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Uranium series dating of stalagmites from Blanchard Springs Caverns, U.S.A.

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Abstract—Because stalagmites are enriched in ^{234}U beyond the equilibrium value at the time of deposition, they are potentially datable by measuring their progress toward equilibrium. Procedures for uranium–thorium and uranium disequilibrium dating of speleothems were developed, making use of alpha spectrometry for thorium determinations and mass spectrometry for uranium determinations. The stalagmites tested were generally beyond the age range of the U–Th age dating method, and, as a result, $^{234}U/^{238}U$ ratios provided the most useful dating technique. The estimated age range for a stalagmite from Blanchard Springs is 135,000 to 785,000 years BP with an interval of slow or suspended growth from about 320,000 to 570,000 years BP.

INTRODUCTION

THE SUBJECT of cave chronology is growing in importance. Knowledge of cave growth rates will further the understanding of development in modern and ancient karst areas and also contribute to the potential use of speleothem as an element in paleoclimate research (e.g. HENDY and WILSON, 1968; DUPLESSY *et al.*, 1970). Because of the limited range of radiocarbon dates, Th and U dates are developed here.

FORNANCA-RINALDI (1968) demonstrated the potential of the $^{230}Th/^{238}U$ ratio in speleothem dating. Shortly thereafter NGUYEN and LALOU (1969) investigated methods of uranium series dating of stalagmites in Southern France. Their conclusions were based on data from a seemingly typical, but short-lived stalagmite, from which the possibility of uranium disequilibrium dating could not be realized.

P. THOMPSON (1970, 1971) developed a paleotemperature profile using speleothems dated by $^{230}Th/^{234}U$ ratios. His work on uranium disequilibrium dating was inconclusive because there was a short active time span for most of his samples (various intervals from 0 to 140,000 years BP) and the older sample material was found in a dry portion of the cave where drip water was not available. More recently P. THOMPSON *et al.* (1975) have investigated $^{234}U/^{238}U$ ratios in West Virginia caves.

In sum the few analyses by previous researches indicate that uranium disequilibrium in stalagmites does not yield systematic ages; however, their observations have been based on relatively young, short-lived speleothems in which short-term variations may have introduced large errors into their age data. In a small speleothem that has developed continuously over a period of five or six hundred thousand years, analysis of 1 or 2 in. segments of its length may include numerous fluctuations of the initial uranium isotope ratio. Thus, the age of each segment will be determined from the average of several fluctuations, and, for this reason, older stalagmites that develop over long periods of time may give systematic and realistic age data when younger, short-lived but faster growing stalagmites yield poor results.

Uranium chemistry in speleothems

Uranium in speleothems is derived from the limestone above the cave. Because U-carbonates are very soluble in slightly acidic water the uranium is leached from the limestone and carried in solution by downward percolating rain water. Thorium has a tendency to form insoluble compounds and has a high affinity for clay mineral surfaces. As a result, it is generally not carried in solution, but, if so, it is carried on clay particles suspended in the water (BARKER and SCOTT, 1958).

Uranium isotopes are fractionated in the solution process, and ^{234}U is preferentially removed from the weathered limestone. As a result the $^{234}U/^{238}U$ activity ratio of the water becomes greater than one (CHERDYNTSEV *et al.*, 1955; THURBER, 1962). The ^{234}U enrichment is attributed to: (1) increased mobility of radiogenic daughter products caused by alpha recoil-induced displacement of the residual nucleus within the crystal lattice (THURBER, 1963; KU, 1965) and (2) change of oxidation state of uranium during radioactive decay. The oxidized uranium is then preferentially leached because of the strong complexes that are formed between the carbonate and uranyl ions (CHERDYNTSEV *et al.*, 1955). Exceptions to this high ratio have been noted in aquifers of North Florida (KAUFMAN *et al.*, 1969).

Two methods of dating are potentially available. The U–Th method (BARNES *et al.*, 1956), where the growth of ^{230}Th from alpha decay of ^{234}U is used to determine ages up to 350,000 years BP, and the uranium disequilibrium method (CHERDYNTSEV *et al.*, 1955; THURBER, 1962) where the age is determined from the difference between the assumed initial $^{234}U/^{238}U$ ratio and the present-day ratio, giving ages back to 1·5 million years BP. Speleothems are datable by these methods only if certain criteria are met.

(1) For the U–Th method to succeed there must be no ^{230}Th present when the system closed. Samples free of detrital thorium are generally obtainable by selecting stalagmites with white or clear calcite that are free of detrital minerals. Systematic variation of uranium and thorium isotope ratios in closely spaced analyses along the length of a stalagmite (showing no excess ^{230}Th beyond the equilibrium value) is partial evidence that the system has remained closed.

(2) The initial uranium ratio for each sample must be known in order to use the $^{234}U/^{238}U$ method. Although it is impossible to determine the uranium ratio in the drip water during past times, it may be assumed that the uranium ratio during deposition is approximately the same as the present-day ratio. This is best estimated from repeated analyses of drip water in the immediate vicinity of the stalagmite being dated. This is a weak point in the uranium disequilibrium dating technique.

(3) The sample system must have remained closed since deposition. Stalagmites vary in their ability to meet this criterion. Selection of samples with minimum visible porosity and generally solid interiors minimizes but does not exclude the possibility of contamination.

SAMPLE SELECTION AND PREPARATION

Because stalagmites grow in vertical increments with very little lateral accretion, they are more suitable for age analysis than stalactites which grow from the ceiling in a series of concentric cones. The study specimens were collected at scattered locations within Blanchard Springs Cavern, Stone County, Arkansas, in the foothills of the Ozark Mountains (Fig. 1). X-Ray analysis revealed nothing but calcite. After being sectioned longitudinally the three that showed the least porosity (and no visible signs of recrystallization) were selected for analysis and numbered BS1, BS2 and BS3. These stalagmites were further prepared by cutting them into segments 5 cm long and trimming off the outside growth layers leaving the remaining inner portions for analysis. The trimmed samples weighed 100–200 g each. These samples were crushed to ± 5 mm fragments before analysis (THOMPSON, 1973).

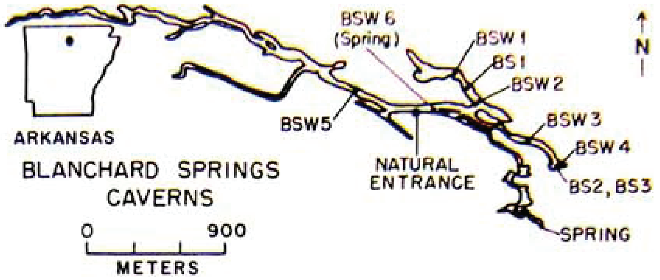


Fig. 1. Map of Blanchard Springs Caverns. The locations of stalagmites BS1, 2, and 3 and water samples BSW-1 to 6 are shown indicating their proximity to each other and to the natural entrance of the cave.

ANALYTICAL PROCEDURES

The ^{230}Th activity of the calcium carbonate was determined by alpha spectrometry, whereas uranium isotope ratios and quantitative uranium determinations of both speleothems and ambient cave water were made using isotope dilution mass spectrometry techniques.

Water samples were spiked with ^{233}U and evaporated to dryness with concentrated HNO_3 and perchloric acid to destroy any organic material present. Uranium was then extracted with tri-butyl phosphate (TBP) (THOMPSON *et al.*, 1973).

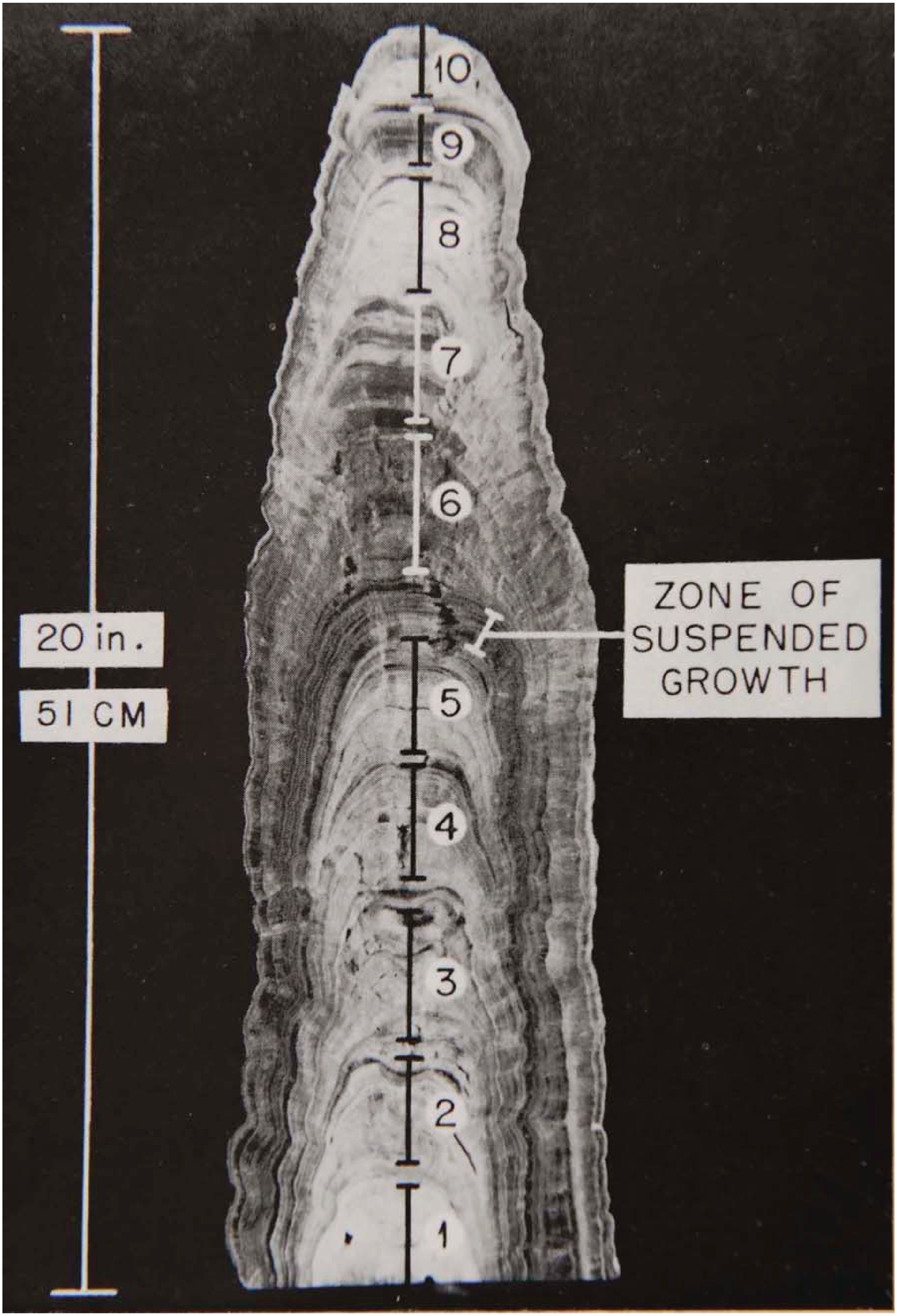
Mass spectrometry

Isotopic uranium determinations were made on a two-stage mass spectrometer of 12 in. radius and 90° magnetic deflection. After extraction, uranium samples in the form of $UO_2(NO_3)_2$ were redissolved and evaporated on to canoe-shaped pre-cleaned rhenium filaments in 0·05 N HNO_3. The samples (10–100 ng U) were run at approximately 1800°C at a pressure of 1×10^{-8} torr. An NBS natural uranium standard was run routinely with each group of samples to check instrument performance.

Using mass spectrometry, uranium determinations can be easily made on small (1 or 2 g) samples containing as little as 0·1–0·5 ppm uranium. The accuracy of the $^{234}U/^{238}U$ ratio determinations by this technique is ± 3 per cent.

Alpha spectrometry

After deposition on to a stainless steel planchette, thorium samples were counted in a methane gas flow proportional counter of 2π geometry to determine the total alpha radiation. This measurement was made within minutes


10
9
8
7
6
5
4
3
2
1
20 in.
51 CM
ZONE OF SUSPENDED GROWTH

after the thorium was deposited on the planchette to minimize interference in the count rate by growth of daughters from the ^{228}Th spike. The total alpha emission was used for computing the per cent recovery of ^{230}Th. Ortec detectors of 1 cm active surface diameter coupled with a 400 channel pulse-height analyzer were used to measure the alpha emission. The energy resolution of this equipment was 45 keV at the 5 MeV level. Background counts were low (1–2 counts/hr/400 channels), and background corrections were not applied. All samples were counted to at least 1000 counts. The analytical error of the thorium determinations was estimated to be within 5 per cent.

CONFIDENCE LIMITS

The confidence limits of the uranium ratio ages are difficult to estimate, but are believed to be quite large. If the initial ratio of deposition in stalagmite BS2 varied as much as 10 per cent of the assumed value, 1·54 (approximately the range of variation observed in the Blanchard Springs cave water analyses), variation in age could be up to ±100,000 years. Considering analytical uncertainty and possible loss of ^{234}U due to alpha recoil displacement, the confidence limits become slightly larger, perhaps ±120,000 years in older material where alpha recoil is more significant. Uncertainty of this magnitude precludes meaningful dating of many young stalagmites, but for older deposits, from 800,000 to 1,500,000 years old, the uncertainty reduces to the order of 10 per cent of the age.

If the stalagmite system was open during its history, the ^{234}U/^{238}U and ^{230}Th/^{234}U age estimates may be erroneous. However, the data may be considered more reliable if certain conditions are met. If, in a young stalagmite, the ^{234}U/^{238}U and ^{230}Th/^{234}U ages agree along the entire length of the stalagmite, then the ages may be reliable. (By 'reliable age data', it is meant that the system has been closed and the confidence limits are equal to the analytical uncertainty.) If 2 or more stalagmites from a single cave are dated by uranium isotopes (preferably using initial ^{234}U/^{238}U ratios close to the sample) and they show good agreement in the age of obvious correlative features such as major periods of suspended growth or dissolution, then the ages are probably reliable. If a young stalamite is dated along its entire length by closely spaced analyses and shows systematic variation that conforms well to the stalagmite morphology, then the age data is probably reliable.

Table 1. Analytical data from water samples

Sample	U-Content µg/l	$\frac{^{234}U}{^{238}U}$	Notes
1	0.119	1.40	Water streaming from cave roof: sample contained large sediment fraction.
2	0.130	1.59	Fast drip.
3			Analysis rejected due to artificial contamination
4	1.200	1.54	Slow drip (less than 1 drop/5 min) adjacent to BS2 and BS3.
5	1.142	1.57	Slow drip (about 1/min).
6.	0.174	1.68	Sample from spring water inside cave.

DISCUSSIONS AND RESULTS

Initial uranium ratios

To use the uranium disequilibrium method, it is absolutely essential to have some knowledge of the original isotopic ratios in the water that forms the stalagmite. Since there is no way these past ratios can be measured, they must be estimated from ratios in the modern waters (Table 1). This approach is subject to error (P. THOMPSON *et al.*, 1975); however, this can be partially accommodated if enough data are obtained.

Five usable water samples were collected and analyzed quantitatively and isotopically for uranium (Fig. 1). One water sample, BSW4, was collected within a few meters of stalagmites BS2 and BS3, but no water was available within 150 meters of BS1. The ^{234}U/^{238}U ratios and uranium concentrations of the drip water vary from place to place with a cave (Table 1). This may explain the high ^{234}U/^{238}U ratios of stalagmite BS1 where the average of the whole stalagmite was higher than the isotope ratio in any of the water samples analyzed. Furthermore, there is temporal variation in uranium ratios (P. THOMPSON *et al.*, 1975). Analyses of the drip water over a period of months or years is necessary to determine the nature of these short-term changes.

Because of this place to place variability, it is necessary to use the uranium ratio of drip water close to the stalagmite of interest. Where this is lacking, an average value of the cave water is the only alternative, however, the range of confidence will be the range of the values of the initial ratios. This average can be calculated from the data of Table 1. Fortunately the average obtained (1·556) and the value in the water sample close to stalagmites BS2 and BS3 are very close (1·54 in BSW4). It may be seen in Table 1 that the water samples furthest from this mean were obtained in rapidly flowing situations. In sharp contrast the range in uranium ratios in water falling at a drip rate is remarkably small. It is tempting to speculate that the ^{234}U/^{238}U ratio is relatively constant for dripping, stalagmite-forming, water. If future work verifies this then a major drawback to the use of uranium ratios will be moderated.

Stalagmite BS2

In retrospect this sample gave the most satisfactory results and is discussed first and in detail. The most distinct physical features of this sample were (Fig. 2): (1) the numerous growth increments, visible due to color variations (amber, clear, white), (2) the lack of single crystal cleavage, instead a tendency to break apart between the concentric growth layers, (3) a zone pended growth. The data indicate that the stalagmite developed over a long period of time; perhaps 650,000 years.

When the ^{230}Th/^{234}U ratios of stalagmite BS2 are plotted against their height above the base of the stalagmite, a modified ^{230}Th growth curve is roughly defined (data curve Fig. 4). For comparison two theoretical growth curves for ^{230}Th are included. Curve A is for a growth interval of 0–800,000 years BP, whereas curve B is for an interval of 0–400,000 years. Increments 9 and 10 (at the top of the stalagmite) lie within one confidence interval of curve A and indicate some correlation of the U–Th data with the U isotopic ages. Increment 1 (at the base) lies within one confidence interval of isotopic equilibrium indicating that point 1 could be 400,000 years or older. The remainder of the data points deviate considerably from both A and B curves indicating that there has been migration of uranium and/or thorium.

Because no ^{232}Th was visible in any of the alpha spectra, we assume that little or no detrital ^{230}Th was incorporated into the stalagmite during deposition. Further support for this belief is the near-absence of silicon in the samples which were analyzed for their trace element content. In no sample did silicon exceed 20 ppm indicating a lack of detrital minerals and probable lack of detrital thorium. No insoluble residue was observed in any sample reported here. Therefore, the possibility of detrital ^{230}Th contamination is not considered as an explanation for the excess ^{230}Th observed in increment 6 nor the mismatch of the U–Th and U/U dates of BS2.

A possible explanation of this age mismatch is based on mobilization of both uranium and thorium. Before the uranium isotopes reach equilibrium the most frequent decay reaction in the stalagmite is the transformation of ^{234}U to ^{230}Th. Therefore all the thorium in the stalagmite is authigenic, and has been displaced from its lattice position by alpha recoil. This makes it subject to subsequent leaching by percolating water, the same mechanism used to explain ^{234}U/^{238}U disequilibrium in water (THURBER, 1963; KU, 1965). Because of the low concentrations of ^{230}Th in stalagmites (typically less than 2 parts per 10^{-9}), loss of very small amounts due to recoil effects may significantly lower the ^{230}Th/^{234}U ratio, making the ages calculated younger than the actual age.

Some ^{234}U is also subject to loss due to displacement by recoil energy. This will be only a small fraction initially, but will increase with time. After 500,000 years nearly 75 per cent of the ^{234}U in the stalagmite will be authigenic and may occupy radiation damaged positions within the lattice. After 800,000 years 89 per cent of the ^{234}U will be authigenic. As a result, by 800,000 years, the rate of ^{234}U loss due to recoil effects may be nearly the same as the rate of ^{230}Th loss. As the proportion of authigenic ^{234}U approaches 100 per cent, ^{234}U and ^{230}Th may be lost from the stalagmite in equal proportions and will cause the ^{230}Th/^{234}U ratio in the stalagmite to approach equilibrium.

If the proposed mechanism has produced the observed variation in the U–Th data, it should also effect the ^{234}U/^{238}U ratios in the lower part of the stalagmite. These effects cannot be distinctly observed in the uranium isotope data, but the discontinuity in the decay curve attributed to suspension of growth (Fig. 3), may be partially due to lowering of the ^{234}U/^{238}U ratio by recoil effects.

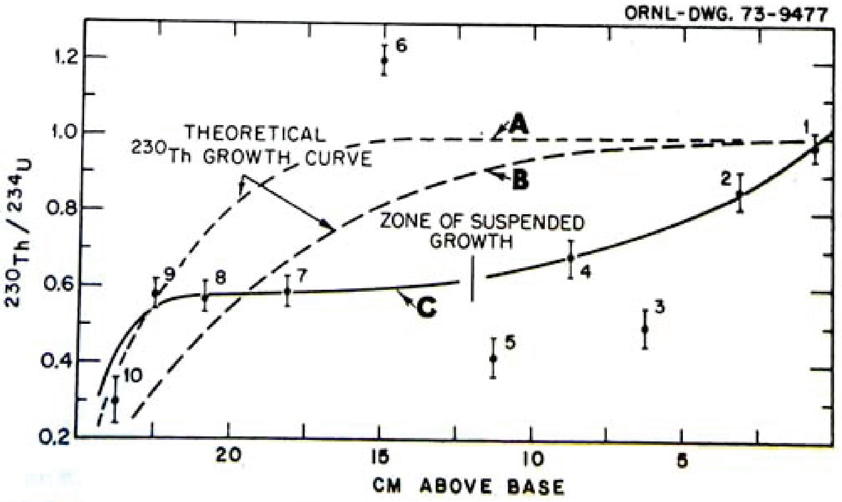


Fig. 4. Plot of thorium–uranium data for stalagmite BS2. Curves A and B are theoretical curves for the change in the ^{230}Th/^{234}U ratio for the time intervals 800,000 and 400,000 years, respectively. Curve C is an approximate fit to the observed data.

If the age of BS2 is inferred from the U–Th data it may be about 400,000 years old at the base and have grown increasingly faster upwards through the central portion, and then slower again from increment 9 to increment 10 at the top. Such a variable growth rate has been inferred by NGUYEN and LALOU (1969), LABEYRIE *et al.* (1969) and P. THOMPSON (1970, 1971). However, in this case the relative growth rates suggested by the U–Th data disagree with the growth history indicated by the morphology of the sample. The U–Th age data show a 182,000 year span of time from increment 1 to 2 at the base of the stalagmite; however, no despositional break is indicated in the morphology. In addition, the data suggest that growth has been relatively rapid from increment 4 to increment 9 and does not allow time for the depositional hiatus clearly indicated by the presence of solution cavities and brown ferruginous layers between increments 5 and 6. This mismatch between the U–Th growth data and the apparent morphological growth history is an important point and is evidence that the uranium–thorium age estimates may be incorrect.

In contrast, the uranium disequilibrium dates conform well with the stalagmite morphology. They indicate relatively steady, slow growth (about 1 mm/1000 years or 1 in. per 25,000 years), both above and below the dark ferruginous layer. An interval of about 125,000 years is indicated in the zone between increments 5 and 6 where ferruginous layers and solution cavities have developed.

It was noted also that the $^{234}U/^{238}U$ ratio of the water sample BSW4, taken adjacent to stalagmites BS2 and BS3, was nearly the same as the average for the cave (Table 3). In fact, all the water samples that were falling at a drip rate have remarkably similar uranium ratios. It is possible that this slow flow averages out uranium ratio fluctuations. If all the samples had been collected from slowly dripping sources the variation in uranium ratios might have been much smaller. In any case, it seems logical that a water sample collected over a long period of time would provide a better representative value of the depositional ratio in a particular area of the cave than a sample collected over a period of a few minutes or hours.

Stalagmite BS1

This sample appeared to have developed in 4 major increments with short periods of suspended growth between each.

The uranium isotope ratio of BS1 is high and varies somewhat irregularly (Table 2). The lowest ratio, $1{\cdot}56 \pm 0{\cdot}03$, is at the base of the sample as expected. However, the relative youth of this sample and lack of a nearby water sample to give the initial uranium ratio precludes a viable age estimate by the uranium ratio method. In this case $^{230}Th/^{234}U$ ratios probably give better age estimates.

The uranium concentration is very low, about 0·025 ppm and, because the thorium concentration is correspondingly low, only one thorium determination was made. The $^{230}Th/^{234}U$ ratio obtained, $0{\cdot}60 \pm 0{\cdot}04$, indicates the age at the base sample to be approximately 97,000 ± 6000 years BP (Table 2). Its average rate of growth based on the U–Th data is about 10 mm/1000 years, ten times that of BS2.

Stalagmite BS3

The stalagmite was sampled at 4 places along its length. Analyses showed that the $^{234}U/^{238}U$ ratio of this stalagmite is $1{\cdot}08 \pm 0{\cdot}03$ with no significant variation along its length. The $^{230}Th/^{234}U$ ratio was in excess of equilibrium for the whole stalagmite (Table 2). No ages could be computed from the $^{230}Th/^{234}U$ ratios but the uranium isotope data indicated that the stalagmite may have developed within a short time interval about 700,000 years ago.

The absence of ^{232}Th is evidence that no detrital thorium was incorporated into the stalagmite to provide the excess ^{230}Th observed. It must be assumed therefore, that in both stalagmite BS3 and interval 6 of BS2, uranium was lost essentially without thorium. Removal with little or no uranium fractionation is suggested because of the $^{234}U/^{238}U$ ratios in all the samples remained greater than one, and, in the case of interval 6 of BS2, the $^{234}U/^{238}U$ ratio conforms very well to the decay curve.

All of the samples deficient in uranium contained numerous cavities that appeared primary in origin, i.e. formed in the stalagmite during deposition. These cavities may have been instrumental in causing uranium loss by permitting water to percolate through the stalagmite.

SUMMARY AND CONCLUSIONS

Age estimates based on $^{230}Th/^{234}U$ and $^{234}U/^{238}U$ ratios do not agree. Which ratio yields the most nearly correct estimates cannot be conclusively demonstrated from the data thus far gathered; however, the data are sufficient to indicate that the $^{234}U/^{238}U$ estimates are to be preferred. The major support for this conclusion is the good match between $^{234}U/^{238}U$ dates and physical changes along the axis of stalagmite BS2. Further support is the systematic decrease in isotopic ratio along the axis of BS2 and the equality of the growth rates both above and below the ferruginous zone. Although stalagmites are known to have quite variable short-term growth rates, it seems reasonable to calculate an average rate when the time involved is in the hundreds of thousands of years range. The fact that these average rates of growth agree quite well both above and below the ferruginous zone of BS2 is support for the reliability of the uranium ratio dates.

The water samples from widespread locations in the cave showed variable uranium isotope ratios. This is attributed to low permeability of the limestone and the fact that stalagmite-forming waters enter the cave moving downward along essentially vertical joints and do not mix before entering the cave. For this reason it is essential that uranium ratio age estimates be based on water collected close to the analyzed stalagmite. If possible, the water samples should be collected over a period of months, or, even years to reduce the potential bias of short-term isotopic variations.

The small samples (in the order of 1 g) useable in mass spectrometry makes this the preferred analytical method. These small samples permit much more detailed dating of a stalagmite. This may lead to insights about rates of growth and detailed variations in isotopic ratios.

The ^{230}Th/^{234}U ratios of stalagmites BS2 and BS3 indicated that these stalagmites systems have been open to migration of uranium, and/or thorium. The excess thorium along the entire length of stalagmite BS3 and in section 6 of BS2 indicates loss of ^{234}U possibly due to alpha recoil effects or by leaching of uranium without significant isotopic fractionation. The latter alternative seems more likely because: (1) the excess thorium ratios are associated with samples that contained primary cavities which would permit water to percolate through the stalagmite, (2) none of the ^{234}U/^{238}U ratios were less than one, and the ^{234}U/^{238}U ratio of section 6 of BS2 fits well on the decay curve in Fig. 3. In stalagmite BS2 migration of both uranium and thorium is believed to have taken place. This is indicated by the fact that ^{230}Th/^{234}U ratios are spuriously low in the central and lower portions of the stalagmite, this is attributable either to secondary enrichment in ^{234}U, or loss of ^{230}Th. Secondary uranium enrichment is not favored because this would act to increase the ^{234}U/^{238}U ratios of the stalagmite, giving a distorted ^{234}U decay curve. This effect was not observed; if anything the ratios were lower than expected.

A model involving both ^{234}U and ^{230}Th loss in response to alpha recoil effects is proposed where ^{230}Th is initially produced at a faster rate than it is lost (top of stalagmite). As ^{230}Th production slows down the rate of recoil loss more or less equals the ^{230}Th production (older central portion), thus causing the ^{230}Th/^{234}U ratios to remain less than 1 for a long period of time. In the oldest basal portion of the stalagmite there is increased loss of ^{234}U due to recoil effects causing the ^{230}Th/^{234}U ratio to increase and approach equilibrium. This conclusion is based on the observation that the ^{230}Th/^{234}U ratios plotted against their height in the stalagmite, depict a highly modified ^{230}Th growth curve, whose shape is best explained in terms of ^{230}Th and ^{234}U loss.

Confidence limits for these ages are very large because they must be based on speculation about the possible range of initial ratios variation and loss of ^{234}U by recoil effects, in addition to analytical uncertainty. An estimated ±120,000 years is suggested for the confidence limits of the stalagmite BS2 age data, but these limits may be greatly reduced if additional correlative age data can be obtained by dating nearby stalagmites that display the same episodic sequence of growth and dormancy in their morphology.

In sum this study shows that some stalagmites are open to migration of ^{230}Th and ^{234}U, and random or isolated stalagmite dates should be regarded with caution. Morphology and age of a stalagmite seems to have profound effects on the closure of the system and greatly complicates interpretation of the age data. Reliable U–Th ages have been obtained on young stalagmites (P. THOMPSON, 1970, 1971) but there is evidence from stalagmite BS2 that this system may not be reliable after 150,000 years. The uranium disequilibrium dating method has a severe limitation in that the initial isotope ratio is not known, but is worth further investigation because this technique seems to give realistic age data for some slowly deposited stalagmites that are well beyond the range of other dating methods.

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