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NATIONAL SPELEOLOGICAL SOCIETY

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The Society serves as a central agency for the collection, preservation, and dissemination of information in fields related to speleology. It also seeks the preservation of the unique faunas, geological and mineralogical features, and natural beauty of caverns through an active conservation program.

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Uranium - Series Dating of Speleothems

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ABSTRACT

Uranium-series disequilibrium methods can be used to determine the age of macrocrystalline calcite speleothems, provided: 1)—the specimens have sufficient uranium concentration, 2)—the initial state of the system can be determined, 3)—the system has not been subject to post-depositional alteration or migration of radioisotopes, and 4)—isotope ratios exhibit a progression toward secular equilibrium with time. The 230Th/234U method, with a range of 2000-300,000 B.P., has been the most successful of the three uranium-series methods which have been applied to speleothems.

Analyses for speleothems from seven North American karst areas have been selected to illustrate the application of speleothem chronology to such geological problems as rates of erosion and sedimentation, the ages of river canyons and terraces, the time and duration of base level stands, speleothem growth rates, the time and duration of low sea level stands, and glacial chronology for the late Pleistocene of North America.

INTRODUCTION

The Pleistocene epoch, the last 1 to 2 million years of geologic history, has witnessed and recorded profound changes in the physical and biological nature of the earth. Not only is the Pleistocene characterized by global episodic periods of warm and cold climate which may be unique to that period, but also the origin and history of mankind has occurred totally within it.

In order to decipher the geologic record of the Pleistocene, it is necessary to relate events to an absolute time scale. Due to insufficient technique for quantitative measurement, this has been and currently remains one of the most active and controversial topics in modern geology. A suitable dating method for the entire Pleistocene does not exist. ^{14}C dating is considered reliable only within the past 40,000 to 50,000 years and the K/Ar method is of limited application because suitable deposits are scarce. Ranges of the uranium-series disequilibrium methods cover portions of most of the Pleistocene, but only the $^{230}Th/^{234}U$ method has been developed to the point of reliability. In this paper, we discuss this method in detail and illustrate several applications of speleothem chronology to Pleistocene geology.

URANIUM AND THORIUM GEOCHEMISTRY

The actinide series contains those elements with atomic numbers 89-103, all of which are radioactive. Only two of the elements, uranium and thorium, have sufficiently long-lived nuclides to occur in large quantities in nature. Shorter-lived daughter products do, however, naturally occur in the decay schemes of the long-lived uranium and thorium isotopes (Fig. 1).

Although chemically similar, certain of the actinide-series elements exhibit important differences. Most notable are the many oxidation states of uranium (3+, 4+, 5+, 6+) and the absence of the 3+ valence state of thorium and protactinium.

Oceanic concentrations of uranium and thorium average 2 ppb and 0.02 ppb, respectively (Adams, et al., 1959). The strong depletion of thorium with respect to uranium is a result of differential mobilization during the weathering

of terrestrial rocks (Fig. 2). Because of its high ionic potential, the Th^{4+} ion is quickly absorbed or precipitated as insoluble hydrolysates when brought into solution. Uranium, although also present in the 4+ valence state in primary igneous minerals, is readily oxidized during weathering to the uranyl ion (UO_2^{2+}), which contains uranium in the 6+ valence state and forms several soluble complexes.

Once present in the marine environment, uranium is subsequently incorporated into carbonate sediments by chemical precipitation. Because biologic factors to some extent control this process, the average carbonate is enriched with respect to the sea water from which is was precipitated. Thus, the average marine limestone contains about 2 ppm uranium and less than 0.1 ppm thorium (Adams, et al., 1959).

Following lithification, diagenesis, uplift and subsequent exposure, karstification of the carbonate rocks occurs, once again remobilizing uranium and thorium. As before, uranium tends to form soluble complexes and to remain in solution, whereas thorium, with its strong affinity for clay minerals, is quickly removed from solution. During this weathering process, uranium isotopes are fractionated, ^{234}U being enriched in ground waters with respect to its parent ^{238}U. This is attributed to two factors: the change in oxidation state from ^{238}U to ^{234}U (Koide and Goldberg, 1963) and the increased mobility of the radiogenic daughter products ^{234}Th and ^{234}U, which occupy radiation-damaged lattice sites as a result of alpha-recoil-induced displacement within the crystal lattice (Ku, 1965; Kaufman, et al., 1969; and Kigoshi, 1971).

This enrichment of ^{234}U in natural systems during weathering was first recognized by Cherdyntsev (1955). Later, Thurber (1962, 1964) demonstrated that the $^{234}U/^{238}U$ ratio of the oceans is constant at 1.15 ± .02, but Isabaev et al. (1960), Thurber (1964), Kronfeld (1971), and P. Thompson, et al. (in press) have shown that the ratio for fresh waters is highly variable, ranging up to 12.2, although most measured values fall within the range 1.1 to 3.0. Once in solution, the uranium is transported as the soluble anionic carbonate complex $(UO_2(CO_3)_3)^{4-}$. Upon encountering a cave, carbon-dioxide-charged ground waters may become supersaturated due to the degassing of CO_2, which causes the uranyl carbonate complex to dissociate to UO_2^{2+} and CO_2. As a result, the uranyl ion UO_2^{2+} is coprecipitated with calcite, forming a thorium-free closed

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238U SERIES

238U
(4.51 x 10^9 y)
α ↓
234Th
(24.1 d)
β ↓
234Pa
(1.18 m)
β ↓
234U
(2.47 x 10^5 y)
α ↓
230Th
(7.52 x 10^4 y)
α ↓
226Ra
(1602 y)
⇣
206Pb
(stable)

232Th SERIES

232Th
(1.4 x 10^10 y)
α ↓
228Ra
(6.7y)
β ↓
228Ac
(6.13h)

232U
(72y)
α ↓
228Th
(1.910y)
α ↓
224Ra
(3.64d)
α ↓
220Rn
(54.4s)
α ↓
216Po
(0.16s)
⇣
208Pb
(stable)

235U SERIES

235U
(7.13 x 10^8 y)
α ↓
231Th
(25.6h)
β ↓
231Pa
(3.25 x 10^4 y)
α ↓
227Ac
(21.6y)
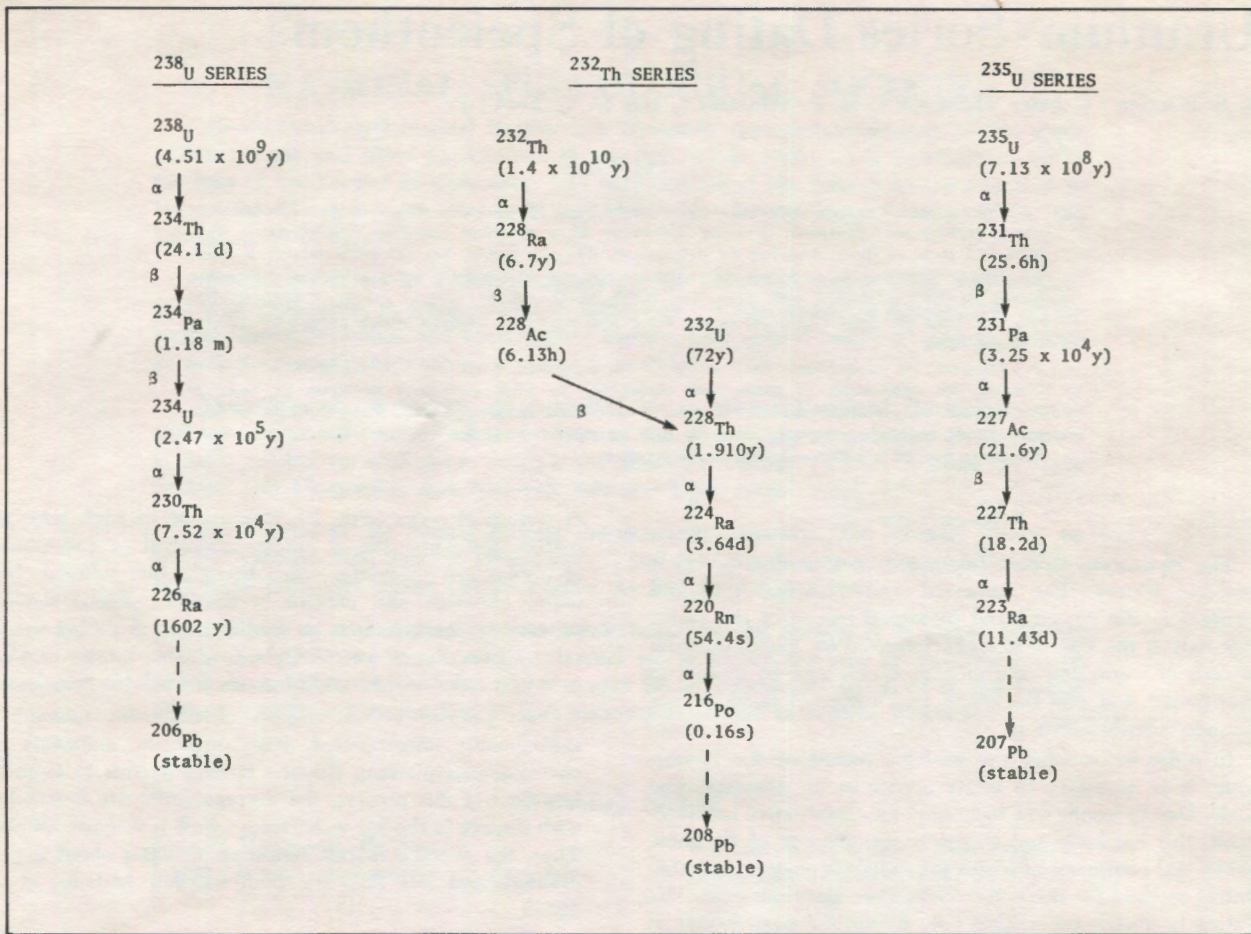β ↓
227Th
(18.2d)
α ↓
223Ra
(11.43d)
⇣
207Pb
(stable)

Fig. 1. Uranium and thorium decay series, indicating mode of decay and half-life for the nuclides of the respective decay series.
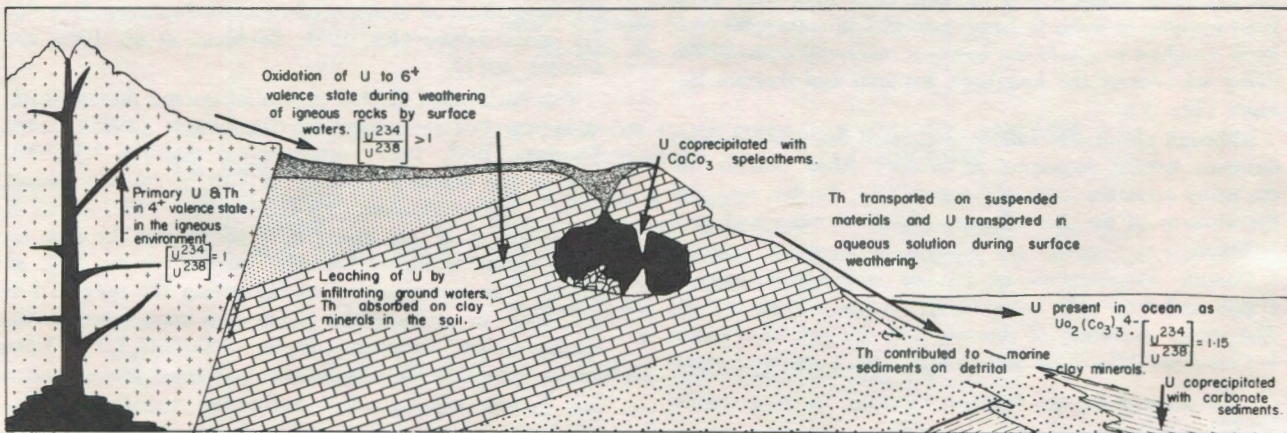

Fig. 2. Idealized schematic diagram of the geochemical behavior of uranium and thorium during weathering and transportation in the surface and near-surface environments.

system enriched in ^{234}U to the same extent as the parent water. The concentration of uranium incorporated into the calcite depends on several factors, including the provenance of the source materials and the geochemical properties of the depositional environment. Uranium concentrations in speleothems have been found to range from about 10 ppb to 100 ppm (Harmon, et al., 1974).

AGE DATING, THEORY AND METHODS

Radiometric methods for age dating depend upon the spontaneous transmutation of a certain amount of one unstable nuclide to another over a fixed period of time. The daughter may be itself radioactive. This radioactive decay occurs at a fixed rate, according to the general law

$$N_t = N_o^x e^{-\lambda_t} \qquad (1)$$

where N_t indicates the number of atoms of a certain nuclide at some time t, N_o the number of atoms of that nuclide at $t = o$, and λ the decay constant given in terms of sec -1 (which is a measure of the probability of the nuclide decaying within a certain period of time).

When the daughter product is absent initially from the host material, the radioactive decay of the parent nuclide is described by Equation 1 and the age of the deposit can be simply determined from the relationship

$$N_t^d = N_t^{p} (e^{\lambda_p t} - 1) \qquad (2)$$

where N_t^d and N_t^p are the respective amounts of daughter and parent at time t.

If, however, the system initially contains both radioactive parent and daughter, the added factor of isotopic equilibrium must be considered. Should the parent be longer-lived than the daughter, i.e. $\lambda_d > \lambda_p$, then a state of isotopic equilibrium will eventually be reached. When this occurs, the rate of decay of the daughter is as rapid as its rate of formation from the parent. Given that the initial amounts of both parent and daughter present in the system are known and that the parent is much longer-lived than the daughter, then the age of the system can be determined from a combined form of Equations 1 and 2 where

$$N_t^d = (\frac{\lambda_p}{\lambda_d - \lambda_p})(N_o^p)(e^{-\lambda_p t} - e^{-\lambda_d t}) + N_o^d e^{-\lambda_d t}. \qquad (3)$$

If, at some point after equilibrium has been reached, the system is disturbed such that an isotopic fractionation occurs between parent and daughter, the radioactive clock is once again reset and the parent-daughter decay may be used once more as a dating method until such time as secular equilibrium is again realized.

The range of any dating method is dependent on the rate at which decay occurs. This decay rate is most commonly expressed in terms of "half-life", i.e. the time required for the original number of atoms of a nuclide present to decrease by one-half. The half-life is related to the inverse of the decay constant, thus, the longer the half-life, the greater the range of the dating method.

The uranium-series dating methods discussed in the sections of this paper that follow are based upon the disequilibrium between the long-lived nuclides ^{238}U and ^{235}U, and their shorter-lived daughters.

The $^{234}U/^{238}U$ Method

Because natural waters are enriched in ^{234}U, carbonates precipitated from them are also enriched. The subsequent decay of the excess ^{234}U atoms in the carbonate host, under closed system conditions, can be used to date the deposit until such time as secular equilibrium between ^{234}U and ^{238}U is reached. The 248,000 year half-life of ^{234}U makes the range of the method about $5 \times 10^4 - 1.5 \times 10^6$ years, about three-fourths of Pleistocene time. The elapsed time t since deposition (age) of a carbonate rock can thus be determined from the relationship

$$\left[([\frac{^{234}U}{^{238}U}])_t - 1 \right] = \left[([\frac{^{234}U}{^{238}U}])_o - 1 \right] \left[e^{-\lambda_{234} t} \right]^* \qquad (4)$$

if the initial activity ratio $[\dfrac{^{234}U}{^{238}U}]_o$ and the activity ratio at time "t" $[\dfrac{^{234}U}{^{238}U}]_t$ are known. The fact that this initial activity ratio cannot be directly determined for ancient deposits severely limits application of the method. Indirect estimations of the initial $^{234}U/^{238}U$ ratio for speleothem deposits can be made by comparison with modern samples and waters from the same area by assuming that the $^{234}U/^{238}U$ ratio in the water has been constant with time. P. Thompson, et al. (in press) have shown that the $^{234}U/^{238}U$ ratio of seepage waters entering a cave can vary significantly from location to location within it and from month to month at a given location, the average ratio differing significantly with time in the speleothem which is being deposited.

Thus, the prospects of dating secondary carbonates by the $^{234}U/^{238}U$ method are not promising. The method may, however, find limited application in extending ages of deposits for which portions can be dated by another, more reliable, method and for which the initial $^{234}U/^{238}U$ ratios for several growth layers are observed to be constant throughout time.

The $^{230}Th/^{234}U$ Method

The $^{230}Th/^{234}U$ method of dating carbonates is based upon the assumption that uranium is co-precipitated with calcite or aragonite from waters essentially free of thorium. Subsequently, ^{230}Th is produced by the radioactive decay of ^{234}U and ^{238}U. Because the carbonate was free of thorium at the time of deposition, the amount of ^{230}Th present at any subsequent time t is a direct measure of the age of the sample. Taking into account the initial disequilibrium of ^{234}U, the age of a sample is determined from the relationship

$$(5)$$

$$[\frac{^{230}Th}{^{234}U}]_t = (\frac{1-e^{-\lambda_{230} t}}{[\frac{^{234}U}{^{238}U}]_t}) + (\frac{\lambda_{230}}{\lambda_{230} - \lambda_{234}})(1 - \frac{1}{[\frac{^{234}U}{^{238}U}]_t})(1 - e^{-(\lambda_{230} - \lambda_{234}) t})$$

where $[\dfrac{^{230}Th}{^{234}U}]_t$ and $[\dfrac{^{234}U}{^{238}U}]_t$ are measured activity ratios at time t, λ_{230} is the decay constant of ^{230}Th, and λ_{234} is the decay constant of ^{234}U. With the ^{230}Th half-life of

72,500 years, this method has a potential range of about 1000-350,000 years BP. A graphical solution of Equation 3 for various values of t and $[\frac{234U}{238U}]_o$ is shown in Fig. 3. Note the minor effect of changes in the initial $^{234}U/^{238}U$ ratio upon the younger isochrons.

Should thorium-bearing, detrital minerals be contained within the carbonate host or present in vugs or as surface coatings, the measured age would be too high because of the addition of non-radiogenic ^{230}Th. Since this detrital ^{230}Th is always accompanied by ^{232}Th, a rough correction for the detrital thorium component can be made using the $^{230}Th/^{232}Th$ ratio in observed modern samples.

The $^{231}Pa/^{235}U$ Method

The chemical behavior of protactinium in aqueous solution is very similar to that of thorium, so that secondary carbonates are also protactinium-free. Thus, the post-depositional accumulation of ^{231}Pa, the second daughter product in the ^{235}U decay chain (Fig. 1), should be a direct measure of the age of the sample according to the relationship

$$[\frac{231Pa}{235U}]_t = (1-e^{-\lambda_{231}t}) \qquad (6)$$

where $[\frac{231Pa}{235U}]_t$ is the measured activity ratio and λ_{231} is the decay constant of ^{231}Pa. The half-life of ^{231}Pa is 32,500 years so that this method has a limit of about 200,000 years BP.

A prohibitive factor with this dating method is the low ^{235}U and thus lower ^{231}Pa concentrations of secondary carbonates. Given the constant lithospheric $^{238}U/^{235}U$ abundance ratio of 137.4 to 1, the $^{231}Pa/^{235}U$ method can only be utilized in samples with uranium concentrations greater than a few ppm.

Suitability of Speleothems for Age Dating

Extensive study by Thurber, et al. (1965) has shown that carbonate materials can be reliably dated by the uranium-series disequilibrium methods only if certain basic criteria are met. These are:

(1) sufficient uranium concentration must be present in the sample to allow accurate determination of activity ratios in a relatively short counting time,

(2) the initial isotopic state of the system must be known,

(3) no loss or gain of uranium or thorium can have occurred since the time of deposition, and

(4) disequilibrium ratios of the radioisotopes must exhibit a progression toward secular equilibrium with time.

It is possible, in most cases, to perform experimental tests to determine whether or not specific samples meet these requirements. Uranium concentrations and isotope activity ratios can be analytically measured. The closed system assumption can be tested by a comparison of ages determined by two different methods and by the internal consistency and stratigraphic correlation of ages determined by a single method. The $^{230}Th/^{234}U$ and $^{231}Pa/^{235}U$ methods require that no ^{230}Th or ^{231}Pa be present at the
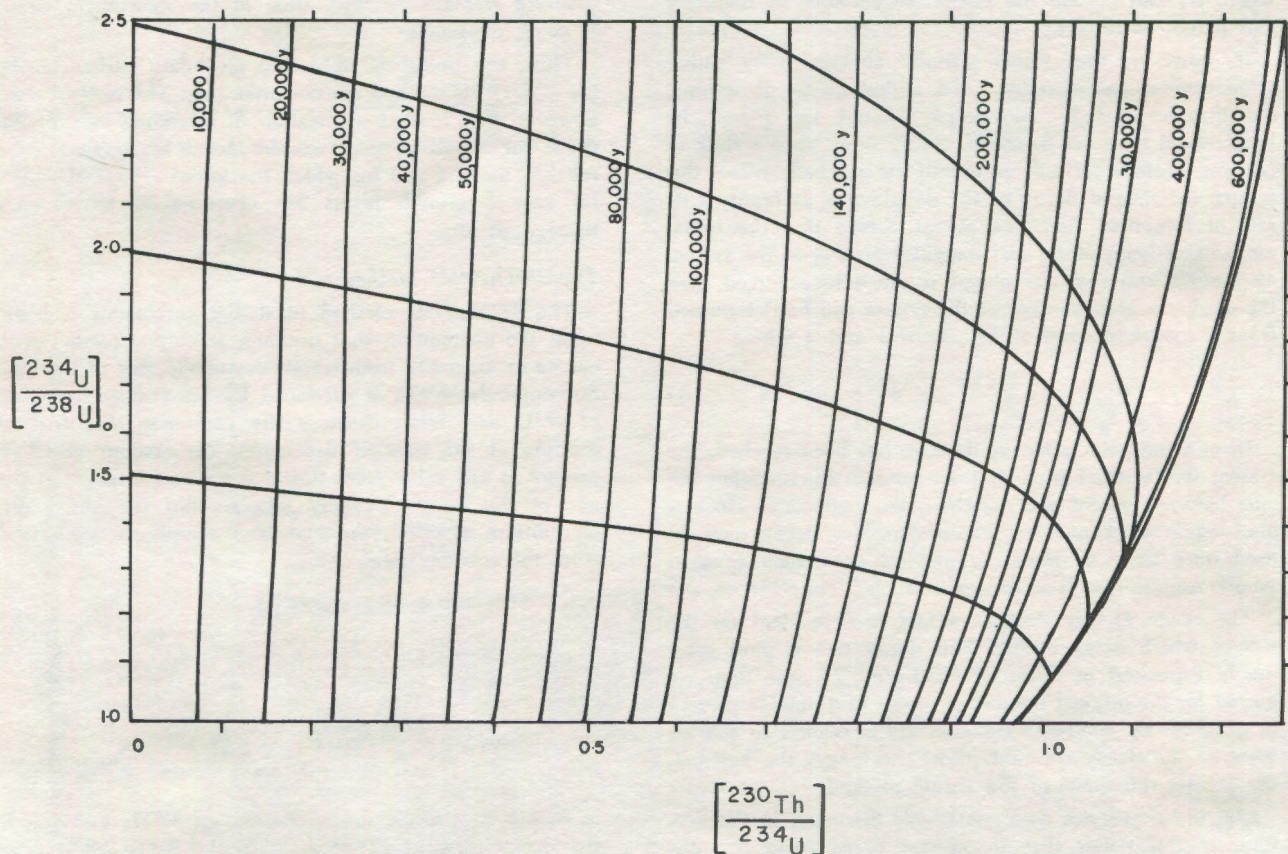

Fig. 3. Graphical representation of the growth of 230Th towards secular equilibrium with 234U in a closed system initially containing no 230Th. The near-vertical lines of the graph depict isochrons of t, the time elapsed since initial emplacement of 234U in the host material.

time of deposition, an assumption that can also be analytically tested. It is, however, not possible to directly determine the initial $^{234}U/^{238}U$ ratio of a sample. An indirect estimation of this value has to be made if this particular method is to be used.

P. Thompson (1973) and P. Thompson, et al. (1974) have shown that pure calcite speleothems, with well defined and preserved internal stratigraphy and showing no signs of diagenetic alteration and post-depositional erosion, generally meet the above conditions. Stalactites, stalagmites, and flowstone, the most abundant speleothem forms, are usually developed by slow precipitation of $CaCO_3$ when CO_2 escapes from ground waters percolating through cavernous carbonate rock. Thus, such deposits tend to be macrocrystalline, to have a low porosity, and not to be subject to diagenetic alteration or leaching once deposition has ceased. In addition, speleothems tend to be geographically widespread and well preserved over long spans of time.

ANALYTICAL METHODS

In order to accurately determine the $^{234}U/^{238}U$, $^{230}Th/^{234}U$, or $^{231}Pa/^{235}U$ activity ratio of a speleothem, it is first necessary to extract sufficient quantities of radiochemically pure uranium and thorium from the carbonate host. This is accomplished in a five-step process developed by P. Thompson (1974). The extraction and purification techniques used are designed to discriminate against both trace element and radiochemical contamination.

Twenty to 100 grams of carbonate material are dissolved in 2N HNO_3 and a measured amount of $^{232}U/^{228}Th$ tracer and $FeCl_3$ are added. Samples not entirely soluble are filtered and the insoluble residue weighed. Next, the solution is brought to boiling and then made alkaline, which results in the coprecipitation of uranium and thorium with $Fe(OH)_3$. This precipitate is washed with distilled water, dissolved in 9N HCl, and the iron removed by ether extraction. Uranium is separated from thorium by anion exchange Dowex 1-XB resin in a chloride form and foreign ions subsequently separated from thorium by anion exchange using the same resin in a nitrate form. Uranium and thorium are then recovered from their respective ion-exchange media by elution with O.1N HCl.

Additional solvent extractions ultimately isolate pure uranium and thorium. Uranium is quantitatively transferred from aqueous solution into O.2M thenoyltrifluoroacetone (TTA) in benzene at a pH of 3.5 whereas thorium is transferred into the same medium at a pH of 1.2. The pure solutions of uranium and thorium in TTA/benzene are evaporated onto steel discs for radioactive counting.

Alpha particle spectrometry is used to measure the radioactivity of the extracted uranium and thorium. Under vacuum, the decay of the isotopes of interest, ^{232}Th, ^{230}Th, ^{228}Th, ^{238}U, ^{235}U, ^{234}U, and ^{232}U produce alpha particles which strike a surface-barrier semiconductor with a characteristic energy. This signal is amplified and analyzed to produce a composite energy spectrum. A typical thorium spectrum is illustrated in Fig. 4A. The peaks shown are, from left to right, ^{232}Th, ^{230}Th, the artificial tracer ^{238}Th, and its daughter products ^{224}Ra, ^{212}Bi, ^{220}Rn, and ^{216}Pb. Similarly, Fig. 4B illustrates a typical uranium spectrum. The peaks shown from left to right are ^{238}U, ^{234}U, and the artificial tracer ^{232}U and its daughter products.

Peak amplitudes are related to the concentration of each isotope present. Thus, peak-area ratios are a direct measure of activity ratios.

The precision with which isotope ratios can be measured using the Nuclear Data Model 1100 analyzer system and Ortec 950 mm² silicon surface-barrier detector arrangement at McMaster University is 1-5%. The resulting age determinations are accurate ±0.5 to 2%, if 50 to 100 micrograms of uranium are extracted from a sample. To date, 0.03 ppm is the lowest uranium concentration for which an age of reasonable precision has been determined.

SOME PREVIOUS SPELEOTHEM RESULTS

Rosholt and Antal (1962) first attempted to date speleothems by uranium series disequilibrium methods. Analyzing several European stalagmites, they found very low uranium concentrations and evidence of post-depositional leaching
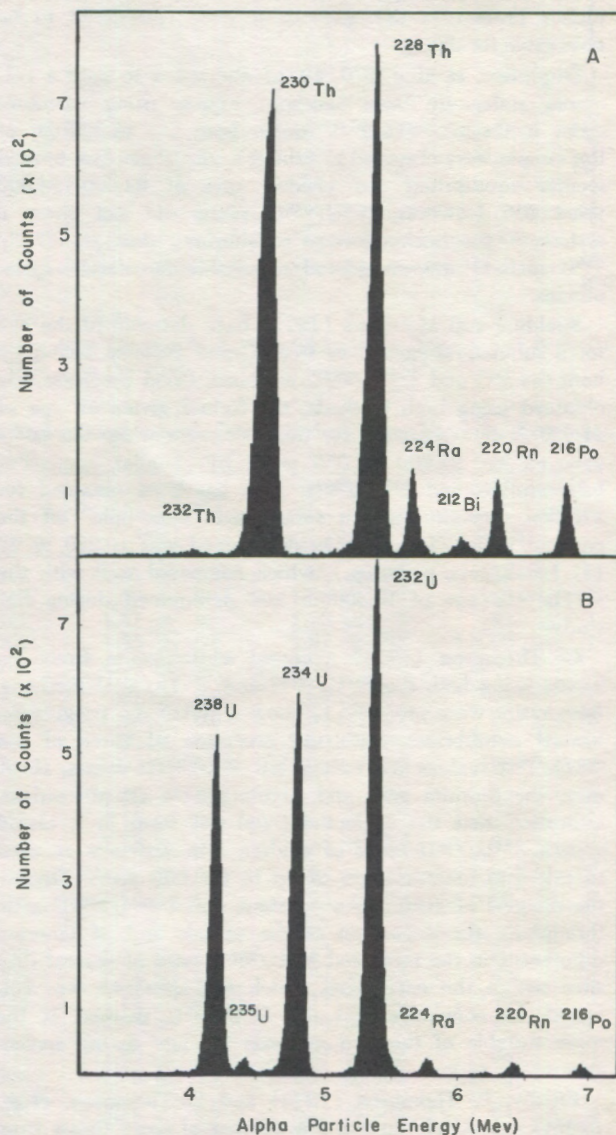

Fig. 4. Typical alpha particle spectra of the isotopes of thorium (A) and uranium (B).

which led them to conclude that such deposits were not acceptable for ^{230}Th/^{234}U or ^{231}Pa/^{235}U age dating.

Cherdyntsev, *et al.* (1965) were the first to actually date speleothem material utilizing uranium-series methods. Working with stalactites and travertines from a Russian cave, they found good agreement between ^{230}Th/^{234}U and ^{231}Pa/^{235}U ages, concluding that speleothem materials were very suitable deposits for dating the late Pleistocene. Variations were, however, observed in ^{234}U/^{238}U at a single site over long periods of time as well as from region to region.

Fornaca-Rinaldi (1968) analyzed speleothems from several Italian caves for their ^{230}Th/^{238}U ratios, assuming a ^{234}U/^{238}U ratio of unity. If the initial ^{234}U/^{238}U ratio of these deposits was, in fact, near unity, the resulting error in ages would not be great, because the samples dated were less than 50,000 years old (see Fig. 3). If, however, the samples contained a large initial excess of ^{234}U, high ^{230}Th/^{238}U ages would result from the incorrect assumption. It was also shown in this work that no detrital thorium was co-precipitated with uranium in several of the speleothems analyzed. Other samples with thorium attributable to detrital phases present in the speleothem were considered to be unsuitable for dating.

Duplessey, *et al.* (1970, 1971) attempted to date a columnar stalagmite from Southern France using uranium-series methods. ^{230}Th/^{234}U ratios from top to bottom of the sample were observed to exhibit a steady increase toward secular equilibrium and yielded ages of 92,000-124,000 years BP. However, ^{234}U/^{238}U ratios did not show a systematic progression toward equilibrium; thus, the ^{234}U/^{238}U method was considered unsuitable for dating speleothems.

Spalding and Matthews (1972) have determined the age for a submerged stalagmite from Grand Bahama Island by both the ^{14}C and ^{230}Th/^{234}U methods. Good precision was obtained using both methods, the former giving an age of $21,900 \pm 600$ years BP for the stalagmite while the latter gave an age $22,000 \pm 350$ years BP. Similar agreement between ^{14}C and ^{230}Th/^{234}U ages has been obtained for a fallen stalactite from a submerged "blue hole" off the coast of Belize. The ^{14}C age determined was $10,220 \pm 40$ (L. Land, pers. commun.), which compared well with the ^{230}Th/^{234}U age of $10,300 \pm 200$ determined during this study.

G. Thompson (1973) analyzed a stalagmite from Arkansas using both the ^{234}U/^{238}U and ^{230}Th/^{234}U methods. Both ratios were observed to show a systematic progression toward equilibrium, with the exception of three of ten ^{230}Th/^{234}U values and two of ten ^{234}U/^{238}U values. However, the thorium ages and uranium ages are discordant, indicating that the speleothem did not form in a closed system. ^{234}U/^{238}U ratios of modern drip waters were used to calculate uranium ages of up to 600,000 years. Despite the dangers of assuming a constant initial ^{234}U/^{238}U ratio throughout the deposition of the sample and of ignoring differences in the measured ^{234}U/^{238}U ratio of several drip sites within the cave from which the specimen was collected, he concludes that the ^{234}U/^{238}U method is the more suitable of the two methods for age dating speleothems.

Finally, P. Thompson (1973) and P. Thompson, *et al.* (1974) extensively analyzed a number of speleothems from Canada, Mexico, and West Virginia. In all three areas, he found that the ^{230}Th/^{234}U method gave reliable ages between 2,000 and 300,000 years BP, but that the ^{234}U/^{238}U method could not be used because initial ratios could not be accurately determined. ^{231}Pa/^{235}U ages agreed well with ^{230}Th/^{234}U ages in the few cases where the comparison was made.

Thus, it appears that speleothems are suitable material for age dating by the ^{230}Th/^{234}U method if care is taken to select only pure, macrocrystalline calcite samples which have no detrital contamination and show no signs of post-depositional alteration. Cherdynstev, *et al.* (1965) and P. Thompson (1973) have shown that the ^{231}Pa/^{235}U method can be used when uranium concentrations are sufficiently great to allow accurate counting of ^{231}Pa or ^{227}Th, the fourth daughter of the ^{235}U decay series. It does not appear that the ^{234}U/^{238}U method will find application to the dating of speleothems, except in the few cases where it might be used to extend ages of deposits for which portions can be dated by another method.

Geochemical Studies

Uranium concentrations for 125 speleothem samples analyzed to date average 3.20 ppm (range: 0.03 to 94.3 ppm) and have a median value of 0.90 ppm (P. Thompson, 1973; this study). Specimens from karst areas in the Cordillera of western North America have the highest uranium concentrations measured (mean = 5.44 ppm), while those from caves in the carbonate islands of the Caribbean and western Atlantic have the lowest concentrations (mean = 0.22 ppm). Speleothems from the Appalachians and the interior plateau areas of the United States generally have intermediate uranium contents (mean = 1.91 ppm). A comparison of the general stratigraphy of these regions suggests that differences in speleothem uranium concentrations may be related to the presence or absence of organic-rich shales; those areas with extensive shales overlying the caves exhibit the greatest uranium concentrations. An example from Kentucky directly illustrates this point. Five speleothem analyses from the caves of Mammoth Cave National Park, an area of limestone overlain by thin shales and sandstones, have an average uranium concentration of 0.7 ppm. In contrast, five speleothem analyses from Pulaski County, an area some 100 km to the east, where the carbonates are overlain by extensive black shales and sandstones, average 11.8 ppm uranium.

From geochemical considerations, it would be expected that the amount of uranium in a secondary carbonate would show an inverse correlation with the ^{234}U/^{238}U ratios at the time of deposition. In Fig. 5, the uranium contents of selected samples from Canada, West Virginia, Kentucky, Mexico, and Bermuda are plotted against initial ^{234}U/^{238}U ratios, as determined from the ^{230}Th/^{234}U age of the particular analysis. A general negative correlation is suggested, but more striking is the consistency of uranium contents and activity ratios. This is true not only from region to region, but from cave to cave and speleothem to speleothem. This is not unreasonable, considering that not only amounts and types of soil and overlying rock, climate, and characteristics of carbonate solution vary from region to region; but that lithologies, soil and rock volumes exposed to leaching, and catchment areas for specific depositional sites are likely to change only slowly with time.

Activity ratios and uranium concentrations for some typical speleothems which meet the criteria for reliable age determination listed earlier are given in Table 1. ^{230}Th/^{234}U
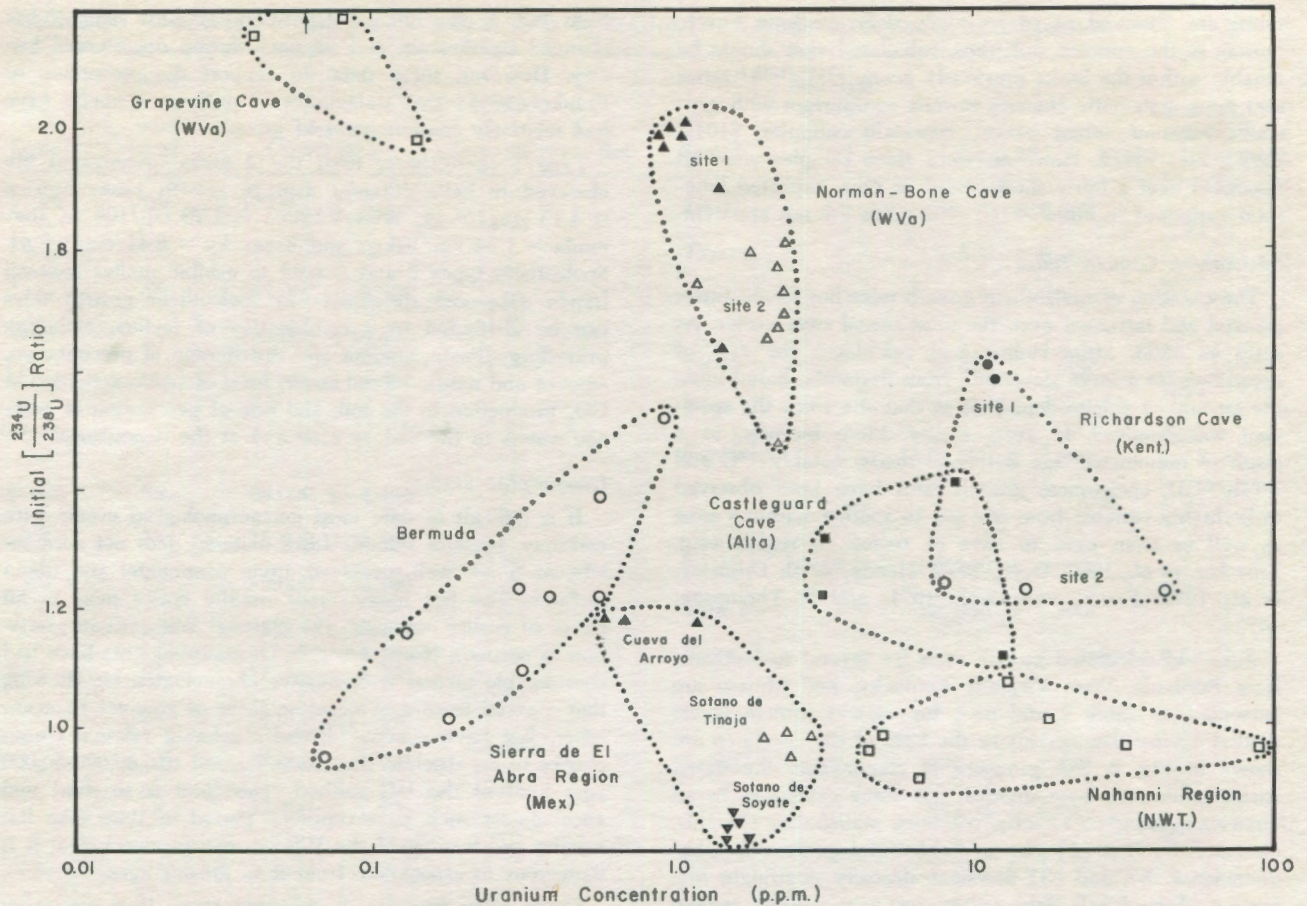
Grapevine Cave (WVa)

2.0

Norman–Bone Cave (WVa)

site 1

1.8

site 2

Initial $\left[\frac{234U}{238U}\right]$ Ratio

site 1

Richardson Cave (Kent.)

Castleguard Cave (Alta)

Bermuda

1.2

site 2

Cueva del Arroyo

Sotano de Tinaja

1.0

Sierra de El Abra Region (Mex)

Sotano de Soyate

Nahanni Region (N.W.T.)

0.01   0.1   1.0   10   100

Uranium Concentration (p.p.m.)

Fig. 5. Total uranium concentration vs. [234U/238U]₀ for selected speleothems from Canada, West Virginia, Kentucky, Mexico, and Bermuda. [234U/238U]₀ ratios determined are based upon the 230Th/234U age. Data from this study and P. Thompson (1973).

TABLE 1. Activity ratios and uranium concentrations for some typical speleothems from Mexico, West Virginia, Kentucky, and Bermuda which meet the criteria for reliable age dating.

Sample ID	Cave	Distance Above Base (cm)	U conc (ppm)	$\left[\frac{^{230}Th}{^{234}U}\right]$	$\left[\frac{^{234}U}{^{238}U}\right]$	$\left[\frac{^{234}U}{^{238}U}\right]_0$	$\left[\frac{^{230}Th}{^{232}Th}\right]$	Ref.
67002	Norman Bone (W. Virginia)	89	0.98	.819 ± .018	1.61 ± .03	1.97 ± .06	135	1
		48	1.65	.843 ± .017	1.60 ± .03	1.98 ± .05	146	1
		29	1.53	.854 ± .022	1.51 ± .02	1.85 ± .05	187	1
		24	1.07	.895 ± .002	1.55 ± .03	1.97 ± .08	>1000	1
		7	0.98	.884 ± .002	1.58 ± .02	2.00 ± .06	357	1
71003	Sótano de Tinaja (Mexico)	98	2.5	.073 ± .003	.973 ± .02	.962 ± .02	94	2
		74	2.4	.173 ± .004	.994 ± .01	.994 ± .01	87	2
		44	2.0	.285 ± .004	.992 ± .02	.991 ± .02	70	2
		2	2.8	.367 ± .006	.938 ± .02	.928 ± .02	100	3
71042	Cueva del Arroyo (Mexico)	43	1.2	.376 ± .008	1.16 ± .02	1.18 ± .02	42	3
		22	0.59	.472 ± .013	1.15 ± .02	1.18 ± .02	26	3
		1	0.65	.644 ± .024	1.13 ± .01	1.18 ± .02	91	3
72023	Wilkenson Quarry Fissure Cave (Bermuda)	6	0.37	.386 ± .016	1.20 ± .01	1.23 ± .03	>1000	3
		1	0.29	.616 ± .017	1.18 ± .02	1.24 ± .02	>1000	3
73036	Crystal Cave (Bermuda)	51	0.50	.675 ± .006	1.31 ± .02	1.42 ± .03	20	3
		45	0.80	.829 ± .008	1.31 ± .01	1.54 ± .02	43	3
		30	1.0	.824 ± .024	1.11 ± .02	1.17 ± .02	46	3
		4	0.30	.785 ± .021	1.06 ± .02	1.10 ± .03	46	3
74011	Richardson Cave (Kentucky)	28	11.2	.123 ± .003	1.55 ± .02	1.57 ± .02	90	3
		6	10.4	.157 ± .004	1.56 ± .02	1.59 ± .02	>1000	3
74012	Richardson Cave (Kentucky)	22	7.5	.189 ± .008	1.21 ± .01	1.22 ± .02	61	3
		9	12.3	.288 ± .007	1.19 ± .02	1.21 ± .02	48	3
		1	41.0	.478 ± .018	1.20 ± .02	1.24 ± .02	152	3

1 P. Thompson, et al. (in press), 2 P. Thompson (1973), 3 this study.

ratios are observed to progressively decrease from top to bottom of the samples and, thus, calculated ages should be reliable within the limits previously given. $^{234}U/^{238}U$ ratios also show systematic changes toward equilibrium with generally constant initial ratios, especially samples 71042, 73023, and 74012. However, since these samples were all deposited over a fairly short period of time, expected long-term variations in initial $^{234}U/^{238}U$ ratios are not apparent.

Speleothem Growth Rates

The question of speleothem growth rates has for centuries puzzled and intrigued even the most casual cave visitor. As early as 1863, Milne-Holme had calculated the rate of deposition for a large stalagmite from Bermuda, based upon the amount of calcite deposited at that site since the specimen was removed 44 years earlier. More recently, as a result of radiometric age dating methods, notably ^{14}C and $^{230}Th/^{234}U$, speleothem growth rates have been observed to be highly variable from one site to another within a cave as well as from cave to cave or region to region (e.g. Broecker, *et al.*, 1960; Geyh, 1970; Hendy, 1970; Duplessy, *et al.*, 1971; Franke and Geyh, 1971; and P. Thompson, 1973).

Ages and calculated growth rates for several speleothems from Bermuda, West Virginia, Kentucky, and Mexico are presented in Table 2 and ages for various growth layers plotted against distance above the base of the specimen are shown in Fig. 6. For purposes of comparison, the dated speleothems have been divided into three categories based upon morphology: (1) long, columnar stalagmites (height/diameter > 5), (2) short, stubby stalagmites (height/diameter < 5), and (3) flowstone deposits. A straight line passing through all data points for a particular sample would indicate a constant rate of growth. As can be seen

from Fig. 6, the rate of deposition for most samples has changed significantly at least once during depositional history. However, these data do support the contention of Franke (1965) that stalagmites of uniform diameter have had relatively constant rates of growth.

Type 1 speleothems from the 4 areas investigated are observed to have different average growth rates: Mexico = 4.13 cm/10^3 yr, West Virginia = 1.75 cm/10^3 yr, Bermuda = 1.24 cm/10^3 yr and Kentucky = 0.41 cm/10^3 yr. Speleothem types 2 and 3 tend to exhibit similar regional trends. Observed differences in speleothem growth rates can be attributed to a combination of factors, including prevailing climate, amount and distribution of precipitation, amount and nature of soil cover, level of biotic activity and CO_2 production in the soil, and rate of percolation of seepage waters in the vadose zone and at the depositional site.

Geomorphic Studies

It is difficult to date most geomorphological events with certainty, because suitable fossil material does not accumulate, or is not well preserved, upon continental and island surfaces. The last major event usually erases most or all traces of earlier ones, e.g. the classical Wisconsinan glaciation in northern North America. Geomorphologists have had considerable success with relative chronologies, i.e. showing that a given feature or event is older or younger than another, but have extreme difficulty relating relative chronologies to an absolute time scale beyond the 40,000-50,000 year limit of the ^{14}C method. This limit is so short and encompasses such an exceptional period of time (the last waxing and waning of the Wisconsinan glaciers), that it is dangerous to extrapolate from it to greater ages.

Caves often function as sediment traps, thus preserving fossil material which may no longer be present on the surface. In many, there are phreatic sections that are now permanently drained and contain speleothems. Because speleothem deposition cannot commence until such time as a cave is air-filled (drained), the greatest speleothem age for a cave provides a minimum date for the draining event. This is usually the result of the downward shift of a spring consequent upon valley deepening by other, usually non-karstic, processes. Data on the absolute ages of speleothems can thus provide useful information upon the time and duration of base level stands, ages of river terraces, rates of erosion and/or sedimentation, rates of regional tectonic uplift, etc. Three examples from Canada illustrate this point.

In the middle sections of its course through the Mackenzie Mountains, N.W.T., the South Nahanni River flows across a thick sequence of Devonian carbonate rocks. Into these it has cut a series of meandering canyons. First Canyon, over 900 m deep, is the deepest canyon and is the erosional base level of the series. More than 30 phreatic caves are exposed in its walls. Large fossil speleothems are common in the caves and small modern stalactites are present near cave entrances. Speleothems from two caves, Grotte Valerie (500 m above the river) and Trou Claudette (230 m) have been dated (Table 3). Since speleothem deposition cannot have commenced until such time as a cave is drained, some limits on the minimum ages of the caves and the entrenchment history of the South Nahanni River can be determined. The age of the Trou Claudette sample reveals that no more than 230 m of River downcutting could have occurred in the last 275,000 years. Extrapolating for the maximum fluvial relief in the canyon,
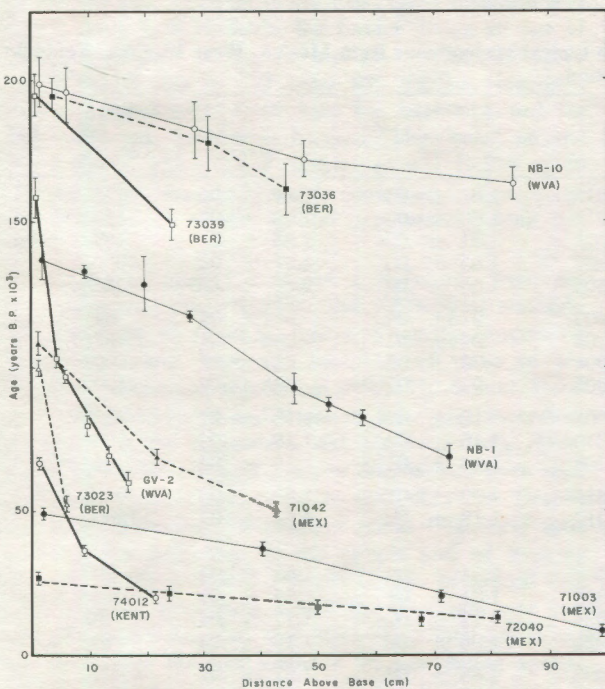

Fig. 6. Age vs. distance above base for growth layers of selected speleothems from Mexico, Kentucky, West Virginia, and Bermuda. A straight line passing through all data points for a particular sample would indicate a constant rate of growth. Data from this study and P. Thompson, *et al.* (in press).

TABLE 2. Comparison of speleothem growth rates in Mexico, West Virginia, Kentucky, and Bermuda.

Sample	Distance Above Base (cm)	Age (Years BP)	Growth Rate (cm/10³yr)	Ref.	Sample	Distance Above Base (cm)	Age (Years BP)	Growth Rate (cm/10³yr)	Ref.
67002	89	163,000 ± 6,800			72041	22	203,900 ±13,900		
(NB-10)	48	173,000 ± 6,900	4.50		Type 1	4	125,500 ± 5,300	0.23	3
Type I	29	183,000 ± 9,700	1.90	1	Kentucky			Avg 0.23	
West	7	195,000 ±10,400	1.84						
Virginia	2	199,000 ± 8,800	1.00		74012	22	22,500 ± 1,000		
		Avg 2.47			Type 1	9	36,500 ± 1,100	0.93	3
					Kentucky	1	68,900 ± 3,500	0.25	
67003	73	69,000 ± 4,400						Avg 0.59	
(NB-1)	58	78,000 ± 2,400	1.67						
Type 1	52	82,000 ± 3,500	1.00		73039	25	149,700 ± 6,600		
West	46	93,000 ± 6,900	0.54	1	Type 2	1	195,800 ± 7,800	0.56	3
Virginia	28	118,000 ± 1,000	1.20		Bermuda			Avg 0.56	
	20	129,000 ±11,200	0.89						
	10	134,000 ± 1,500	2.00						
	2	137,400 ± 7,800	2.67		71042	43	50,000 ± 1,400		
		Avg 1.04			Type 2	22	68,200 ± 2,700	1.17	3
					Mexico	1	108,900 ± 4,200	0.52	
71003	98	8,200 ± 400						Avg 0.81	
Type 1	74	20,600 ± 500	1.94						
Mexico	43	37,000 ± 900	1.82	2,3	73023	6	52,100 ± 2,900		
	2	48,900 ± 800	3.52		Type 3	1	100,400 ± 4,600	0.12	3
		Avg 2.41			Bermuda			Avg 0.12	
					67022	17	60,400 ± 2,900		
72040	81	11,800 ± 800			(GV-1)	14	70,000 ± 3,600	0.31	
Type 1	68	13,100 ± 1,100	10.0		Type 3	10	85,900 ± 3,000	0.25	
Mexico	50	16,100 ± 1,200	6.00	3	West	6	97,200 ± 2,500	0.36	2
	24	21,200 ± 3,100	5.20		Virginia	4	104,500 ± 2,700	0.41	
	2	26,500 ± 2,800	4.35			1	159,000 ± 6,900	0.05	
		Avg 5.85						Avg 0.17	
73036	45	162,000 ± 9,800							
Type 1	30	178,300 ± 9,300	0.94						
Bermuda	4	195,000 ± 6,900	1.44						
		Avg 1.24							

1 P. Thompson, et al. (in press), 2 P. Thompson (1973), 3 this study.

TABLE 3. Activity ratios, uranium concentrations, and calculated ages for speleothems from three Canadian karst areas.

Location	Sample ID	U conc (ppm)	$\frac{^{230}\mathrm{Th}}{^{234}\mathrm{U}}$	$\frac{^{234}\mathrm{U}}{^{238}\mathrm{U}}$	Age (years BP)	Ref.
South	GV-1	4.31	.975 ± .085	.98 ± .01	290,000 ± 50,000	1
Nahanni	GV-2	17.9	.840 ± .030	1.01 ± .01	200,000 ± 20,000	1
River	GV-3	12.9	.850 ± .025	1.05 ± .01	217,000 ± 17,000	1
Area	GV-4	32.6	.01 —	.97 ± .01	<2,000	1
N.W.T.	TC-1	7.6	.960 ± .020	.99 ± .01	275,000 ± 35,000	1
	72026(GV)	93.4	.825 ± .017	.98 ± .01	191,400 ± 11,000	3
	72030(GV)	21.1	.777 ± .009	1.41 ± .03	145,300 ± 6,000	3
	GV = Grotte Valerie (600m above river level)					3
	TC = Trou Claudette (230m above river level)					3
Nahanni	73051:4	4.0	1.078 ± .018	.99 ± .01	>350,000	3
North	73051:5	3.3	1.076 ± .020	1.02 ± .02	>350,000	3
Karst	73052:6	6.7	.935 ± .018	1.03 ± .05	315,100 ± 25,100	3
Area	73056:1	.67	.955 ± .023	.97 ± .01	319,100 ± 27,900	3
N.W.T.						
Crows	CT-1	0.23	.862 ± .026	1.00 ± .02	235,000 ± 19,500	2
Nest	CT-2	0.25	.925 ± .029	1.07 ± .02	296,000 ± 32,500	2
Pass	E-1	0.33	.976 ± .026	1.15 ± .02	>300,000	2
Area	E-2	0.28	.869 ± .026	1.40 ± .02	198,000 ± 13,000	2
Alta.	MS-1	0.12	.595 ± .024	1.10 ± .03	102,500 ± 6,000	2
	MS-2	0.07	.808 ± .032	1.07 ± .04	191,000 ± 16,500	2
	MS-3	—	.873 ± .038	.97 ± .03	273,000 ± 37,000	2
	YP-1	3.1	.756 ± .028	1.21 ± .02	178,000 ± 10,500	2
	GAR-1	3.7	.993 ± .016	1.07 ± .02	>350,000	2
	69001(MC)	1.3	1.05 ± .029	.98 ± .03	>350,000	3
	72025(GAR)	18.1	.853 ± .019	.94 ± .05	219,300 ± 15,900	3
	E = Eagle Cave (1350m above sea level)					
	MS = Middle Sentry (1950m above sea level)					
	MC = Middle Caves (2000m above sea level)					
	CT = Coulthard Cave (2500m above sea level)					
	GAR = Gargantua (2675m above sea level)					
	YP = Yorkshire Pot (2700m above sea level)					

1 Ford (1973), 2 Ford, et al. (1973), 3 this study.

this figure yields a maximum average rate of canyon entrenchment of 0.8 m per thousand years and a minimum age of 1.4 million years for the preserved portion of First Canyon (Ford, 1973). It also yields valuable information on the rate of tectonic uplift of the Nahanni Plateau, into which the canyon is incised, and the time of tectonism in this part of the Mackenzie Mountains.

The Nahanni "North Karst" is contained in a 6 to 10 km wide limestone belt which crops out for some 50 km north of First Canyon. Intensively studied by G. A. Brook of McMaster Universtity (ms. in preparation), it is the most accentuated karst landscape in continental North America. Landforms present include pavements, dolines, cenotes, poljes and towers, but the landscape is dominated by systems of great canyons and corridors of solutional origin and periglacial enlargement. Over 100 caves are exposed on cliff faces and walls of the canyons. Most of these are fragments or remnants of larger phreatic cave systems, now dissected and eroded by the development and enlargement of the canyons, and presently are choked with silt and clay, fallen rock, or ice.

Fossil speleothems from several caves have been dated (Table 3). These dates, together with those from the First Canyon area, indicate that major speleothem deposition occurred during the periods 200,000 to 225,000 years BP and 275,000 to > 350,000 years BP. The caves, the oldest

karst landforms of the region, were drained by canyon entrenchment through and below them. The speleothem ages thus indicate that many of the karst canyons must be at least 300,000 to 350,000 years old and so give an indication of the rate of evolution of the karst landforms of the Nahanni Region.

The Crows Nest Pass area of the High Rock Range, Rocky Mountains, is an alpine terrain comprised of severely faulted Devonian and Mississippian limestones. The topography and most of the present landforms are glacial in origin, glaciers having flowed eastward through the pass, dissecting the surrounding area to a local relief of about 1600 m. Over 25 caves are known in the area, most being fragments of fossil phreatic passages that are now exposed due to valley and cirque entrenchment and/or cliff recession. The caves are exposed at all elevations from valley floor to mountain top. Most caves contain both active and fossil speleothems. Ages determined for speleothems from Yorkshire Pot (2700 m ASL), Gargantua Cave (2675 m ASL), Coulthard Cave (2500 m ASL), Middle Sentry Cave (1950 m ASL), and Eagle Cave (1350 m ASL) are given in Table 3.

The succession of ages indicates that the floor of the Pass to which the caves discharged was below 1960 m ASL 275,000 years ago and below 1600 m ASL 200,000 years ago. Given that valley floor elevations are maximum and

Table 4. Activity ratios, uranium concentrations and calculated ages for speleothems from Bermuda.

Location	Sample ID	U conc (ppm)	$\dfrac{230\text{Th}}{234\text{U}}$	$\dfrac{234\text{U}}{238\text{U}}$	Age (years BP)	Ref.
Crystal	73036:11	.50	.675 ± .006	1.31 ± .02	114,400 ± 4,200	1
Cave	73036:10	.80	.785 ± .021	1.06 ± .02	162,000 ± 9,300	1
	73036:12	.10	.824 ± .024	1.11 ± .02	178,300 ± 9,800	1
	73036: 9	.30	.829 ± .008	1.31 ± .01	195,000 ± 6,900	1
	73039: 7	.18	.757 ± .007	1.06 ± .01	149,700 ± 6,600	1
	73039: 6	.07	.830 ± .011	.971± .01	195,800 ± 7,800	1
	73037: 8	.13	.715 ± .010	1.13 ± .01	131,200 ± 6,000	1

1 this study.

their ages minimum, the data suggest that over 60% (900 m) of the present relief had developed at least 275,000 years ago and that at least 85% (1400 m) of the present relief had formed at least 200,000 years ago, before the onset of the penultimate glaciation. Thus, it appears that most of the alpine relief at Crows Nest Pass (and, thus, also in the surrounding mountain ranges) is attributable to earlier glacial and interglacial events of which no surficial evidence at all exists today, (Ford, *et al.*, 1972).

Pleistocene Sea Level History

The tectonically stable, low relief, carbonate islands of the western Atlantic and Caribbean commonly contain caves with abundant speleothems and which are partially or fully submerged in the sea. Their speleothems can be used to date Pleistocene low sea level stands, provided their age can be determined.

Two stalagmites from Crystal Cave in Bermuda were recovered in the growth position from a depth of about 8 m below the sea. A stalactite, fallen from the ceiling, 2 m above present sea level in the cave, was also selected for study. All three specimens consist of macrocrystalline, white calcite covered with thin surface coatings of beige-grey aragonite. $230\text{Th}232$/Th ratios and trace element concentrations of the calcite portions of the samples indicate that no contamination or alteration of the deposits by sea water has occurred.

The ages for these samples (Table 4) indicate that during the period 195,000-150,000 years BP, sea level in Bermuda must have been at least 8 m lower than at present, whereas 130,000 years ago sea level could not have been more than 2 m higher than at present.

Pleistocene Glacial Chronology

Speleothem deposition in caves is dependent on many factors, the most important of which is a source of car-

bonate-bearing recharge water. Periods of severely cold climate, glacial surface ice, periglacial frozen ground, and/or decreased rainfall most often result in a decrease in the amount of seepage water entering a cave and, therefore, in the rate of speleothem deposition. Additionally, cold-climate conditions may cause a drop in the rate of CO_2 production, also producing a decrease in the rate of speleothem deposition or terminating it.

Speleothem ages from caves sampled above 35° North latitude are shown in Fig. 7. These ages are observed to cluster into distinct groups, which can be interpreted broadly in terms of a glacial/interglacial sequence.

It has become evident from recent paleotemperature studies that the picture of Pleistocene glaciation is much more complex than the classical concept of four distinct glacial periods, each separated by a period of warm climate. Rather, the present picture is one of periodic, cold/warm cycles with many superimposed short-term fluctuations. It is these major cycles, each approximately 100,000 years in duration and distinctly recognizable by geologic criteria, to which the classical description applies. The periods of speleothem deposition shown in Fig. 7 support this picture of Pleistocene glacial chronology. It must, however, be stressed that, at present, the correlation observed is tentative and requires additional substantiation.
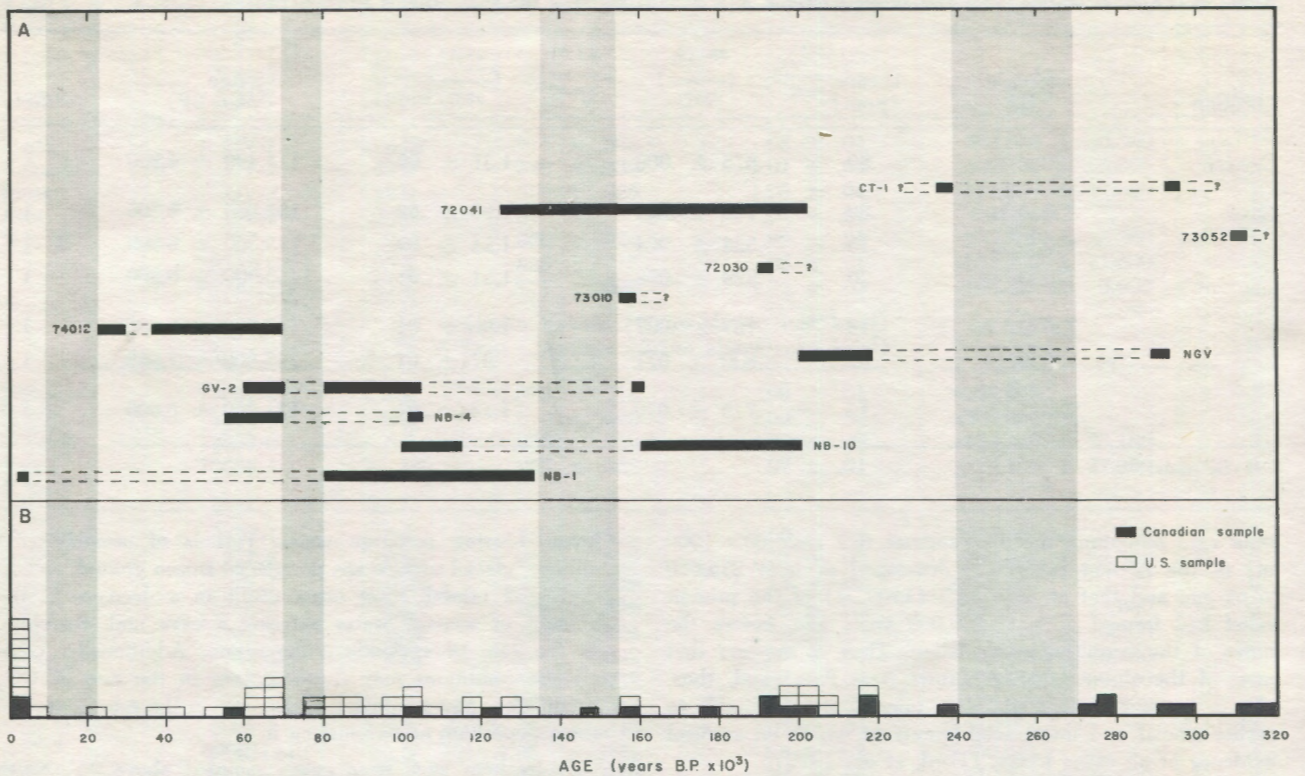
Fig. 7. (A) Periods of speleothem deposition (solid bars) and no deposition (dashed bars) for speleothem samples from karst areas in the United States and Canada above 35°N latitude. Samples NB-1, NB-4, NB-10, and GV-2 from Greenbrier County, West Virginia; 74012 and 72041 from central Kentucky; 73010 and CT-1 from the southern Canadian Rocky Mountains; and 72030, 73052, and NGV from the South Nahanni Region. Question marks indicate that the inception or termination of deposition is not known.

(B) Frequency of speleothem deposition for North America above 35°N latitude, as indicated by age determinations of 70 speleothem samples.

The shaded areas on both Figures A and B indicate times of reduced speleothem growth corresponding to periods of cold climate in northern North America.

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Applelite: A New Calcite Structure From Apple Cave, Orange County, Indiana

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ABSTRACT

A section of the main stream passage in Apple Cave, Indiana contains calcite speleothems on the undersides of several hundred loose rocks within the cave stream. These speleothems are composed of many spindle- or scalenohedron-shaped, crystal-like forms which are composed of even finer-grained crystallites. The crystal-like forms are approximately 60 μm in diameter and 120 μm in length. They possess no optical continuity. The crystallites range in diameter from 1 to 6 μm. These coalesce to give the surface of the applelite a subdued-botryoidal appearance. Two modes of origin are proposed for the formation of applelite: (1) change in hydrologic regime of waters approximately saturated with respect to calcite, and (2) fixation by heterotropic micro-flora.

INTRODUCTION

An apparently new calcite speleothem occurs in Apple Cave, Orange County, Indiana (Figs. 1 and 2). This speleothem consists of crystal-like forms which have the basic shape of spindles or scalenohedra, but are made up of finer-grained crystallites. The crystal-like forms coat the under-
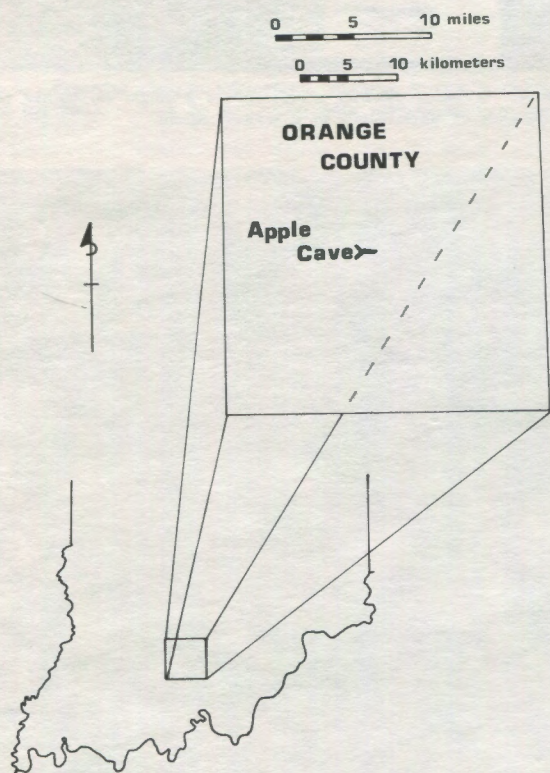
Fig. 1. Partial map of Indiana, showing location of Apple Cave.

sides of hundreds of loose rocks within a short segment of the main stream in the cave. The area where the speleothems are found is approximately 5 m long and 1 m wide. This segment of the cave stream is a bedrock riffle between two

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Fig. 2. Photograph showing the underside of a rock on which calcite has formed; note subdued botryoidal nature of the surface.

pools immediately downstream from the confluence of two cave streams (Fig. 3).

The coating of calcite on observed samples averages 3-5 mm in thickness and thins toward its margin. The mineralogy of the formation was determined by x-ray diffraction as calcite. In broken cross-section, a faint series of parallel and subparallel laminations can be seen with a 10x hand lens. However, the laminations are not visible in thin section or when examined with the scanning electron microscope.

In thin section, individual crystal-like forms are discernible only near the boundary of the deposit. These crystal-like forms do not display optical continuity in thin section and are, thus, not single crystals. Therefore, the term "crystal-like forms" is used to describe them throughout this paper. The crystal-like forms appear as micritic lumps near the edge of the deposit. Elsewhere, the entire deposit is micritic and no distinct crystal-like forms are to be seen.
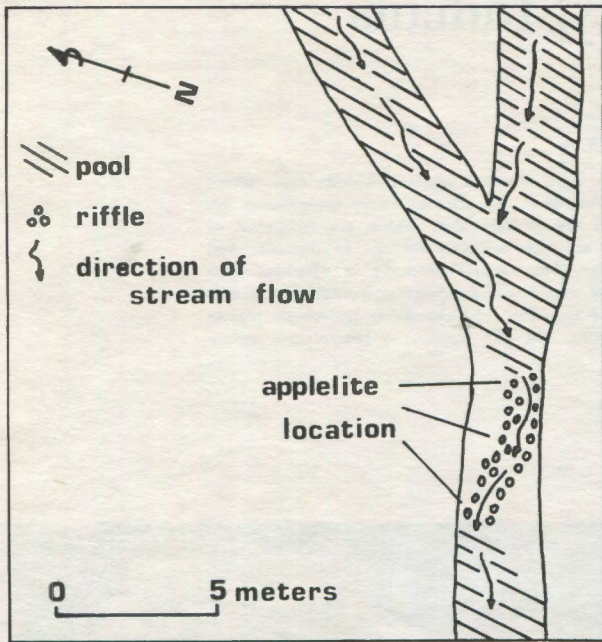
Fig. 3. Map of a portion of Apple Cave, Orange County, Indiana, showing the relationship of Applelite locality to pools and riffles.
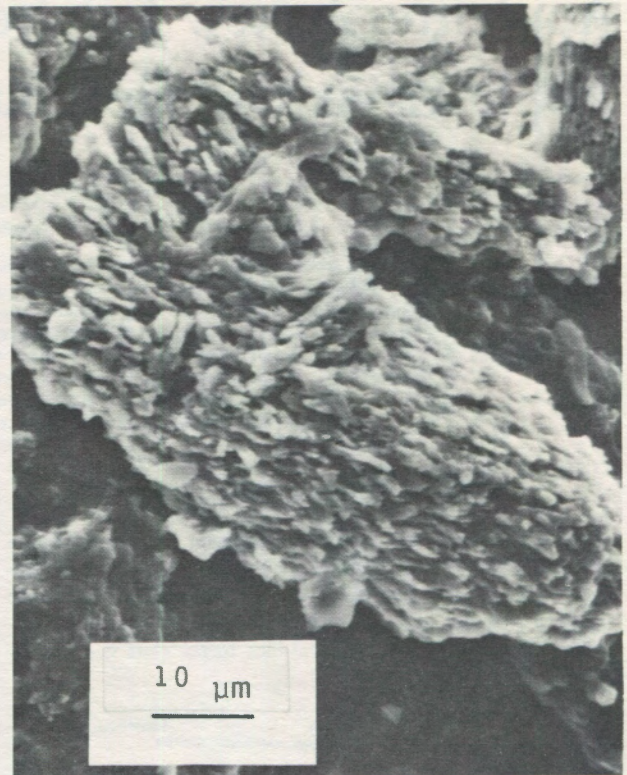

Fig. 4. Scanning electron micrograph of a single crystal-like form, showing its resemblance to a scalenohedron.

Fig. 5. Scanning electron micrograph of a portion of an individual crystal-like form, showing the morphology of the crystallite bundles.
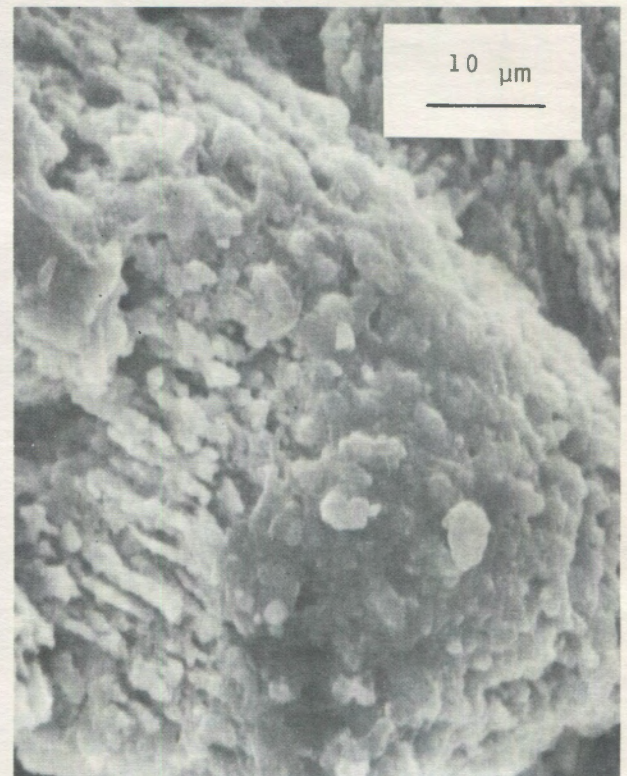

Fig. 6. Scanning electron micrograph of the end of a crystal-like form; note that terminations of individual crystallites are subcircular in cross-section.
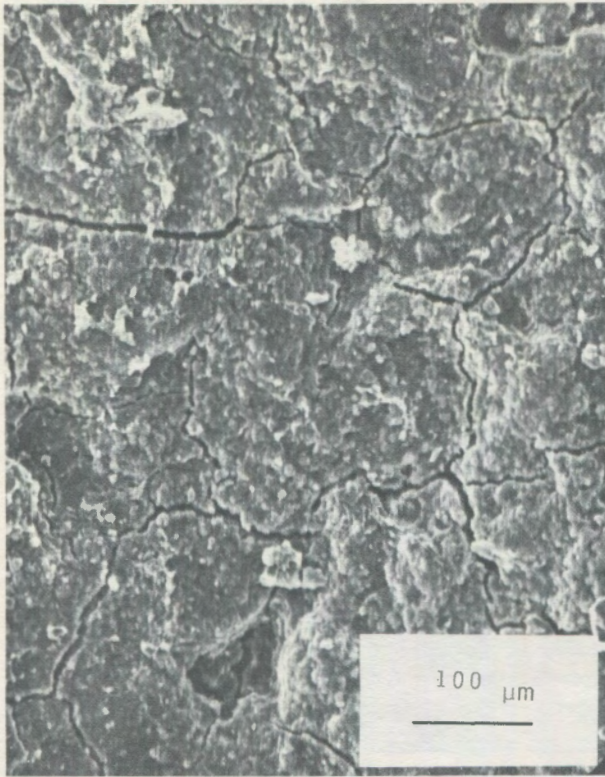
Fig. 7. Scanning electron micrograph, showing surface morphology of the black coating on the rocks; note microdesiccation cracks.
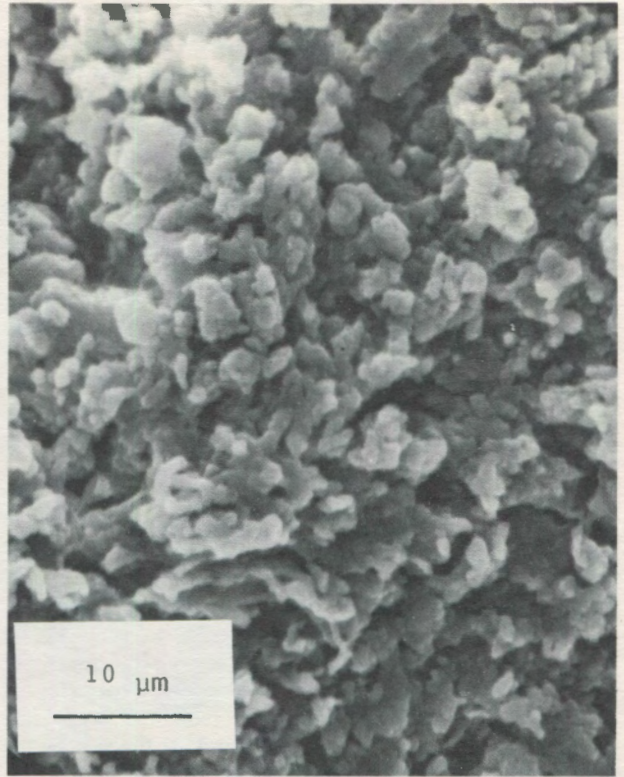
Fig. 8. Scanning electron micrograph of the bottom surface of applelite. Compared with Fig. 6, which is a view of the upper surface, it has a finer texture.
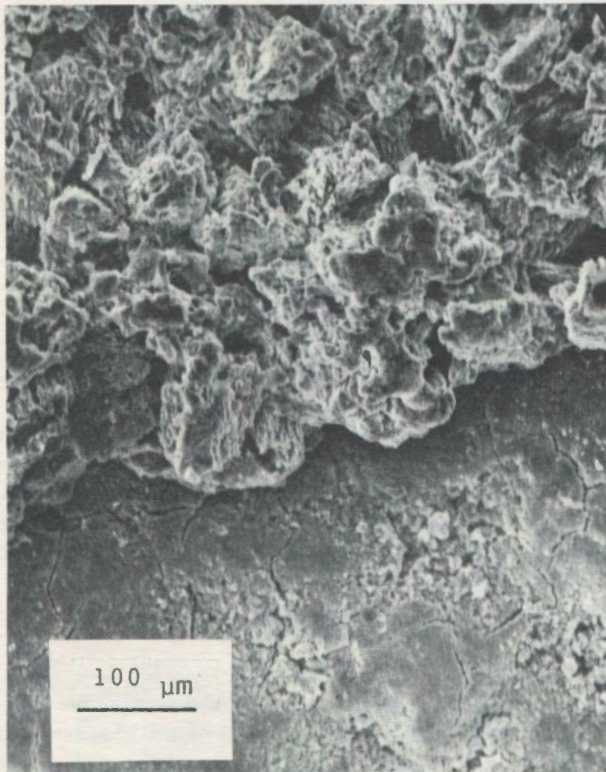
Fig. 9. Scanning electron micrograph, showing microscarp between calcite and exposed rock surface.

Fig. 10. Scanning electron micrograph of the surface of an applelite speleothem. Note that the crystal-like forms are random in orientation. However, 20 to 50 of these coalesce to form a group. A collection of groups form the typical botryoidal surface seen in hand specimens (Fig. 2).

APPLELITE MORPHOLOGY

The crystal-like nature of these deposits is easily seen in scanning electron micrographs. In Fig. 4, it is seen that the crystal-like forms resemble miniature scalenohedral crystals characteristic of calcite in general. However, it can also be seen that each individual scalenohedron is composed of a bundle of generally parallel or subparallel crystallites (Figs. 5 and 6). These crystallites are 1 to 6 μm in diameter and many of them appear to be as long as the crystal-like form (approximately 120 μm).

The rocks on which the calcite is deposited are sandstone cobbles with a black coating. This coating is approximately 200 μm thick and its surface is characterized by what appear to be small-scale desiccation cracks (Fig. 7). Unfortunately, it is not known if the desiccation cracks formed before or after sample removal from the cave. The relationship between this coating and the deposit of calcite on it is not known at this time. However, it appears that some correlation does exist between the two, as rocks in the same locality which have no black coating also lack a calcite coating.

By sliding a dental probe along the surface of the rock, the calcite growth can be separated from the rock. Fig. 8 is a scanning electron micrograph of the calcite growth at the edge of the deposit. It shows the terminal ends of individual crystallites, but does not show the crystal-like forms found at the margin of the deposit, at the side of the rock, and at the surface of the calcite growth.

The contact between calcite and bare rock along the side of the rock specimen (Fig. 9) is characterized by an irregularly shaped microscarp. The crystal-like forms are most distinct there. Fig. 10 shows that the surface of the calcite growth consists of groups of randomly oriented, crystal-like forms. Twenty to 50 of these crystal-like forms coalesce to form a single group. These groups are approximately 1 mm in diameter and give the surface a subdued botryoidal appearance.

POSSIBLE MODES OF ORIGIN

Based on scanning electron microscopy, light microscopy of thin sections, and environmental analysis, two modes of origin seem possible:

1) change in hydrological flow regime of calcite-saturated water, or

2) heterotrophic microfloral fixation

A combination of both is also a possibility.

Varnedoe (1965) has shown fairly well that calcite deposition can be caused by a loss of CO_2 from approximately saturated solutions. This is important in the case of applelite, as their development takes place entirely under water. Thus, evaporation cannot be used to explain the deposition of the calcite.

In the case presented by Varnedoe (1965), changes in the hydrologic regime of the cave stream can trigger deposition of calcite. This is because, in laminar flow, there is little mixing or interchange between adjacent flow layers and, consequently, there is little CO_2 mixing either. However, when laminar flow changes to turbulent flow, eddies are produced which transcend laminar flow layers and mixing can take place. Fig. 3 shows that all of the applelite deposits occur in a riffle between two pools. Keller (1971)

points out that, at low flows, the velocity of the streams in pools is less than their velocity in adjacent riffles. If the flow regime of the stream in the pool is subcritical (Froude Number less than 1) and the flow in the riffle is supercritical (Froude Number greater than 1), mixing of flow layers, a loss of CO_2, and deposition of calcite can take place in the riffles. Although this mechanism appears to present a viable mechanism for the deposition of calcite under certain conditions, it is suggested by Keller (1972) that Froude Numbers greater than 1 are seldom reached, even in streams with steep gradients. However, other changes in flow regime may account for the deposition of calcite.

Morisawa (1968), as well as many others, points out that the discharge over a given reach of a stream (assuming steady-state conditions) remains constant with time and is defined by the equation: $Q = AV$, where Q is discharge, A is cross-sectional area, and V is velocity of the stream at a particular point on the stream. This is important to our discussion because, if Q is constant with time and cross-sectional area decreases, then velocity must increase to maintain the proper discharge. As Varnedoe (1965) points out, an increase in velocity results in a lower vapor pressure in the fluid media and degassing of CO_2 may result. The locality of applelite formation is within a portion of reduced cross-sectional area for the stream and, thus, lowering of vapor pressure due to velocity increase may have been a cause of calcite deposition.

In coating the samples for use in the scanning electron microscope, great difficulty was encountered in producing specimens that did not 'charge' under the electron beam. It was found that the trouble was caused by an excessive amount of organic matter. This problem was solved by boiling the samples in KOH for 45 minutes, undercoating with carbon, and then coating the samples with aluminum. The presence of this organic material, plus the faint laminations visible in broken hand specimens, suggest another possible mode of origin.

Queen (1973) points out that laminations of the type found can result from the binding of floculated clay, silt, and fine sand by heterotropic microflora (bacteria, fungi, and algae). According to Queen, this binding can be accompanied by the precipitation of calcite. However, scanning electron microscopy failed to show any of the characteristic branching filamental networks possessed by fungi, bacteria and algae.

All algae do not have branching networks. Therefore, a small piece of applelite was dissolved in EDTA and a sample of the insoluble residue was obtained. Two slide smears were made of the residue. X-ray diffraction determination of the mineral composition of one smear showed it to be quartz and kaolinite. Using phase-contrast microscopy, the presence of blue-green algae and bacteria was confirmed (Figs. 11 and 12).

The coating on the rocks in Apple Cave has been identified as manganese oxide by x-ray diffraction. Also, the dark-colored sheath surrounding the ovoids of some bacteria was found to be a mixture of iron and manganese oxides. The close spatial relationship between the manganese mineral and the applelite, therefore, suggests that oxidation at the riffle, possibly through the agency of microflora, could have produced deposition of applelite.
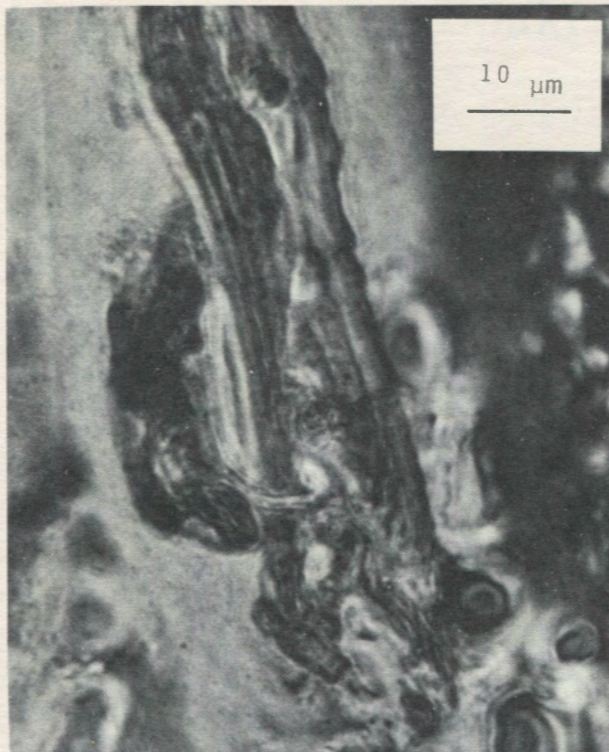
Fig. 11. Photomicrograph, showing a piece of blue-green algal debris, such as is common in the insoluble residue of applelite after EDTA leaching.
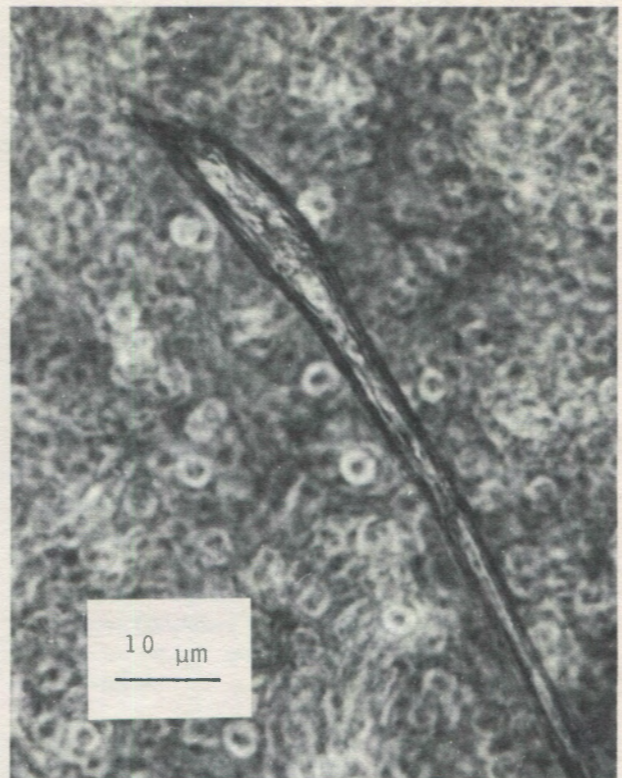

Fig. 12. Photomicrograph, showing the type of bacteria common in the insoluble residue of applelite after EDTA leaching; note dark sheath surrounding ovoid.

CONCLUSIONS

In thin section, applelite appears micritic; in actuality, it is composed of many coalescing crystal-like forms which are, in turn, composed of individual crystallites. The mineralogic makeup of applelite was shown by x-ray diffraction to be calcite. The microcrystalline nature of applelite is readily apparent in hand specimens and in thin-sections. Its microtexture and morphology are easily observed by scanning electron microscopy. The individual crystallites form scalenohedral crystal-like forms approximately 60 μm wide and 120 μm long. These crystal-like forms, in turn, coalesce into groups containing 20 to 50 crystal-like forms. These groups give the surface of applelite a subdued botryoidal appearance.

Two possible modes of origin include:

1) changes in the hydrologic regime of calcite-saturated water of the cave stream, and
2) fixation by heterotropic microflora.

The presence of algae and bacteria in insoluble residues of the applelite strongly suggests that they had at least a partial role in its genesis.

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Cave-Associated Snakes, Elaphe Guttata, In Oklahoma

C. J. McCoy [*]

Black (1974) recently summarized records of reptiles from Oklahoma caves. In his list, two records of the Great Plains Rat Snake, *Elaphe guttata emoryi*, were cited, one previously published by Webb (1970) and the other an original observation from Selman's Cave, Woodward County. Black classified all occurrences of reptiles (including *E. guttata*) in Oklahoma caves as "accidental." Contrary to Black's opinion, *E. guttata* has been reported as a regular cave inhabitant throughout the western Great Plains, commonly entering caves that harbor bat colonies, where the snakes become effective resident predators on the bats. Twente (1955) found *E. guttata* in Oklahoma and Kansas bat caves in both winter and summer and considered snake predation an important limiting factor on bat populations.

The presence of *E. guttata* and bat predation have also been documented in Kansas caves by Hibbard (1934), in Texas caves by Herreid (1961), and in Mexico by Davis (1951). My observations during 1957 and 1958 indicate that the species is also a frequent inhabitant of bat caves throughout western Oklahoma.

On 28 June 1957, a specimen of *E. guttata* was found inside the entrance of Reed Cave No. 2, Harmon County (cave locations in Glass and Ward, 1959). A second individual was discovered a few minutes later at the cave entrance. This cave system is colonized by *Myotis velifer* and *Plecotus rafinesquii*. Rat snakes were observed frequently in Griever Creek Cave, Major County, during both 1957 and 1958. The snakes usually were found climbing on the eroded walls and low ceiling of the cave, which harbors a nursery colony of *Tadarida brasiliensis*. On 4 July 1957, a rat snake was found approximately 150 feet inside the entrance of Selman's Cave, Woodward County, confirming Black's record. This specimen was forced to regurgitate an adult *T. brasiliensis*. Rat snakes were observed on various visits to Merrihew Cave (Cavern II of Twente, 1955), Woods County, in 1957. A snake taken deep in the cave on 28 August 1957 contained two adult *Tadarida*. All specimens of this snake found in the various caves were well-nourished and, apparently, thriving adults.

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The Lessons of Altamira

James J. Kilpatrick °

The essay reprinted below epitomizes the terse, sparkling prose style toward which all contributors should strive. It is at once analytical, descriptive, autobiographical, and introspective. It is sparing, but not miserly. No word, flaunted, dazzles the reader; each contributes its measured share to a panorama in the mind's eye. Every sentence is a limpid thought grasped at first reading, a coherent whole embedded in logical sequence with its neighbors. We read and, having read, understand. More than that, we empathize, for the words convey experience as well as observation. These are the goals of communication.

Here, then, is America's consummate newspaper columnist, James J. Kilpatrick, expounding on The Lessons of Altamira:

Pilgrimages come in many forms. The Catholic goes to Rome, the Muslim to Mecca, the Jew to Jerusalem. The purpose is not only to seek inspiration; the purpose is also to see with one's own eyes, and thus to confirm the transfer of dream to reality. This is about a pilgrimage to Altamira.

I could not tell you when my wife first began talking of the caves. It was a long time ago. She is an artist, a sculptor, a lover of anthropology. Whenever the talk turned to Europe, she would dream anew: Maybe, this time, Altamira. But Altamira is up on the northern coast of Spain, and unless you are beach people, attracted by the lures of Biarritz or San Sebastian, you have to work at getting there. This time we got there.

And it was work. If the planes are not flying from Madrid, you drive north to Burgos, across some of the emptiest land in Europe. At Burgos you leave the main road and cross a range of mountains en route to Santander. By night, in rain and fog, it is heart-in-the-mouth all the way. A little before midnight you arrive at a dimly lit inn at the end of a narrow, crooked street in Santillana. In the morning the rain still is falling—great gray sheets of rain—and even the most determined pilgrim wonders if the trip is worth it.

It is worth it, not merely for the artist or archeologist, but for every man and woman who give even passing thought to the nature of man and to man's survival. In Dante's vision, the gates of hell bore a warning: All hope abandon, ye who enter here. The keepers of the caves of Altamira could post a better sign at the entrance: Here all hope regain.

The story goes back to 1879, when Marcelino Sanz de Sautola returned to Santillana to explore a cave he had heard about. Sautola was only 28. He was not professionally trained in the disciplines of science, but paleontology was his passion. On this trip his nine-year-old daughter Maria was with him. The little girl scrambled ahead of him into the cave, holding her carbide lantern. Suddenly she cried out, "Toros! Toros!" On the ceiling of the cave were the paintings of bison. The paintings had been there, we now know, for 15,000 years.

The Spanish government has carved out discreet steps and walkways for the visitor, and has provided subtly dramatic lighting, but otherwise the caves are just as Sautola found them. The paintings are not stick art. There is nothing crude about them. The bison stand as bison do—stiff-legged, stolid, brute-passive—and here they come alive. In other caves of the region one finds the same confident, brilliant execution of color and design. Fifteen thousand years ago, an artist passed this way.

Silent in the shadows, we seek vainly to summon the human beings who lived here. Who were these cave dwellers of Altamira? How could they have survived the cold, the wet, the incessant perils of existence? Here in this dark cavern they loved, gave birth, suckled young; here the exhausted hunters dragged their quarry. All that mattered, one might suppose, was sheer survival.

But that was not all that mattered. In the midst of this prehistoric community there appeared the artist, the shaggy Michelangelo who squatted on his haunches, squinted through the smoke of a sputtering torch, and decorated the ceiling with works that endure. We reach out and touch them with our hands.

This is a sermon in stone. The lessons of Altamira are as plain as the dark eyes of the bison: Man was, and is, and will be. The creative spark cannot be extinguished. Thirteen thousand years before Christ the human spirit rose from this rubbled floor and brought beauty to a ceiling. It was a perilous time. So, too, is ours today a perilous time. But the pilgrim who goes to Altamira comes from the cave with this serene conviction: We of the 20th century are only prehistory, too; and whatever devastation we barbarians impose upon our planet, the spark will not go out.

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