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SPELEOTHEMS AS PROXY FOR THE CARBON ISOTOPE COMPOSITION OF ATMOSPHERIC CO<sub>2</sub>

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**Abstract.** We have measured the stable isotope ratios of carbon in a suite of recent cave deposits (< 200 years) from the San Saba County, Texas, USA. The methodology for dating these deposits using excess <sup>210</sup>Pb was recently established [Baskaran and Iliffe, 1993]. The carbon isotope ratios of these samples, spanning the time period ~ 1800-1990 AD, reflect the carbon isotope ratio of atmospheric CO<sub>2</sub> for the same period. The pathways by which the δ<sup>13</sup>C of atmospheric CO<sub>2</sub> is imprinted on these speleothems can be explained using a model developed by Cerling (1984). The results suggest that the carbon isotope ratios of speleothems can be used to develop long-term, high-resolution chronologies of the δ<sup>13</sup>C of atmospheric CO<sub>2</sub> and, by implication, the concentration of the atmospheric CO<sub>2</sub>.

Introduction

Speleothems have been widely used as a proxy to retrieve continental paleoenvironmental information. It has been observed that the optimum climatic conditions for speleothem growth are wet and warm environments as opposed to cold and dry weather conditions [Harmon et al., 1975; Ayliffe and Veeh, 1989]. For example, higher speleothem growth rates during interglacial periods has been observed [Harmon et al., 1975]. All stable isotope studies of speleothems published so far have dealt with glacial-interglacial time scales, 10- 500 ka (kilo annum). Oxygen isotope ratios together with radiometric dating of speleothems have provided significant palaeoclimatic information [Hendy, 1971; Harmon et al., 1975; Atkinson et al., 1978; Goede and Harmon, 1983; Ayliffe and Veeh, 1989; Brook et al., 1990; Dorale et al., 1992]. Carbon isotope ratios of cave deposits, on the other hand, have received much less attention.

Recently, we have shown that a large amount of excess <sup>210</sup>Pb (half-life = 22.1 yr) is produced within the crystals of speleothems and that this excess can be utilized to date them [Baskaran and Iliffe, 1993]. Lead-210 is produced from its precursor, <sup>222</sup>Rn (half-life = 3.8 d) at a constant rate. As <sup>222</sup>Rn-containing water in caves drips from stalactites to stalagmites, <sup>210</sup>Pb, the relatively longer lived daughter of <sup>222</sup>Rn, is produced according to the equation

$$[^{210}\text{Pb}] = [^{222}\text{Rn}] \times (1 - \exp(-\lambda_{\text{Pb}} \Delta t))$$

where λ<sub>Pb</sub> is the decay constant of <sup>210</sup>Pb, and Δt is the time for which the water drop is in contact with the calcium carbonate. We report here the stable isotope ratios of carbon from a

relatively young cave deposit system (<200 yr) from the San Saba County in Texas, USA.

Materials and Methods

Three types of speleothems, two normal icicle-shaped stalactites, a tubular soda straw stalactite and a stalagmite were dated using the method of Baskaran and Iliffe (1993). The <sup>210</sup>Pb concentrations and the ages of these samples are given in Baskaran and Iliffe (1993). The altitude of the cave is ~ 570 m and the relative humidity in the cave is near 100%. Details on this cave system are given elsewhere [Smith, 1973]. The calcite samples were reacted with 100% H<sub>3</sub>PO<sub>4</sub> at 25° C and the CO<sub>2</sub> gas was analyzed in a VG OPTIMA Isotope Ratio Mass spectrometer. The isotopic ratios are reported in the usual δ-notation where:

$$\delta \text{‰} = [(R_{\text{Sample}} / R_{\text{standard}}) - 1] \times 1000$$

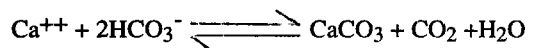
$$\text{and } R = {}^{13}\text{C}/{}^{12}\text{C}$$

The standard used is PEEDEE BELEMNITE (PDB). Analytical precision is 0.05‰ as determined by repeated analysis of pure calcium carbonate.

Results and Discussion

The δ<sup>13</sup>C values of the samples are plotted as a function of time in Figure 1. The δ<sup>13</sup>C values remain relatively constant at about -6‰ until around 1920 and then decrease to a value of about -8.2‰ around 1990. This trend very closely parallels the δ<sup>13</sup>C trend in atmospheric CO<sub>2</sub> deduced from a variety of studies such as the measurement of air trapped in polar ice [Friedli et al., 1986], certain C4 plants [Marino and McElroy, 1991] and direct atmospheric measurements [Keeling et al., 1989]. For comparison, the δ<sup>13</sup>C trend in atmospheric CO<sub>2</sub> based on the compilation and work reported by Marino and McElroy (1991) is reproduced in Figure 2. The δ<sup>13</sup>C variations of atmospheric CO<sub>2</sub> within this century using direct measurements and other proxies are given in Table 1. Along the lines of arguments considered below, we show that under favorable conditions, the δ<sup>13</sup>C value of cave deposits may be preserving a proxy record of the δ<sup>13</sup>C of atmospheric carbon dioxide.

Carbonate precipitation, such as speleothems, from drip waters can be represented by the following overall chemical reaction taking place in nature:



In this, the first step is the dissolution of the parent limestone by the dissolved CO<sub>2</sub> in the percolating waters to form the necessary bicarbonate ions. The CO<sub>2</sub> is almost always derived

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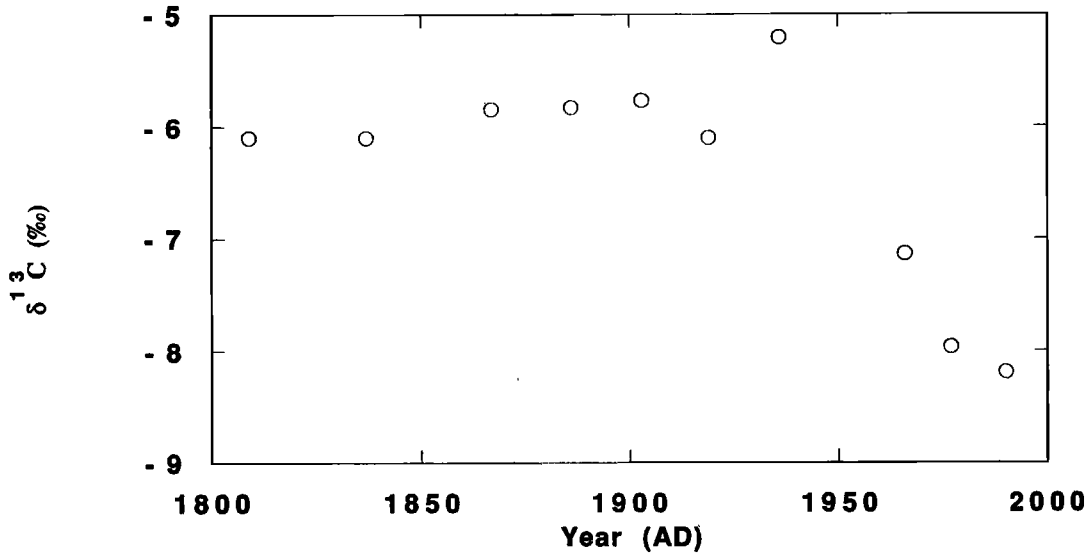


Fig. 1 Values of  $\delta^{13}\text{C}$  (with respect to PDB) of the speleothem samples as a function of time (calendar years BP). The method of calculating the ages is discussed in detail elsewhere [Baskaran and Iliffe, 1993].

from the soil horizon where the partial pressure of  $\text{CO}_2$  exceeds that in the atmosphere by orders of magnitude. When the solution containing the calcium and bicarbonate ions enters the cave atmosphere, precipitation of calcium carbonate takes place either due to degassing of  $\text{CO}_2$  from the solution or by the evaporation of the water leading to calcium carbonate supersaturation. In the cave atmosphere, high humidity (near 100%) generally limits calcium carbonate precipitation to  $\text{CO}_2$  degassing. Isotopically, the bicarbonate in solution reflects the carbon isotopic ratios of the soil  $\text{CO}_2$  and that of the parent limestone. As the reaction given above suggests, the bicarbonate is derived from one carbon each from the  $\text{CO}_2$  and limestone, respectively. However, Quade et al. (1989) have shown that because of complete equilibration between soil  $\text{CO}_2$  and the dissolved bicarbonate in the soil solution, virtually no imprint of the parent limestone is discernible in the precipitated calcium carbonate. This would mean that the carbon isotopic composition of the carbonates is directly related to the isotopic composition of the soil  $\text{CO}_2$ . In turn,

this relationship is governed by the fractionation effects in the system:



where the  $\text{CO}_2(\text{gas})$  represents the soil  $\text{CO}_2$ .

In order to estimate the  $\delta^{13}\text{C}$  of the bicarbonate in solution, it is necessary to evaluate the  $\delta^{13}\text{C}$  of the soil  $\text{CO}_2$ . The  $\delta^{13}\text{C}$  of the soil  $\text{CO}_2$  is related to the  $\delta^{13}\text{C}$  of the biomass. The  $\delta^{13}\text{C}$  values of the biomass, in turn, are determined by the nature of the vegetation. The  $\delta^{13}\text{C}$  values of C3 plants utilizing the Calvin cycle of photosynthesis average around  $-27\text{‰}$  and those of C4 plants governed by the Hatch-Slack cycle of photosynthesis tend to average around  $-13\text{‰}$ , respectively [Smith and Epstein, 1971; Deines, 1980]. The  $\delta^{13}\text{C}$  of soil  $\text{CO}_2$  is modified by processes such as diffusion into and exchange with atmospheric  $\text{CO}_2$ . In general, it has been observed that the latter process is significant only at shallower

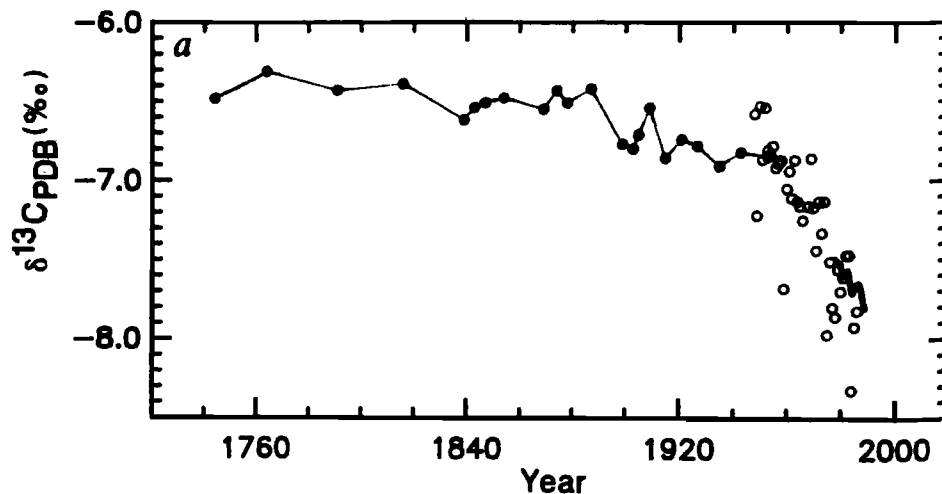


Fig. 2 Values of  $\delta^{13}\text{C}$  of atmospheric  $\text{CO}_2$  (with respect to PDB) as inferred from C4 plants and Siple station ice core samples, as plotted in Marino and McElroy [1991].

depths (~ 50 cm: Cerling, 1984; Wood and Petraitis, 1984). It has also been observed that the  $\delta^{13}\text{C}$  of the soil  $\text{CO}_2$  is relatively heavier in comparison to the  $\delta^{13}\text{C}$  of the soil organic matter.

Cerling (1984) has proposed a model which permits one to evaluate the  $\delta^{13}\text{C}$  of the soil  $\text{CO}_2$ . According to this model, the  $\delta^{13}\text{C}$  of the soil  $\text{CO}_2$  can be calculated knowing the soil respiration rate, the concentration and isotopic content of the atmospheric  $\text{CO}_2$ , isotopic content of the soil respired  $\text{CO}_2$  and the diffusion controlled fractionation of  $\text{CO}_2$  containing the light and heavy isotopic species of carbon. Further, from this model it can be shown that the  $\delta^{13}\text{C}$  of soil  $\text{CO}_2$  is less sensitive to the partial pressure of  $\text{CO}_2$  in the atmosphere but depends strongly on the proportion of C4 biomass in the soils. We adopt this model and the following values to calculate the expected  $\delta^{13}\text{C}$  value of the sample of age 1990 as an illustration: 0.01% soil  $\text{CO}_2$  concentration which is a reasonable estimate based on the soil respiration rate of  $9 \times 10^{-3}$  moles  $\text{m}^{-2} \text{hr}^{-1}$  for temperate grasslands [Wood and Petraitis, 1984; Schlesinger, 1977; Singh and Gupta, 1977]; -23‰ for the  $\delta^{13}\text{C}$  of soil respired  $\text{CO}_2$ ; 1.00440, 1.00846 and 1.00185 for the diffusion dependent fractionation, the fractionation between  $\text{CO}_2$  (gas)-bicarbonate and bicarbonate-carbonate, respectively [Mook et al., 1974; Emrich et al., 1970] at 20° C (the observed cave temperature); 350 ppm and ~ -8‰ for the concentration and  $\delta^{13}\text{C}$  of atmospheric  $\text{CO}_2$  [Keeling et al., 1989], respectively. Using these data, the cave sample is calculated to have a  $\delta^{13}\text{C}$  value of -8.11‰. This value is in excellent agreement with the value of -8.2‰ measured for the year 1990.

It may be noted that the  $\delta^{13}\text{C}$  of -23‰ chosen for the soil respired  $\text{CO}_2$  is somewhat arbitrary in that it is difficult to obtain precise single-year values for the organic matter which is an average of several years. The average age of soil organic matter could be of the order of several decades at least. According to Cerling (personal communication), the "modern (=1993)" vegetation could have shifted by as much as 1‰ compared to the soil organic matter that we have analyzed. If this is the case, then our calculations will further be strengthened. However, we feel this is a reasonable approximation when compared to the actual value of -22‰ that we obtained for the organic matter extracted from the soil collected around one of the samples. A similar calculation using the pre-industrial values of -6.5‰ and 300 ppm for the isotopic content and concentration of atmospheric  $\text{CO}_2$  and -21‰ for the soil respired  $\text{CO}_2$  [Marino and McElroy, 1991; Cerling, 1984] yields a  $\delta^{13}\text{C}$  value of -5.9‰ for the cave samples representing the pre-industrial times. This again is in good agreement with the near-constant values of -6‰ we obtained for the samples prior to 1920. Using the average values of -5.9‰, and -8.2‰ for the pre-1920 and 1990 years, respectively, it is seen that there is an overall  $\delta^{13}\text{C}$  decrease of  $-0.032\text{‰ y}^{-1}$  over the last 70 years (Table 1). This data is in excellent agreement with the long-term decline of  $-0.031\text{‰ y}^{-1}$  for the atmospheric  $\delta^{13}\text{C}$  inferred by other measurements [Marino and McElroy, 1991; Keeling et al., 1989].

The  $\delta^{13}\text{C}$  value of the cave deposit is determined by the isotopic composition of the soil vegetation and atmospheric  $\text{CO}_2$ . The  $\delta^{13}\text{C}$  value of the soil vegetation could have registered a change if the proportion of C3/C4 plants had changed in the study area, a likelihood that we exclude on the premise that this is an undisturbed site and also in the absence

of any documented evidence for this. Presumably, the proportion of C3/C4 vegetation could change by either a change in the local climate or by the influence of man. The latter arises due to changes in cultivation habits or by an increase in the animal population that preferably grazes C4 plants. We have not been able to obtain evidence for any of these factors. Moreover, it would be even less likely that the proportion of C3/C4 plants would change in just such a way to mimic the changes in the  $\delta^{13}\text{C}$  values of atmospheric  $\text{CO}_2$  evaluated from a variety of studies. Another interesting observation that can be made from our data is that, despite a longer residence time of soil organic matter in soils there is a relatively remarkable synchronicity in the  $\delta^{13}\text{C}$  changes of soil organic matter and soil  $\text{CO}_2$ . There are two likely explanations for this. Firstly, the soil  $\text{CO}_2$  is strictly dominated by plant respiration processes and no organic matter derived from extant vegetation is involved in the production of soil  $\text{CO}_2$ . Secondly, the soil organic matter turnover is conspicuously rapid in our study area. These aspects require detailed investigation that would combine not only the stable isotope measurements but  $^{14}\text{C}$  determinations of soil organic matter as well.

As is well known, this decline in  $\delta^{13}\text{C}$  values is related to the increase in concentration of atmospheric  $\text{CO}_2$  released by the consumption of fossil fuel [Keeling et al., 1989]. In the geologic past, forest fires, volcanism or similar events could have caused the changes in the concentration and isotopic ratio of the atmospheric  $\text{CO}_2$ . Therefore, it becomes important to document paleo- $\delta^{13}\text{C}$  variations of atmospheric  $\text{CO}_2$ . Our present work opens up the possibility to carry out this study using cave deposits.

### Conclusion

In this preliminary study we have argued that the  $\delta^{13}\text{C}$  value of atmospheric  $\text{CO}_2$  is recorded in cave deposits via the  $\delta^{13}\text{C}$  of soil  $\text{CO}_2$ . The specific conclusions are:

TABLE 1. Comparison of the estimated  $\delta^{13}\text{C}$  changes in the atmospheric  $\text{CO}_2$ .

Sample	Year	$\delta^{13}\text{C}$ variations (‰ yr <sup>-1</sup> )	Reference
Ice Core	1953 to 1980	-0.026*	Friedli et al. (1986)
C4-Plants	1948 to 1984	-0.031	Marino and McElroy [1991]
Direct Measurements	1956 to 1989	-0.034	Keeling et al. [1989]
+Tree rings	1800 to 1970	-0.012	Freyer [1986]
Cave Deposits	1920 to 1990	-0.032	this study

\* The values were calculated assuming a  $\delta^{13}\text{C}$  value of -7.80‰ in the year 1989 [Keeling et al. 1989].

+ This record represents a very long time period; since most of the  $\delta^{13}\text{C}$  changes took place during the last 35 years, the value reported is very low.

(i) Speleothems can be used as a proxy to obtain  $\delta^{13}\text{C}$  values of atmospheric  $\text{CO}_2$ .

(ii) The overall decrease in  $\delta^{13}\text{C}$  values of atmospheric  $\text{CO}_2$  for the past 70 years,  $-0.032\%$ , is in good agreement with other published values.

Further investigations on fine-scale variations in stable isotopic compositions will enable us to verify the temperature obtained from this study with the meteorological record available for the past 75 years or so.

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