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AGE DETERMINATION OF RECENT CAVE DEPOSITS USING EXCESS ^{210}Pb - A NEW TECHNIQUE

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Abstract. Cave deposits have been widely used as proxy recorders in deciphering palaeoclimate during the last glacial/interglacial maxima (~ 120 ka) [Harmon et al., 1975; Atkinson et al., 1978; Goede and Harmon, 1983; Ayliffe and Veeh, 1989]. Palaeoclimatic studies of cave deposits for the past 1-1000 yr time scale require a precise dating technique, that until now has been lacking. Due to the multiple sources of carbon in speleothems, ^{14}C dates obtained for recently deposited calcite are highly variable and thus, ^{14}C dating techniques are not suitable to obtain speleothem ages for the past 1-1000 years.

Here, we show for the first time that speleothems contain high concentrations of excess ^{210}Pb and that this $^{210}Pb_{excess}$ can be successfully employed to obtain growth rates of speleothems deposited during the last 100 years. Of two specimens analyzed, a tubular "soda straw" stalactite yielded a longitudinal growth rate of 1.1 mm/yr, while a normal icicle-shaped stalactite had a lateral growth rate of 0.028 mm/yr. The mass growth rates of these two speleothems (149 and 78 mg/yr respectively) are comparable within a factor of two. Studies of fine-scale variations in the isotopic composition of recent speleothems will help to corroborate the validity of palaeoclimate records obtained using longer lived isotopes and extending back into Pleistocene.

Introduction

Calcite speleothems are formed when ground water which is supersaturated with $CaCO_3$ enters a cave. Slow outgassing of dissolved CO_2 lowers carbonate solubility in these drip waters and leads to crystalline calcite deposition. If isotopic equilibrium is maintained between HCO_3^- and aqueous CO_2, then the calcite precipitated will be in isotopic equilibrium with the water and variations in $^{18}O/^{16}O$ composition of the calcite will depend on climate alone [Hendy, 1971]. These speleothems preserve a record of long-term fluctuations in the isotopic (oxygen and hydrogen) composition of the recharge waters [Harmon et al., 1976]. Recharge waters that are derived from precipitation contain a climate signal consisting of information on temperature [Harmon et al., 1976] and amount of precipitation [Lawrence and White, 1989]. Previous speleothem investigations using $^{230}Th/^{234}U$ and stable oxygen isotopes indicate that the optimum climatic condition for speleothem growth would be wet and warm environments compared to cold and dry conditions [Harmon et al., 1975; Atkinson et al., 1978; Goede and Harmon, 1983; Ayliffe and Veeh, 1989]. All these earlier studies were confined to speleothems deposited during the last glacial/interglacial maxima (10^3-10^5 yr).

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Prior radiometric growth rate measurements of speleothems [Harmon et al., 1976; Broecker et al., 1960] utilized either ^{14}C or $^{230}Th/^{234}U$. These isotopes yield an average growth rate over a period of 10^3-10^5 years. Also, ^{14}C ages of young speleothems (< 1000 yr) are not reliable due to uncertain sources of the carbon in the calcite. Suitable short-lived radionuclides were not available to determine the short-term (1-100 yrs) growth rates and thus, to our knowledge, there are no published studies reporting growth rates of speleothems using relatively short-lived isotopes such as ^{210}Pb.

^{210}Pb (half life = 22.1 yr) is produced from its gaseous precursor, ^{222}Rn (half life = 3.8 d) at a constant rate. Ground waters have very high concentrations of ^{222}Rn which is derived from the recoil of Rn atoms into the aqueous phase during its production from the U-series decay chain. In addition, measurable quantities of ^{222}Rn have been found in the air in caves from various parts of the world [Breisch, 1968; Quinn 1990]. Most of this ^{222}Rn in the cave air presumably degassed from waters running through or dripping into the cave. As Rn containing water in caves drips from stalactites to stalagmites, the relatively longer lived daughter of ^{222}Rn,

TABLE 1. Weight and ^{210}Pb concentrations* in vertical segments of a soda straw stalactite from Harrel's Cave, San Saba Co., Texas, USA.

Segment Lengths (mm) (top = 0)	Diameter (top x bottom) mm	Weight of segment (g)	^{210}Pb concentra-tion (dpm/g)	Age (yr)+
0-19	18 x 13	4.85	8.09 ± 0.21	106 (98-115)
20-49	12 x 8	4.98	21.3 ± 0.4	84 (71-97)
50-82	9 x 9	4.23	49.5 ± 1.0	55 (41-70)
83-126	7 x 7	3.11	100.6 ± 1.6	20 (0-40)

* Parent-supported ^{210}Pb concentration was found to be < 0.5 dpm/g and hence parent-supported ^{210}Pb was not subtracted from the measured ^{210}Pb concentration.Errors quoted are 1 σ due to counting statistics.

+ The age corresponds to the middle of the segment; numbers in the parentheses denote age range of that corresponding segment.

TABLE 2. Weight and ^{210}Pb concentration* of material scraped from the sides of a normal, icicle-shaped stalactite collected in Harrel's Cave, San Saba Co., Texas, USA

Sample code	Amount of material scraped (g)	Corresponding depth from surface (mm)	^{210}Pb concentration (dpm/g)	Age (yr)+
H3-A	2.10	0-1.54	98.6 ± 3.7	28 (0-55)
H3-B	0.57	1.55-2.34	51.9 ± 1.2	70 (56-83)
H3-C	0.55	2.35-3.13	18.4 ± 0.7	98 (84-112)
H3-D	0.56	3.14-3.93	5.57 ± 0.24	127(113-140)
H3-E	0.50	3.94-4.68	3.61 ± 0.27	154(141-167)
H3-F	0.53	4.69-5.46	1.20 ± 0.16	182(168-195)

* Dimension of the stalactite: 108 mm long; wide and narrow diameters at the top, 47 mm x 18 mm, and at the bottom, 12 mm x 10 mm, respectively. Bottom 25 mm was broken after the first scraping (2.10 g), powdered and ^{210}Pb concentration in the bulk was measured as 3.05 ± 0.17 dpm/g. Parent-supported ^{210}Pb concentration was found to be < 0.5 dpm/g and hence parent-supported ^{210}Pb was not subtracted from the measured ^{210}Pb concentration. Errors quoted are 1 σ due to counting statistics.

+ Age corresponds to the middle of the layer scraped; numbers in the parentheses denote age range of that corresponding section scraped.

^{210}Pb, should accumulate within the growing crystal lattice of stalactites as well as stalagmites. Thus, ^{210}Pb concentrations in speleothems should theoretically offer a mechanism of dating relatively young (≤ 100 yr old) cave deposits.

^{210}Pb has been previously used to date various marine carbonates (such as corals) from both from coastal [Moore and Krishnaswami, 1972; Dodge and Thomson, 1974] as well as deep [Druffel et al., 1990] waters. Moore and Krishnaswami (1972) first introduced the ^{210}Pb-based radiometric method to determine the growth rates of corals. This method is based on ^{210}Pb production from its parent ^{226}Ra ($^{210}Pb/^{226}Ra$ method). In this technique, the initial ^{210}Pb concentration must be insignificant compared to ^{226}Ra concentration and its value be precisely known.

Since drip waters from the ceiling of caves have high concentrations of ^{222}Rn, recently-growing speleothems likewise should contain a large amount of excess ^{210}Pb. With this view, speleothem samples were collected from a central Texas cave (Harrel's Cave, San Saba Co.) and ^{210}Pb concentrations were measured.

Materials and Methods

In order to ascertain if the short-lived isotope ^{210}Pb is present in speleothems in amounts suitable for radiometric age determination, stalactites and stalagmites were collected from a limestone cave in central Texas. A tubular "soda straw" stalactite, a normal icicle-shaped stalactite and a stalagmite were collected from a privately owned cave in San Saba Co., about 160 km northwest of Austin, Texas. Other soda straw

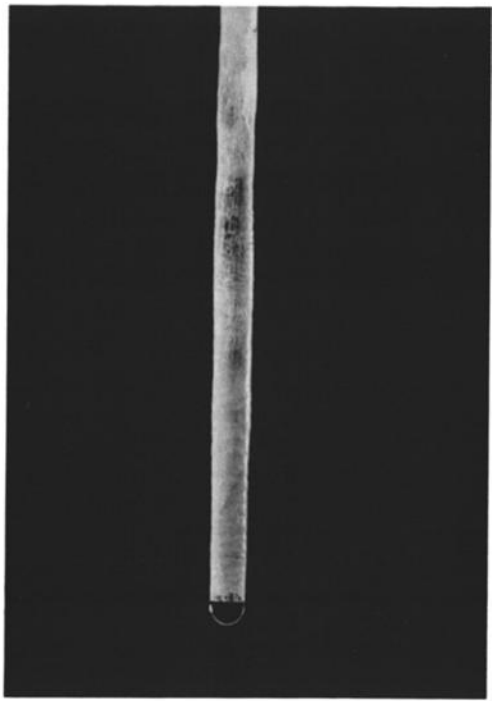

Fig. 1. A soda straw stalactite, showing a drop of water hanging from the tip (Photo by Cristian Lascu).

stalactites were collected from caves near San Antonio, Texas and in the Yucatan Peninsula of Mexico.

Excess ^{210}Pb concentrations were measured in sequential layers to determine the age and longitudinal or lateral growth rates. The tubular stalactite samples were cut into segments and weighed. The icicle type stalactites were scraped beginning with the outer most layer and the scraped powders were weighed. Assuming a uniform scraping on the layers of the icicle-shaped stalactite, the mass of the powder was used to

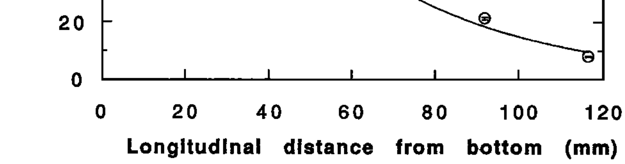

Fig. 2. ^{210}Pb contents of a "soda straw" stalactite from a central Texas cave. The concentration of ^{210}Pb exhibits an exponential decrease with distance from the bottom of the soda straw, the most recently deposited carbonate. This yields a longitudinal growth rate of 1.1 mm/yr, corresponding to a mass growth rate of 149 mg/yr. Since all the data points fall very close to the curve fit indicating incorporation of excess ^{210}Pb had been constant with time, it can be concluded that the growth rate has been uniform during the last 100 yr. Error bars in the y-axis are 1 σ due to counting statistics.

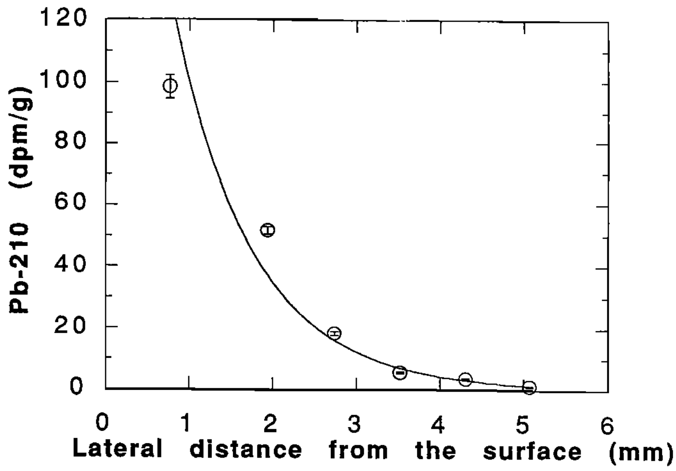

Fig. 3 ^{210}Pb contents of a normal icicle shaped stalactite from a central Texas cave. The outer layer, most recently deposited layer of this stalactite, contains the highest concentration of ^{210}Pb. An exponential decrease occurs inward. This yields a lateral growth rate of 0.028 mm/yr, corresponding to a mass growth rate of 78 mg/yr. These data points indicate constant incorporation of ^{210}Pb, likely resulting from a uniform growth rate during the last 100 yr. Error bars in the y-axis are 1 σ due to counting statistics.

determine the thickness of the layer that was scraped. Samples of this scraped powder or segments of the tubular stalactite were used to determine ^{210}Pb concentrations. A known amount of ^{208}Po spike was added to the powdered carbonate as a yield monitor and the sample subsequently dissolved in 6 M HCl. The solution was centrifuged and the supernatant used for Po plating onto silver planchets (Flynn, 1968). In most samples, no residue remained after acid treatment, indicating presence of pure carbonate. The planchets were assayed for their activity using a solid state surface barrier detector coupled to a S100 Canberra multichannel analyzer. The parent-supported ^{210}Pb concentrations were determined by gamma counting the sample powder on a high purity Ge-Well detector.

Results and Discussion

Excess ^{210}Pb concentrations of two speleothems, a soda straw and a normal stalactite, are presented in Tables 1 and 2, respectively. Soda straw stalactites (Figure 1) are of particular interest. These form as water drips from the cave ceiling producing fragile hollow tubes with a diameter of about 5 mm, equivalent to the size of a water droplet. Some soda straws can extend to a meter or more in length. Growth of soda straw stalactites occurs longitudinally as new rings of calcite form at the tip where drops of water hang before falling. If the central canal becomes plugged, water begins to run down the exterior producing lateral growth that results in characteristic icicle shapes. Thus, all stalactites start as tubular soda straws although subsequently some are transformed into icicle-shaped stalactites.

Characteristically, ^{210}Pb in the outer most layer of icicle-shaped stalactites was the highest, 98.6 dpm/g. Since water was dripping from this speleothem, it was assumed that it was still growing. In the case of soda straw stalactite, the bottom-most segment had the highest concentration, 100.6 dpm/g. The parent-supported ^{210}Pb concentration in these samples (= ^{226}Ra concentration) was < 0. 5 dpm/g. Potential sources of ^{210}Pb in growing speleothem crystals could arise from ^{222}Rn dissolved in the dripping water and ^{210}Pb produced from ^{222}Rn in the cave air. Since the ^{210}Pb concentration in the cave soil (clay layers) is negligible compared to the speleothem concentration, we presume that the contribution of ^{210}Pb to speleothems from ^{222}Rn present in the cave air is negligible. The ^{210}Pb concentration in the soda straw increases from top to bottom as the bottom corresponds to the latest growth. In the cases of icicle-shaped stalactites and stalagmites, excess ^{210}Pb concentration decreased with depth from the outer surface.

Growth Rates

Previously, no data existed on short-lived isotope-based growth rates for cave deposits. Traditionally, growth rates were obtained from repeated measurements of stalactites. Such growth rates were variable, ranging from a few tenths of a millimeter to as much as 2 millimeters per year [Moore and Sullivan, 1978].

In the present study, ^{210}Pb concentration is plotted against the median longitudinal distance from the bottom tip in each of four segments of a soda straw (Figure 2). For the second sample, an icicle-shaped stalactite, ^{210}Pb concentration is plotted against lateral depth (Figure 3). In both specimens, ^{210}Pb values of increasingly older samples fit an exponential curve, thus suggesting that the production of ^{210}Pb has been constant with time. Also, the near-ideal fit indicates that the growth was uniform and there was no break in the continuous growth. Stalactite growth rates were determined from the best fit to the exponential curve through the ^{210}Pb concentrations using the following equation:

$$^{210}Pb(x) = {}^{210}Pb_s\, e^{(-\lambda/s)d} \qquad (1)$$

where $^{210}Pb_s$ and $^{210}Pb(x)$ are the activities of excess ^{210}Pb in the most recent layer (s) and at any other layer (x), λ is the decay constant (=0.0311 yr^{-1}), d is the distance between the two layers, and s is the growth rate (mm/yr). The longitudinal growth rate in the soda straw is 1.1 mm/yr so that this 126 mm long tubular stalactite corresponds to an age of 115 yr. The lateral growth rate for the normal stalactite is 0.031 mm/yr. Since this 23 mm diameter stalactite formed from a soda straw having a central canal with a diameter of 5 mm, the deposition around this soda straw would have taken 581 yr.

An inner core sample of the normal stalactite was analyzed for ^{14}C by AMS (at Lawrence Livermore National Lab). It yielded an age of 7460 yrs BP (John Southon, written communication). Even though the ^{210}Pb-extrapolated age assumed a continuous and constant growth rate, the ^{14}C age is very likely to be incorrect due to unknown amounts of mixing of fresh with dead carbon Theoretically, when one molecule of H_2CO_3 containing CO_2 from decomposing organic matter in soil (fresh carbon), combines with one molecule of $CaCO_3$ from limestone (dead carbon) to produce two HCO_3^- ions. When this HCO_3^- solution enters a cave and degasses CO_2 to precipitate calcite, the radiocarbon content of a resulting speleothem should be only 50% that of fresh carbon. In practice, however, presently growing stalactites have been found to contain about 90% of the radiocarbon content expected from fresh carbon [Broecker et al., 1960].

Even though the longitudinal and lateral growth rates are different, the mass accumulation rates of these two samples are comparable, within a factor of two (soda straw = 149 mg/yr; normal stalactite = 78 mg/yr). This lateral growth rate compares closely to the rate obtained for a travertine deposit from a California cave by the ^{14}C method, 0.06 mm/yr (6.2 cm in 1000 yr; Broecker et al., 1960), and the rates obtained for temperate caves by $^{230}Th/^{234}U$ method, 0.05-0.1 mm/yr [Harmon et al., 1975]. The rate of deposition of speleothems, expressed as the annual increase in its longitudinal length or lateral diameter, is controlled by climatic factors [Ayliffe and Veeh, 1989]. In order to separate local from climatic factors, the variation in speleothem growth rates within a particular cave must be assessed. It should be possible to extrapolate a continuation of the observed constant growth rate back several thousands of years to time periods in which the age can be directly compared with those obtained using long lived nuclides such as $^{230}Th/^{234}U$ or ^{14}C.

Samples of a stalagmite from the same cave and stalactites from other caves (Hills and Dales Cave, Bexar Co., Texas, located ~ 170 km distant and Grutas de Tzab-Nah, Yucatan, Mexico) contained elevated levels of ^{210}Pb. A fossil stalagmite which was found overturned on the floor of the San Saba Co. cave did not contain any measurable ^{210}Pb indicating that the stalagmite stopped growing at least about 150 years ago. Thus, excess ^{210}Pb concentration data can be used to determine if any speleothem has been growing in the last 100-150 years or not. It also appears that presence of excess ^{210}Pb concentrations in speleothems is a common feature of newly depositing speleothems and can be routinely used to determine age and growth rates of all such recent cave deposits.

Conclusion

From this investigation, we conclude that:

(i) Presently-growing speleothems contain high concentrations of excess ^{210}Pb and this excess can be successfully employed to determine the growth rates of speleothems deposited during the last 100 years.

(ii) The growth rates determined in this study are comparable with those obtained in prior studies using repeated measurements or long lived isotopes.

(iii) Mass growth rates of soda straw and icicle-shaped stalactites from a single cave are also comparable.

(iv) The presence or absence of excess ^{210}Pb concentration in the speleothems can be used to determine if any deposition has occurred over the last 150 years or so.

With careful sampling, it may be possible to obtain 1-3 years of time resolution in cave deposits (stalactites and stalagmites) and thus climatological parameters such as temperature and/or precipitation can be determined from the stable isotope record. Such a reconstruction of recent palaeoclimate can be compared to the historical meteorological record available for the past 100-150 years to test the validity of such data and the potential for extrapolations back to periods ranging from thousands to hundreds of thousands of years ago.

Further investigations on the fine-scale variations in the isotopic composition of recent speleothems will help to corroborate the validity of palaeoclimate records obtained using longer-lived isotopes and extending back to Pleistocene. The two speleothems investigated appear to have grown continuously. However, more detailed sampling would be needed to detect brief lapses in deposition. Also, the variability in growth rates within a cave during the last 100 years will be of great significance in evaluating the use of speleothems as proxy climatic recorders.

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