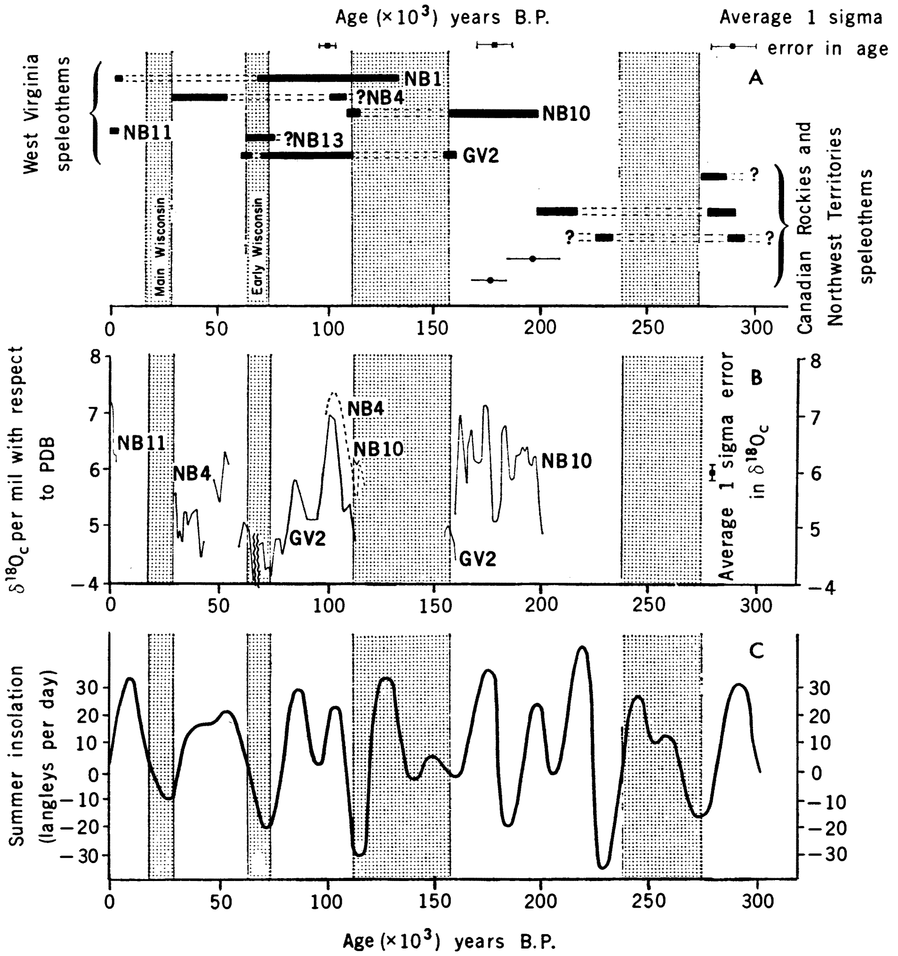

Fig. 1. (A) Periods of speleothem deposition (solid bars) and zero deposition (broken lines) in West Virginia, the Crowsnest region of the southern Canadian Rockies, and the Nahanni region of the Northwest Territories. Single age determinations are shown by the circles. Question marks indicate that the start or finish of the period of deposition is not known. (B) Variations in the $^{18}O/^{16}O$ ratio for some West Virginia speleothems. The curves are visually fitted to 110 points uniformly distributed through the measured intervals. The wavy line in the GV2 record represents a short period of erosion. The more recent NB4 record is based on a single age determination and an estimated average growth rate of 1 cm per 10^3 years; the error will be somewhat larger than indicated by the error bars in (A). The cold periods inferred from the isotopic and age data are indicated by the stippling. (C) The summer insolation curve for latitude 60°N, drawn from data in (*13*). Present-day radiation values are zero on the scale. A positive change represents an increase in insolation; a negative change represents a decrease.

The warm period predicted from the insolation curve at 127,000 years B.P. has not been recognized yet in West Virginia because no stable isotope record was obtained from NB1. However, a high sea-level stand (indicating slightly warmer climatic conditions than at present) has been widely recognized at 125,000 ± 6,000 years B.P. (*12*). The $\delta^{18}O_c$ minimum and maximum at 170,000 ± 7,000 and 175,000 ± 7,000 years B.P., respectively, may be correlated with the insolation maximum and minimum at 175,000 and 185,000 years, respectively.

The speleothem ages from the Canadian Rockies and Northwest Territories are too few and imprecise to allow a detailed comparison with the insolation curve (see Fig. 1A). Two speleothems did show evidence of an inactive phase between 280,000 ± 20,000 and 230,000 ± 20,000 years B.P. In all, three speleothems became inactive between 275,000 and 290,000 years B.P., which is good evidence for the onset of the cold period predicted by the insolation curve at 275,000 years B.P.

The positive correlation between the summer insolation curve of the Northern Hemisphere and the speleothem curves suggests that it is the cool summers that control the accumulation of glacial ice. The insolation theory also predicts that, under certain conditions, an insolation maximum in the Northern Hemisphere is accompanied by an insolation minimum in the Southern Hemisphere with the result that certain glacial advances and retreats should be out of phase in the two hemispheres. Because of the widespread distribution of caves in both the Northern Hemisphere and the Southern Hemisphere, speleothem age and isotopic data could help to resolve once and for all this controversial theory of climatic change.

PETER THOMPSON
HENRY P. SCHWARCZ
Department of Geology,
McMaster University,
Hamilton 16, Ontario, Canada
DEREK C. FORD
Department of Geography,
McMaster University

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5. Oxygen isotope ratios are given in per mil deviation from the ratio of a standard,

$$\delta^{18}O_c = [(^{18}O/^{16}O)_c/(^{18}O/^{16}O)_s - 1] \times 1000$$

where c is the sample of calcite and s is the standard. The standard for oxygen analyses is Pee Dee belemnite (PDB), as described by H. Craig [*Science* **133**, 1833 (1961)].
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Elemental Mercury Evolution Mediated by Humic Acid

Abstract. *Elemental mercury is formed in aqueous solution by the chemical reduction of mercuric ion in the presence of humic acid. The reduction proceeds via first order kinetics (rate constant, 0.009 hour^{-1}) and is depndent on* p*H. The reaction mechanism involves interaction of the ionic metal species with the free radical electrons of the humic acid.*

Most studies of mercury in the environment have been concerned either with dialkyl and diaryl organomercurials or with ionic mercury species, principally mercuric and methylmercuric ions, since these forms represent the mercury species most often introduced into the environment. However, Bongers and Khattak (*1*) have shown that anaerobic sediments treated with ionic mercury exhibit release of elemental mercury, and methylmercuric ion is converted to elemental mercury in lake sediments in the presence of microorganisms, with subsequent loss of the volatile Hg^0 (*2*).

Strohal and Huljev (*3*) have shown by radiotracer experiments that mercuric ion forms a strong but reversible complex with humic acids (they report a stability constant of 1.7×10^5 for the complex), and Szilagyi (*4*) has shown that soil humic material is capable of reducing ferric iron to ferrous iron in aqueous solution. The possibility that ionic mercury is reduced to the highly volatile elemental form by naturally occurring, ubiquitous humic acids has led us to investigate this possible pathway of mercury mobilization in the environment.

Humic acid was obtained from a farm pond sediment near the University of Georgia, Athens (*5*). Extraction and purification were accomplished by standard procedures (*6*); the purified material had the following composition, in percentages by weight: C, 48.9; H, 6.8; O, 28.0; N, 5.3; S, 1.7; and ash, 9.3. One milligram of the purified humic acid in 1 ml of 0.1*N* KOH solution was added to a 50-ml solution containing 200 μg of Hg^{2+} as $HgCl_2$ and 5 μc of carrier-free $^{203}Hg^{2+}$ and buffered to the desired *p*H with borate. Controls at each *p*H were identical solutions without the humic acid. All experiments were performed at ambient temperatures (25°C). High-purity N_2 was bubbled through the reaction solutions and volatile mercury was trapped in a potassium permanganate–sulfuric acid liquid trap. Measurements of evolved mercury were made by removing the acid-permanganate trap, clearing the trap with 5 ml of 25 percent hydroxylamine hydrochloride solution (weight to volume), and subsequently counting a portion of the solution. Sealed standards were prepared and counted along with the samples to correct for decay and daily counter fluctuations. Control experiments have shown that less than 10 percent of the activity in the traps was lost during clearing with hydroxylamine solution (*7*).

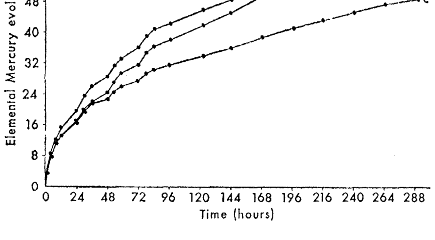

Fig. 1. Evolution of Hg^0 plotted against time at *p*H (a) 6.5, (b) 7.5, and (c) 8.2.

Elemental mercury is evolved at a slow but significant rate, which appears to be *p*H-dependent. Figure 1 shows plots of the elemental mercury released as a function of time at three different *p*H values. Almost 33 percent of the initial mercuric ion added to the solution was reduced to elemental mercury after 290 hours at *p*H 6.5, while 24 percent evolved over the same period at *p*H 8.2. All three curves show almost identical release for the first 8 hours and then diverge. This behavior would seem to suggest two reaction rates and perhaps two different reaction mechanisms and rate constants for these reactions.

Since an inordinate period of time would have been required to reach 99 percent completion of the reaction, the following method of evaluating the data was employed. The process was assumed to be describable by first-order kinetics, and a preliminary estimate of the rate constant (k^*, hour^{-1}) was obtained from the half-life equation. The half-life was taken as the time necessary to acquire half of the total quantity of Hg^0 evolved. The amount evolved at equilibrium or in infinite time (y_∞) was estimated from the preliminary rate constant (k^*) and the last data point (y', t')

$$y_\infty = y'/(1 - e^{-k^*t'})$$

The rate constant was then recalculated as the slope of the right member of Eq. 2, where y_t represents the concentration of evolved Hg^0 at any time t

$$\left(\ln \frac{y_\infty - y_t}{y_\infty} = -kt\right) \qquad (2)$$

The curve calculated from Eq. 2 for the reaction at *p*H 6.5 is a straight line with the general equation $a = -0.090 - 0.009b$, with a correlation coefficient $r = .99$. Similar plots for *p*H 7.5 and *p*H 8.2 are described by $a = -0.06 - 0.008b$ ($r = .99$) and $a = -0.155 - 0.009b$ ($r = .98$), respectively. These curves show that the reactions are first order over the entire time period examined. The close agreement of the rate constants for the three experiments indicates that *p*H influences the total amount of mercury which may be reduced, but is not involved in the rate-determining reaction.