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GROWTH MECHANISMS OF RECENT SPELEOTHEMS FROM CASTLEGUARD CAVE, COLUMBIA ICEFIELDS, ALBERTA, CANADA, INFERRED FROM A COMPARISON OF URANIUM-SERIES AND CARBON-14 AGE DATA

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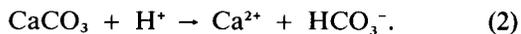
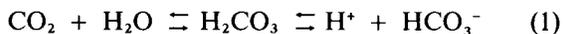
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ABSTRACT

Uranium-series and conventional ^{14}C ages have been determined for six recent soda-straw speleothems from different locations in Castleguard Cave, Alberta. Allowing for detrital thorium contamination of some samples, ^{14}C ages are consistently greater than $^{230}\text{Th}/^{234}\text{U}$ ages by about 8000 to 10,000 yr. Analysis of the HCO_3^- content of a modern calcite-depositing, seepage water gave a ^{14}C age of 4100 yr. These results, and values of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of the speleothem calcite, indicate that production of "dead" CO_2 by oxidation of carbonaceous deposits in rocks overlying the cave may be occurring, thus accounting for the growth of speleothems. Alternatively, isotopic exchange between seepage water and rock carbon may also account for the low ^{14}C activities in each speleothem. Various other mechanisms to explain this anomaly are considered.

INTRODUCTION

Limestone dissolution by groundwater containing dissolved carbon dioxide is summarized by the following equations:



Dissolution continues until the groundwater is saturated with calcium carbonate. On entering a cave, the reverse process may occur by equilibration with the cave atmosphere, causing deposition of calcite or aragonite in the form of speleothems:



In temperate and tropical climates this process is generally caused by a combination of loss of CO_2 from groundwater seepage entering a cave and evaporation of that water. The former mechanism predominates in passages that have a high relative humidity; both processes occur together in caves of low humidity. In both situations, the seepage water is almost always enriched in CO_2 (as HCO_3^- ion) relative to standard atmospheric levels, due to additional gas uptake from decaying organic matter, and plant root and bacterial respiration in soils above the cave. It is this extra source of CO_2 which provides the driving force for more limestone dissolution and consequent abundant speleothem deposition in caves in warm areas.

In contrast, caves in cold climates generally have little vegetation at the surface above them and, as is the case

at Castleguard Cave, may be overlain by a thick ice cover for part of their length (Figure 1). The absence of any additional soil CO_2 suggests that speleothems are unlikely to be found in Castleguard Cave under the ice cover, but as exploration has shown (Harmon et al., 1983, this symposium), this is not so. Recent soda-straws and stalagmites are found throughout the Headward Complex, which lies at shallow depth beneath the central Columbia Icefield. Their presence was explained initially as an effect of evaporation. From measurements of temperature and relative humidity, however, Atkinson (1979) suggested that the amount of evaporation occurring was insufficient to account for the size of speleothems. He also observed that the concentration of HCO_3^- in speleothem waters was similar to that which can be supported by standard atmospheric CO_2 alone (Atkinson, 1979). This apparently ruled out the possibility of a CO_2 -degassing mechanism for the speleothem deposition and, therefore, any additional CO_2 sources such as overlying vegetation. Instead, Atkinson (1983, this symposium) has proposed precipitation of calcite by dissolution of gypsum and dolomite in the rocks overlying the cave.

If the seepage water from which calcite precipitation occurs is derived from melting ice and firn, then it is likely that this water is depleted in CO_2 relative to atmospheric levels, as shown by measurements of PCO_2 in glacier and snowmelt waters in the area (Ford, 1971). Uptake of some CO_2 to attain near-atmospheric levels is therefore indicated. Two possible sources are proposed here: (1) the decay of organic substances under the ice, formed during earlier Holocene times when the ice cover did not extend as far over the cave as at present; (2) oxidation of organics and hydrocarbons present as discrete horizons in the bedrock (e.g., black shales).

One possible method of resolving this question of the source of CO_2 for speleothem formation is to examine the isotopic character of these deposits, in particular, the carbon isotopic content.

Both radiocarbon and uranium-series ages may be determined for a speleothem (Hendy, 1970; Thompson et al., 1974). In pure, unaltered calcite speleothems, U-series ages are a best estimate of the true age because ^{14}C ages are influenced by dilution with "dead" carbon obtained from the rock. The difference between ^{14}C and

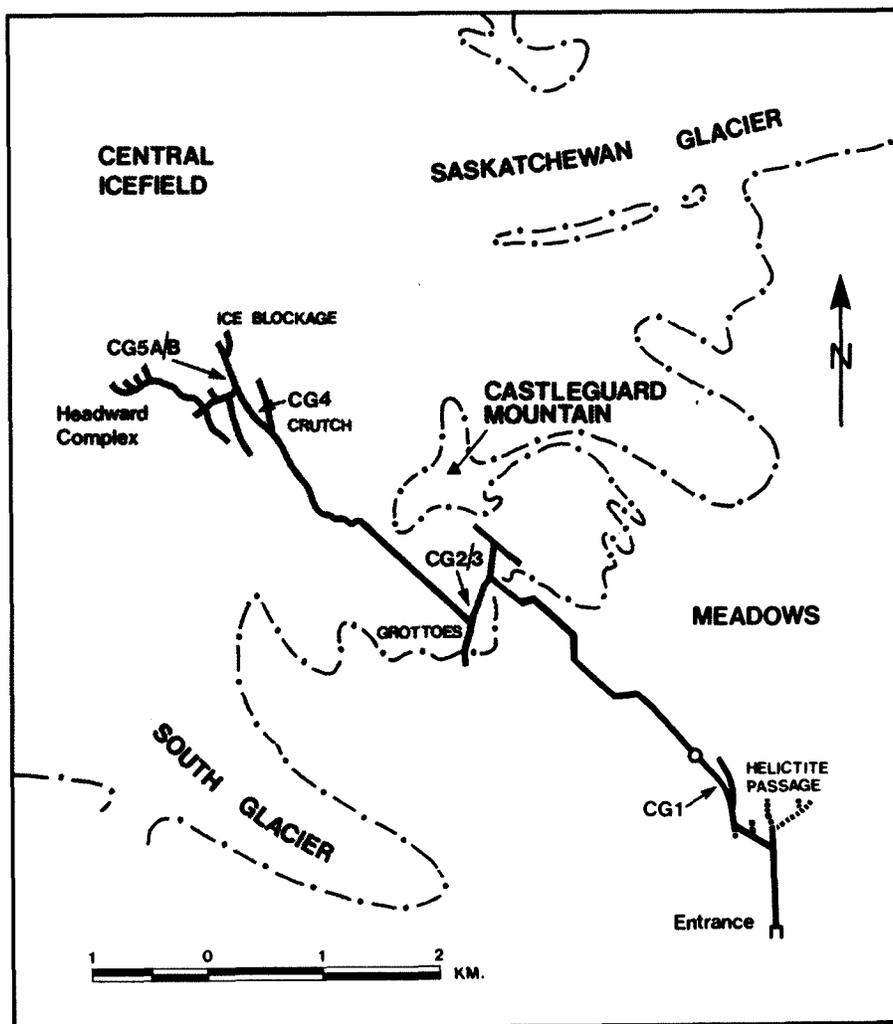


FIGURE 1. Plan of Castleguard Cave, showing the extent of modern glacier ice cover and the locations of recent speleothem samples discussed in this paper.

U-series ages for a given deposit will give an indication of the source of carbon for that deposit. Similarly, the ^{13}C content may indicate whether carbon in solution is derived from organic matter, bedrock, the atmosphere, or some combination of these.

The relationship between carbon sources, dissolution mechanisms, and carbon isotopic content of limestone groundwaters has been considered in detail by several workers, including Hendy (1971), Deines et al. (1974), and Wigley et al. (1978). These authors have used the ^{13}C content of groundwater to indicate whether rock dissolution is occurring under open or closed system conditions (i.e., when groundwater is open to, or isolated from, a CO_2 source during dissolution). These problems also arise in application of ^{14}C dating of groundwater and speleothems (Hendy, 1970; Wigley, 1975). The main question concerns the value of the correction factor, Q (the fraction of modern carbon in the deposit), in the age equation:

$$A = QA_0e^{-\lambda t} \quad (4)$$

where A and A_0 are the measured and modern ^{14}C activities, respectively, t is the age, and λ is the decay constant of ^{14}C . Generally Q lies between 0.5 (closed system) and 1.0 (open system), but as Wigley (1975, 1976) has shown, Q may not always be estimated precisely from the ^{13}C content of groundwater CO_2 sources. It may also be influenced by pH changes and incongruent dissolution of carbonate minerals (i.e., a continuous process of dissolution and precipitation, in which a small cumulative isotopic fractionation occurs).

In this paper we attempt to show how ^{14}C and U-series dating, coupled with stable isotopic data, can be used to distinguish between the various sources of carbon in recent soda-straw speleothems and seepage water entering Castleguard Cave. All samples were collected over a five-day period in April 1980.

ANALYTICAL METHODS

Samples of broken soda-straw stalactites were collected from the four different locations in Castleguard Cave shown in Figure 1. Each sample was crushed and a small aliquot dated by the $^{230}\text{Th}/^{234}\text{U}$ method according to the procedure described by Gascoyne (1977). Approximately 30 g of each was then dated by the ^{14}C method. These samples were ultrasonically cleaned in distilled water, dried at 90°C , and reacted with HCl to yield CO_2 . The CO_2 was next reacted with Li to form Li_2C_2 and hydrolyzed to yield acetylene gas. The acetylene was cleaned and polymerized to benzene and counted for ^{14}C activity in a modified liquid scintillation counter. Details of the ^{14}C laboratory are given in Nelson and Hobson (1982).

One site was found in the Grottoes (Figure 1) where calcite deposition was occurring from a single source that was dripping rapidly enough at the end of the winter season to permit collection of sufficient HCO_3^- in a short time span. A column packed with ion exchange resin was installed on the tip of this source for 4 d to collect the HCO_3^- , using a method similar to that described by Hendy (1970). The column was prepared as an upper bed of

anion exchange resin, preconditioned with NaF, and a lower bed of cation exchange resin in the Na^+ form. Water flowed from base to top with an outer input level tube to prevent drying out of the resin beds. In this arrangement, incoming water was first decationized and then deanionized, so that HCO_3^- was trapped in the upper resin bed. During operation, care was taken to isolate the seepage water from the cave atmosphere to prevent any CO_2 exchange before the water entered the column.

In the laboratory, the anion resin was flushed with NaCl solution, and the bicarbonate/carbonate precipitated as SrCO_3 , by addition of SrCl_2 and ammonia. Because unused F^- was flushed from the column, the precipitate was contaminated with SrF_2 but this was found to cause no interference in the subsequent determination of ^{14}C and ^{13}C contents. For ^{14}C , CO_2 was generated by addition of HCl, as described above.

All soda-straw powders and the prepared SrCO_3 ($\delta^{13}\text{C}$ only) were analyzed for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ using the mass spectrometer technique described in Gascoyne (1980).

RESULTS

Sample descriptions and the uranium-series age data are listed in Table 1. Samples CG 4, 5A, and 5B display slight ^{232}Th contamination (seen as $^{230}\text{Th}/^{232}\text{Th}$ ratios less than 20) due to incorporation of detrital sediments in the calcite of the speleothem. Uranium-series ages for these deposits are likely to be slightly lower than those listed because sediments generally contribute unsupported ^{230}Th (Schwarcz, 1980). Sample CG2 is strongly contaminated with ^{232}Th ; therefore, its age is probably much less than the value of 8900 yr quoted.

In Table 2, the radiocarbon measurements are reported

in terms of absolute percent modern and as conventional ^{14}C ages, as defined by Stuiver and Polach (1977). The radiocarbon ages are in themselves not meaningful, given that the value(s) for Q in equation 4 is (are) unknown, but they serve here as a convenient means for comparison with the uranium-series measurements. The yield of CO_2 from the drip-water sample (CG 2E) was very small (ca. 0.25 g) for ^{14}C dating and consequently the uncertainty on the determined age is large.

Stable isotopic compositions of the soda-straws and the single HCO_3^- precipitate are also given in Table 2.

DISCUSSION

The age determinations summarized in Table 2 clearly show that the conventional ^{14}C age (determined from raw ^{14}C activity without correction for dilution by inactive carbon) is greater than the $^{230}\text{Th}/^{234}\text{U}$ age for all samples. Allowing for detrital Th contamination in some samples, the age difference, Δ , appears to be fairly constant throughout the cave and equal to about 8000 to 10,000 yr. This difference is much greater than might be anticipated for either open or closed system rock dissolution and indicates that, at the time of formation, the fraction of modern carbon in the deposit, Q , must have been between 0.3 and 0.35. These results support the contention that part of the source of CO_2 in the groundwater was derived from oxidation of inactive carbonaceous substances in the rock overlying the cave. In fact, it is possible that *all* of the CO_2 comes from inactive carbon sources because some active CO_2 is likely to be incorporated by exchange with cave air during calcite precipitation, and this may entirely account for the observed activity.

Conversely, these results can be explained in terms of incongruent dissolution of bedrock, whereby ^{14}C is continuously lost to a calcite precipitate and is replaced by dead carbon from the bedrock, before reaching the cave. The constancy of Δ for all sites, however, argues against this mechanism, because the amounts of incongruent dissolution are likely to vary from one depositional site to the next. The fact that most $\delta^{13}\text{C}$ values for calcites are close to equilibrium with bedrock (ca. 0 to 2‰) does not negate this argument, because ^{14}C depletion from solution is essentially an unidirectional process and continues until all ^{14}C is removed.

The single ^{14}C analysis of seepage HCO_3^- ion appears to contradict the possibility of a totally dead carbon source for the calcite speleothems because Δ is only 4100 yr. It is difficult to discount this result as an effect of contamination because, if anything, contamination should be from dead carbon sources (e.g., ion exchange resins) which would *increase* Δ . Although reasonable pre-

TABLE 1
Sample descriptions, radiometric data, and $^{230}\text{Th}/^{234}\text{U}$ ages of recent speleothems from Castleguard Cave

Sample	Location	U (ppm)	Th	$^{234}\text{U}/^{238}\text{U}$	$^{230}\text{Th}/^{232}\text{Th}$	$^{230}\text{Th}/^{234}\text{U}$	$^{230}\text{Th}/^{234}\text{U}$ Age $\pm 1\sigma$ (yr)
CG 1	Straws, Helictite Passage	3.0	0.0	1.434 ± 0.025	>1000	0.024 ± 0.002	2600 ± 200
CG 2	Active stalactite piece, Grottoes	0.4	0.14	2.757 ± 0.342	1.7	0.079 ± 0.055	8900^{+6500}_{-6200}
CG 3	Straws, Grottoes	11.4	0.04	1.092 ± 0.011	69	0.073 ± 0.002	8300 ± 300
CG 4	Straws, Crutch Passage	3.7	0.12	1.167 ± 0.021	11	0.098 ± 0.006	$11,100 \pm 700$
CG 5A	Large stalactite, Ice Passage	5.5	0.07	1.072 ± 0.016	10	0.038 ± 0.002	4200 ± 200
CG 5B	Straws, Ice Passage	4.6	0.05	0.981 ± 0.016	15	0.052 ± 0.003	5800 ± 300

TABLE 2
Summary of ^{14}C age data, $^{230}\text{Th}/^{234}\text{U}$ ages, and stable isotopic analyses of speleothems from Castleguard Cave

Sample	^{14}C data		$^{230}\text{Th}/^{234}\text{U}$ age (ka)	Δ (ka) (^{14}C -Th/U)	$\delta^{13}\text{C}$ (as ‰ PDB)	$\delta^{18}\text{O}$
	pM ^a	^{14}C age (ka) ^b				
CG 1	25.8 ± 0.1	10.8 ± 0.1	2.6 ± 0.2	8.2 ± 0.2	0.0	-15.9
CG 2	22.5 ± 0.4	11.9 ± 0.2	$\leq 8.9^{+8.5}_{-8.2}$	≥ 3	+0.4	-17.2
CG 3	10.4 ± 0.4	18.1 ± 0.3	8.3 ± 0.3	9.8 ± 0.4	-0.6	-15.8
CG 4	10.3 ± 0.4	18.2 ± 0.3	$< 11.1 \pm 0.7$	> 7.1	+0.3	-16.6
CG 5A	18.3 ± 0.1	13.6 ± 0.1	$< 4.2 \pm 0.2$	> 9.4	+1.6	-18.5
CG 5B	14.4 ± 0.4	15.6 ± 0.2	$< 5.8 \pm 0.3$	> 9.8	-1.5	-18.4
CG 2E	59.5 ± 3	4.1 ± 0.4	0 ^c	4.1	-4.1	N.A.

^aAbsolute percent modern, as defined by Stuiver and Polach (1977).

^bConventional ^{14}C age, corrected to $\delta^{13}\text{C} = -25\text{‰}$, as defined by Stuiver and Polach (1977); 1 ka = 1000 yr BP.

^cAssumed age.

N.A. Not applicable.

cautions were taken to prevent CO₂ exchange with cave air, or absorption by reagents, no satisfactory blanks could be run and so the possibility of atmospheric contamination still exists. However, the low $\delta^{13}\text{C}$ value for HCO₃⁻ (-41‰) argues for minimal contamination because atmospheric CO₂ would tend to give the bicarbonate a positive $\delta^{13}\text{C}$ value; $\delta^{13}\text{C}$ of atmospheric CO₂ is -7‰ and fractionation of ¹⁸O between HCO₃⁻ and CO₂(g) is about 10‰ at the prevailing temperatures. Unfortunately, only one accessible, fast-dripping, yet depositing, site was found in the cave over the period of the field work, so no other data are available to resolve this problem.

The Δ calculated for the HCO₃⁻ sample implies Q is 0.62, indicating some open system dissolution with an active CO₂ source. This may simply be atmospheric CO₂, but because the Grottoes lie just at the edge of the permanent ice cover, a recent organic source of CO₂ is also probable. A further argument against the role of dead organic carbon sources contributing to HCO₃⁻ in seepage

waters is the absence of an expected trend of increasing CO₂ age, and hence Δ , away from the cave entrance (i.e., towards, and then under, the ice field). Similarly, no trend is visible in $\delta^{13}\text{C}$ or $\delta^{18}\text{O}$ of calcites. The $\delta^{13}\text{C}$ values are high compared to speleothems in temperate caves. This may be due either to CO₂ derived entirely from rock carbonate and the atmosphere, or to rock plus organic-derived CO₂ (low $\delta^{13}\text{C}$) with kinetic isotope fractionation during precipitation, causing enrichment of ¹³C in the calcite. The variability of $\delta^{18}\text{O}$ values (2.7‰) may be due to different temperatures of formation and varying $\delta^{18}\text{O}$ seepage water. Part of this variation may also be due to evaporation, because this would cause ¹⁸O enrichment in the aqueous phase and consequently in the calcite precipitate. Evidence of some evaporation in the main passages of the cave is indicated by the fact that the Ice Blockage passage has the least air flow (and therefore the least potential for evaporation) and contains those speleothems with lowest $\delta^{18}\text{O}$ values (CG 5A and 5B).

CONCLUSIONS

Age differences between U-series and ¹⁴C dating methods for recent speleothems in Castleguard Cave are found to be fairly constant and larger than expected. High ¹⁴C ages may be due to CO₂ in groundwater derived from the oxidation of dead carbonaceous deposits in the bedrock. This hypothesis is supported by stable isotopic analysis of the speleothems, but an anticipated trend of increasing ¹⁴C age as the proportion of active carbon decreases in the feed water was not seen. Analysis of a single depositing seepage water also argued against this mechanism but, because no blanks could be run or other sites

sampled, this result may not be significant. More data are needed from both near and far reaches of the cave to determine the relative variations in ¹⁴C activity in bicarbonate of seepages.

These results have raised more questions about the sources of CO₂ and modern speleothem depositional mechanisms than they have answered but it is hoped that they show, to some extent, how complex dissolution-precipitation processes in natural situations can be investigated by means of both chemical and stable/radioactive isotopic methods.

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