

## FORMATION OF $^{13}\text{C}/^{12}\text{C}$ ISOTOPE RATIOS IN SPELEOTHEMS: A SEMI-DYNAMIC MODEL<sup>1</sup>

MAREK DULINSKI

Institute of Physics and Nuclear Techniques  
Academy of Mining and Metallurgy, Krakow, Poland

and

KAZIMIERZ ROZANSKI

Isotope Hydrology Section, IAEA, Vienna, Austria

**ABSTRACT.** A theoretical approach towards predicting the carbon isotope composition of carbonate cave deposits is presented. The proposed model simulates time variations of both the chemical and isotopic composition of the carbonate solution and deposited calcite in the course of  $\text{CaCO}_3$  precipitation. Two phases of the precipitation process are distinguished and treated separately: initial outgassing of the solution until a certain degree of supersaturation of  $\text{CO}_3^{2-}$  ions is reached and subsequent precipitation of  $\text{CaCO}_3$  related to further outgassing. Precipitation rates of  $\text{CaCO}_3$  predicted by the model agree fairly well with literature data. The model predicts  $\delta^{13}\text{C}$  values of deposited calcite within a range of ca  $-16$  to  $+3\%$  depending on temperature, chemical and isotope parameters of the initial solution and actual degree of the precipitation process.

### INTRODUCTION

Speleothems are deposits of calcium carbonate found in limestone caves (stalagmites, stalactites and flowstones). They are formed by precipitation from seepage water entering through the roof or walls of the cave which becomes supersaturated with  $\text{CaCO}_3$ . Several models describing the evolution of the carbon isotope composition of precipitated carbonates have been proposed (eg, Hendy 1971; Dreybrodt 1982; Salomons & Mook 1986).

The most comprehensive analysis of the  $\text{CaCO}_3$  precipitation process was made by Hendy (1971). He describes mathematically  $\text{CaCO}_3$  precipitation under equilibrium conditions for both open and closed systems. He also presents first attempts towards kinetic treatment of isotopic exchange in the reaction chain  $\text{CO}_{2g} \rightleftharpoons \text{CO}_{2w} \rightleftharpoons \text{HCO}_3^-$  and formulates physical and chemical conditions to be fulfilled for equilibrium fractionation of carbon and oxygen isotopes during speleothem formation processes.

Salomons and Mook's (1986) theoretical approach to the formation of  $^{13}\text{C}$  content of precipitated carbonate is in fact, very similar to Hendy's model, with some simplifications.

Both these models assume that outgassing of the solution and precipitation of  $\text{CaCO}_3$  occur simultaneously from saturated solution. They also assume that isotopic equilibrium is maintained between gaseous and dissolved  $\text{CO}_2$ .

Dreybrodt's model (1982) refers to specific conditions in caves situated under glaciers or in bare karst areas where precipitation of  $\text{CaCO}_3$  may be due to geothermal effect. This model was proposed to explain very high  $\delta^{13}\text{C}$  values of speleothems (up to  $+10\%$ ) from the high mountain caves of the Alps (Geyh, Franke & Dreybrodt 1983).

Recent isotope investigations of streams precipitating  $\text{CaCO}_3$  revealed that deposition of  $\text{CaCO}_3$  starts, in fact, from supersaturated solutions, with activity of  $\text{CO}_3^{2-}$  ions equal to ca  $2.2 \cdot 10^{-5}$  mol/L (Uzdowski, Hoefs & Menschel 1979); Dandurand *et al* 1982; Michaelis, Uzdowski & Menschel 1985). Also, the assumption of full chemical and isotopic equilibrium in the solution cannot be strictly valid because the rate of removal of  $\text{CO}_2$  from the solution, especially at initial stages of the outgassing process, is much larger than its production rate of  $\text{HCO}_3^-$  ions. Consequently, kinetic isotope relationships rather than equilibrium should be used. Our model will hopefully eliminate many simplifying assumptions made in the above-mentioned models.

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THE H<sub>2</sub>O-CO<sub>2</sub>-CaCO<sub>3</sub> SYSTEM

The H<sub>2</sub>O-CO<sub>2</sub>-CaCO<sub>3</sub> system, under full chemical equilibrium conditions can be described by the following equations (Buhmann & Dreybrodt 1985)

$$(\text{H}^+)(\text{OH}^-) = K_{\text{W}}(\text{H}_2\text{O}) \quad (1\text{a})$$

$$(\text{CO}_2) = K_{\text{H}}P_{\text{CO}_2} \quad (1\text{b})$$

$$(\text{CO}_2) = K_{\text{O}}(\text{H}_2\text{CO}_3^{\circ}) \quad (1\text{c})$$

$$(\text{H}^+)(\text{HCO}_3^-) = K_1(\text{H}_2\text{CO}_3^*) \quad (1\text{d})$$

$$(\text{H}^+)(\text{CO}_3^{2-}) = K_2(\text{HCO}_3^-) \quad (1\text{e})$$

$$(\text{H}^+)(\text{HCO}_3^-) = K_4(\text{CO}_2)(\text{H}_2\text{O}) \quad (1\text{f})$$

$$(\text{H}^+)(\text{HCO}_3^-) = K_3(\text{H}_2\text{CO}_3^{\circ}) \quad (1\text{g})$$

$$(\text{Ca}^{2+})(\text{CO}_3^{2-}) = K_{\text{C}}(\text{CaCO}_3^{\circ}) \quad (1\text{h})$$

where  $(\text{H}_2\text{CO}_3^*) = (\text{H}_2\text{CO}_3^{\circ}) + (\text{CO}_2)$ ,  $K_{\text{H}}$  – solubility of CO<sub>2</sub> in water and the expressions in brackets represent activity of individual ions in the solution. The presence of CaCO<sub>3</sub><sup>o</sup> and CaHCO<sub>3</sub><sup>+</sup> molecules can be ignored because of their low concentration in the solution, usually <1% of the total amount of all other carbonic components (Langmuir 1984). Also, the condition of electroneutrality of the solution should be fulfilled

$$c_{\text{H}} + 2c_{\text{Ca}} - c_{\text{OH}} - c_{\text{HCO}_3^-} - 2c_{\text{CO}_3^{2-}} = 0 \quad (2)$$

where  $c$  represents the concentration of the given ion in the solution (in mol/L). The equilibrium constants quoted in Eqs (1a)–(1h) are temperature-dependent (see eg, Buhmann & Dreybrodt 1985).

In a natural environment, limestone dissolution occurs usually with participation of biogenic CO<sub>2</sub> originating from plant respiration and decay of dead organic matter. The soil layer is the principal reservoir of biogenic CO<sub>2</sub> where its partial pressure can be up to two orders of magnitude higher than in the bulk atmosphere.

Limestone dissolution may proceed along two extreme routes:

1) under open-system conditions where the solution is always in contact with the reservoir of CO<sub>2</sub>,

2) under closed-system conditions where the solution is isolated from the reservoir of gaseous CO<sub>2</sub> before dissolution begins. In nature, the dissolution process mostly should be considered as a mixture of these extreme situations.

In an open system, with chemical and isotopic equilibrium between the CO<sub>2</sub> reservoir and the solution, the chemical composition of the solution can be determined from Eqs (1a)–(1h) and (2). The carbon isotopic composition of individual ions in the solution can be calculated using the equilibrium isotopic enrichment constants listed in Table 1. It is evident that, under open-system conditions, the isotopic composition of all carbonic compounds present in the solution is controlled by the isotopic composition of the gaseous CO<sub>2</sub>.

Under closed-system conditions, carbon atoms in the solution originate from two sources, the soil CO<sub>2</sub> and dissolved limestone rock. Again, assuming full chemical and isotopic equilibrium in the solution, the carbon isotope composition of individual carbonate compounds in the solution can be calculated for each step of the dissolution process.

Figure 1 shows the evolution of the isotopic composition of HCO<sub>3</sub><sup>-</sup> ions and total dissolved inorganic carbon (TDIC) in the solution during dissolution, for values of temperature and partial pressure of CO<sub>2</sub> typical for cave environments. The calculations were based on the iterative method proposed by Hendy (1971). We assumed the δ<sup>13</sup>C of soil CO<sub>2</sub> equal

TABLE 1  
Equilibrium isotope enrichment coefficients  $\epsilon_{A,B}$  (‰) for the CO<sub>2</sub>-H<sub>2</sub>O-CaCO<sub>3</sub> system at 5° and 15°C. Data after Mook, Bommerson & Staverman (1974), Vogel, Grootes & Mook (1970), Thode, Shima, Rees & Kirshnamurthy (1965), Salomons & Mook (1986).

TEMPERATURE 5 °C						
A	B	CO <sub>2g</sub>	CO <sub>2w</sub>	HCO <sub>3</sub> <sup>-</sup>	CO <sub>3</sub> <sup>2-</sup>	CaCO <sub>3</sub>
CO <sub>2g</sub>		+	+ 1.15	-10.20	- 9.61	-10.09
CO <sub>2w</sub>		- 1.15	+	-11.35	-10.74	-11.24
HCO <sub>3</sub> <sup>-</sup>		+10.31	+11.48	+	+ 0.60	+ 0.11
CO <sub>3</sub> <sup>2-</sup>		+ 9.70	+10.86	- 0.60	+	- 0.49
CaCO <sub>3</sub>		+10.19	+11.37	- 0.11	+ 0.49	+
TEMPERATURE 15 °C						
A	B	CO <sub>2g</sub>	CO <sub>2w</sub>	HCO <sub>3</sub> <sup>-</sup>	CO <sub>3</sub> <sup>2-</sup>	CaCO <sub>3</sub>
CO <sub>2g</sub>		+	+ 1.10	- 9.02	- 8.54	- 9.43
CO <sub>2w</sub>		- 1.10	+	-10.12	- 9.63	-10.53
HCO <sub>3</sub> <sup>-</sup>		+ 9.10	+10.22	+	+ 0.49	- 0.41
CO <sub>3</sub> <sup>2-</sup>		+ 8.61	+ 9.72	- 0.49	+	- 0.90
CaCO <sub>3</sub>		+ 9.52	+10.64	- 0.41	+ 0.90	+

to -25‰ vs PDB which is the mean value occurring on areas covered by C<sub>3</sub> plants. The δ<sup>13</sup>C of limestone carbonate was fixed at the level of +1‰ vs PDB. As shown in Figure 1, the δ<sup>13</sup>C<sub>TDIC</sub> values at the saturation point vary between -15‰ and -19‰ under open-system conditions, whereas the corresponding values for the closed system are in the range of -13‰ to -15‰. The corresponding δ<sup>13</sup>C values for HCO<sub>3</sub><sup>-</sup> ions in the solution lie in the range of -14.9‰ to -16.1‰ and -13‰ to -14‰, for open- and closed-system conditions, respectively. There is only a slight dependence of δ<sup>13</sup>C<sub>HCO<sub>3</sub><sup>-</sup></sub> on temperature because changes of equilibrium fractionation factors with temperature are compensated by parallel changes of the molar ratios of carbonic molecules in solution.

#### FORMATION OF SPELEOTHEMS

Under natural conditions, calcite speleothems are formed when a thin film of carbonate solution depositing CaCO<sub>3</sub> flows down the given specimen. For a theoretical description of this process, a planar model has been proposed (Fig 2). The liquid film is assumed to be ca 0.01cm thick, which is the value most frequently observed in nature. A constant pH value across the film was further assumed (Hoover & Berkshire 1969) which considerably simplifies numerical calculations. In view of the isotope and chemical data for carbonate precipitating springs (*cf* Introduction), the formation process of speleothems was divided into two parts: 1) outgassing of the solution without precipitation of CaCO<sub>3</sub> until a certain degree of supersaturation of the solution is reached, 2) simultaneous outgassing of the solution and precipitation of CaCO<sub>3</sub>. In both cases, the δ<sup>13</sup>C<sub>TDIC</sub> and δ<sup>13</sup>C of precipitated CaCO<sub>3</sub> were calculated as functions of the time elapsed since the beginning of the outgassing process.

#### Outgassing of the Solution

During the release of CO<sub>2</sub> from the solution, the conversion rate of HCO<sub>3</sub><sup>-</sup> to CO<sub>2w</sub> is usually much faster than the backward reaction. Thus, the reaction CO<sub>2w</sub> → HCO<sub>3</sub><sup>-</sup> was omitted from the calculations. Further, we assumed that the solution preserves the initial

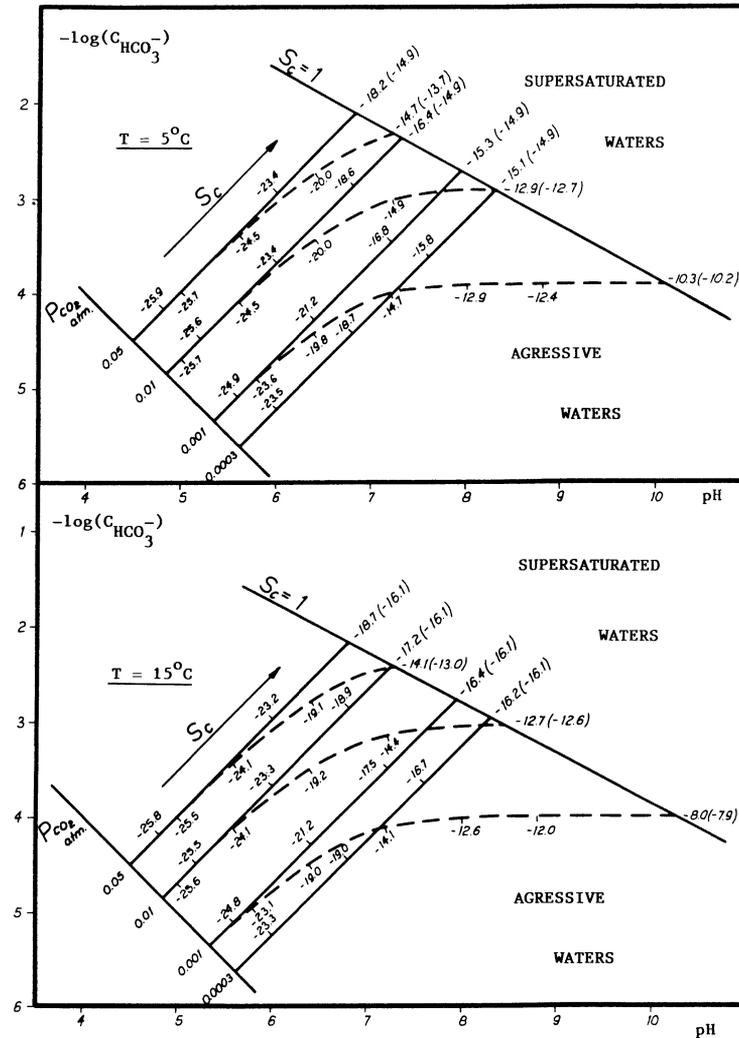
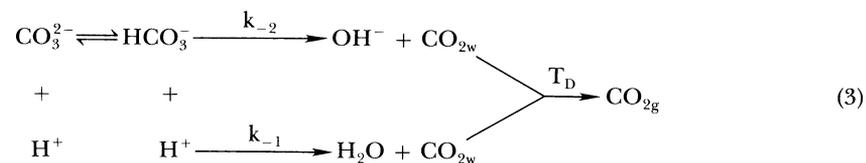


Fig 1. Dissolution of  $\text{CaCO}_3$  in water under closed- (----) and open- (—) system conditions at  $+5^\circ$  and  $+15^\circ\text{C}$ . Numbers labeling the curves indicate  $\delta^{13}\text{C}$  values of the TDIC. Numbers in parentheses are  $\delta^{13}\text{C}$  values of  $\text{HCO}_3^-$  in the saturated solution ( $S_c = 1$ ). The input  $\delta^{13}\text{C}$  values are  $-25$  and  $+1\text{‰}$  vs PDB for soil  $\text{CO}_2$  and limestone carbonate, respectively.

concentration of  $\text{Ca}^{2+}$  ions during removal of  $\text{CO}_2$ . Based on these assumptions, the outgassing of the solution can be described by



where the reaction  $\text{CO}_3^{2-} + \text{H}^+ \rightleftharpoons \text{HCO}_3^-$  is fast (Dreybrodt 1980). Conversion of  $\text{HCO}_3^-$  to  $\text{CO}_{2w}$  can be treated as a simultaneous, pseudo-first-order reaction. Consequently, temporal

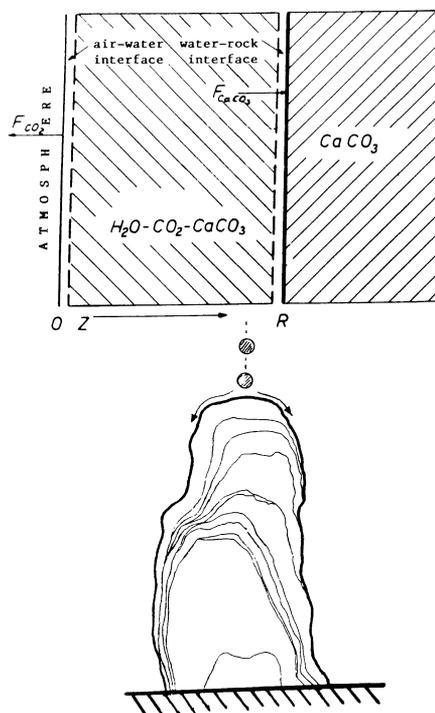


Fig. 2. Schematic representation of processes on the surface of the growing speleothem

variations of concentration of  $\text{HCO}_3^-$  ions in the solution can be expressed by

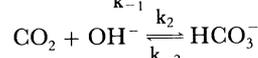
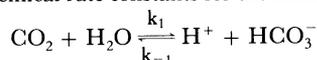
$$c_{\text{HCO}_3^-}(t) = c_{\text{HCO}_3^-}^{\text{atm}} + \{c_{\text{HCO}_3^-}^{\circ} - c_{\text{HCO}_3^-}^{\text{atm}}\} \text{EXP}(-k_{\text{HCO}_3^-} t) \quad (4)$$

where  $c_{\text{HCO}_3^-}(t)$ ,  $c_{\text{HCO}_3^-}^{\circ}$ ,  $c_{\text{HCO}_3^-}^{\text{atm}}$  represent concentrations of  $\text{HCO}_3^-$  ions at the time instant  $t$ ,  $t = 0$  and in equilibrium with the atmospheric  $\text{CO}_2$ , respectively. The rate constant  $k_{\text{HCO}_3^-}$  in Eq (4) depends on the pH of the solution and is equal

$$k_{\text{HCO}_3^-} = k_{-2} + k_{-1}c_{\text{H}^+} \quad (5)$$

where  $k_{-2}$  and  $k_{-1}$  are the rate constants of the reactions shown in Eq (3). Numerical values of  $k_{-2}$  and  $k_{-1}$  are listed in Table 2.

TABLE 2  
Chemical rate constants for the reactions



(according to Buhmann & Dreybrodt 1985)

Temperature [°C]	$k_1$ [1/s]	$k_2$ [L/mol*s]	$k_{-1}$ [L/mol*s]	$k_{-2}$ [1/s]
0	$2.3 \cdot 10^{-3}$	995	6966	$4.4 \cdot 10^{-6}$
5	$4.2 \cdot 10^{-3}$	1574	11096	$9.7 \cdot 10^{-6}$
10	$7.5 \cdot 10^{-3}$	2449	17673	$2.1 \cdot 10^{-5}$
15	$1.3 \cdot 10^{-2}$	3753	28136	$4.4 \cdot 10^{-5}$

We further assumed that diffusion is a principal mechanism responsible for transport of  $\text{CO}_{2w}$  across the film thickness. The solution of a one-dimensional diffusion equation with a homogeneous source of  $\text{CO}_{2w}$  (reservoir of  $\text{HCO}_3^-$  ions), for the time intervals fulfilling the condition  $D_{\text{CO}_2} t/R^2 > 0.4$ , can be expressed by

$$c_{\text{CO}_{2w}}(t) = \frac{8}{\pi^2} \left( \text{EXP}(-t/T_D) \{c_{\text{CO}_{2w}}^o - c_{\text{CO}_{2w}}^{\text{atm}}\} + \frac{\{c_{\text{HCO}_3^-}^o - c_{\text{HCO}_3^-}^{\text{atm}}\} T_D k_{\text{HCO}_3^-}}{1 - T_D k_{\text{HCO}_3^-}} * \right. \\ \left. * \{ \text{EXP}\{-k_{\text{HCO}_3^-} t\} - \text{EXP}\{-t/T_D\} \} \right) + c_{\text{CO}_{2w}}^{\text{atm}} \quad (6)$$

where  $c_{\text{CO}_{2w}}(t)$ ,  $c_{\text{CO}_{2w}}^o$  and  $c_{\text{CO}_{2w}}^{\text{atm}}$  are the average concentrations of  $\text{CO}_{2w}$  in the liquid film at the time  $t$ , at  $t = 0$  and in equilibrium with atmospheric  $\text{CO}_2$ , respectively.  $T_D$  stands for characteristic constant of  $\text{CO}_2$  decrease in the solution and is expressed as

$$T_D = \frac{4R^2}{\pi^2 D_{\text{CO}_2}} \quad (7)$$

where  $R$  is the film thickness (in cm) and  $D_{\text{CO}_2}$  is the diffusion coefficient of  $\text{CO}_2$  in water (in  $\text{cm}^2/\text{s}$ ). The temperature dependence of  $D_{\text{CO}_2}$  was adopted after Buhmann & Dreybrodt (1985).

The net mass and isotope fluxes of  $\text{CO}_2$  through the air-water interface can be expressed as a difference between corresponding fluxes “out” and “into” the solution (Siegenthaler & Munnich 1980)

$$F = F_{\text{as}} - F_{\text{sa}} = w * (K_{\text{H}} P_{\text{CO}_2} - c_s) \quad (8)$$

$$F^{13} = w^{13} \alpha_{\text{CO}_{2g}-\text{CO}_{2w}} K_{\text{H}}^{13} R_{\text{a}} P_{\text{CO}_2} - w^{13} \alpha_{\Sigma-\text{CO}_{2w}}^{13} R_{\Sigma} c_s \quad (9)$$

where

- $F, F^{13}$  = net fluxes of  $^{12}\text{CO}_2$  and  $^{13}\text{CO}_2$ , respectively
- $w, ^{13}w$  = transport velocities of  $^{12}\text{CO}_2$  and  $^{13}\text{CO}_2$  molecules through the liquid film
- $^{13}R_{\text{a}}, ^{13}R_{\Sigma}$  =  $^{13}\text{C}/^{12}\text{C}$  isotope ratios of atmospheric  $\text{CO}_2$  and TDIC in solution
- $P_{\text{CO}_2}$  = partial pressure of atmospheric  $\text{CO}_2$
- $K_{\text{H}}$  = solubility of  $\text{CO}_2$  in water
- $\alpha_{\text{CO}_{2g}-\text{CO}_{2w}}$  = equilibrium fractionation factor between gaseous and dissolved  $\text{CO}_2$
- $\alpha_{\Sigma-\text{CO}_{2w}}$  = effective equilibrium fractionation factor between TDIC and  $\text{CO}_{2w}$  in solution
- $c_s$  = concentration of  $\text{CO}_{2w}$  in bulk solution.

Dividing Eq (9) by Eq (8) and transforming the isotopic ratios  $R$  into corresponding  $\delta$  values we obtain

$$\delta^{13}C_{\text{F}} = \left( \frac{\alpha_{\text{as}} c_{\text{CO}_2}^{\text{atm}} \{ \delta^{13}C_{\text{CO}_2}^{\text{atm}} 10^{-3} + 1 \}}{K_{\text{H}} P_{\text{CO}_2} - c_{\text{CO}_{2w}}} - \frac{\alpha_{\text{sa}} c_{\text{CO}_{2w}} \{ \delta^{13}C_{\Sigma} 10^{-3} + 1 \}}{K_{\text{H}} P_{\text{CO}_2} - c_{\text{CO}_{2w}}} - 1 \right) * 1000 \quad (10)$$

where  $\alpha_{\text{as}} = \alpha_{\text{CO}_{2g}-\text{CO}_{2w}} * ^{13}w/w$  and  $\alpha_{\text{sa}} = \alpha_{\Sigma-\text{CO}_{2w}} * ^{13}w/w$ . The above formula represents the  $\delta^{13}\text{C}$  value of the net flux of  $\text{CO}_2$  through the interface.

Calculations of the evolution of  $\delta^{13}C_{\text{TDIC}}$  during the outgassing process started from the parameters of the solution saturated with  $\text{CaCO}_3$ . Based on Eqs (4) and (6), for the time step  $\Delta t$ , the actual concentrations of  $\text{CO}_{2w}$  and  $\text{HCO}_3^-$  ions were calculated. Assuming chemical activity coefficients of all carbonic molecules equal 1, we evaluated the concentration of hydrogen ions  $\text{H}^+$  using conditions of electroneutrality and the assumption of chemical

equilibrium between  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  ions. After computation of the concentrations of other ions in solution, the ionic strength was used (Garrels 1960) to calculate activity coefficients, which in turn, were applied to calculate the concentrations of carbonic compounds in solution more accurately. The iterative process was repeated until successive changes in activity coefficients were  $<10^{-4}$ . The values of  $\Delta c_{\text{TDIC}}$ ,  $\delta^{13}\text{C}_{\text{TDIC}}$ , and isotopic composition of all carbonic compounds remaining in the solution were then computed. Since the kinetic fractionation factor for the  $\text{HCO}_3^- \rightarrow \text{CO}_{2\text{w}}$  reaction is unknown, the equilibrium values have been adopted. The computation was performed for successive intervals  $\Delta t$ , until the activity of  $\text{CO}_3^{2-}$  ions necessary for initiation of  $\text{CaCO}_3$  precipitation process was reached ( $\sim 2.2 \cdot 10^{-5}$  mol/L).

The degassing process was simulated for four carbonate solutions with different initial parameters. The results are summarized in Figure 3. The initial, fast increase of  $\delta^{13}\text{C}_{\text{TDIC}}$  is caused by release from the solution of large amounts of  $\text{CO}_{2\text{w}}$  with low  $^{13}\text{C}$  content. A further increase of  $\delta^{13}\text{C}_{\text{TDIC}}$  proceeds slowly because the  $\text{CO}_{2\text{w}}$  reservoir is exhausted and the outgassing rate is controlled by the  $\text{HCO}_3^-$  ions. At  $5^\circ\text{C}$ , after the first 20 sec, the  $\text{HCO}_3^-$  ions entirely control the outgassing process. The influence of atmospheric  $\text{CO}_2$  on the isotope composition of the solution is negligible because the flux of  $\text{CO}_2$  "out" of the solution is much larger than the backward flux. In Figure 3 it becomes clear that solutions of similar origin (closed or open system), start to precipitate calcite earlier for higher partial pressures of  $\text{CO}_2$  at the time of their formation.

Temperature is an essential parameter accelerating the outgassing process. An increase in temperature slightly decreases the difference in  $\delta^{13}\text{C}_{\text{TDIC}}$  between saturated and outgassed solutions. As in Figure 3, this difference is in the range of 3-4‰. It should be noted that final values of  $\delta^{13}\text{C}_{\text{TDIC}}$  may in reality be slightly lower because in the calculations we assumed isotopic equilibrium between carbonate compounds in solution. Escape of  $\text{CO}_2$  to the atmosphere is a fast process and the  $\text{HCO}_3^-$  ions probably are not able to reach equilibrium with  $\text{CO}_2$  remaining in solution.

#### Precipitation of $\text{CaCO}_3$

When the activity of  $\text{CO}_3^{2-}$  ions in solution reaches ca  $2.2 \cdot 10^{-5}$  mol/L, both outgassing and precipitation of  $\text{CaCO}_3$  proceed simultaneously. It is a well-known experimental fact that precipitation of 1 mole of  $\text{CaCO}_3$  is accompanied by release of 1 mole of gaseous  $\text{CO}_2$  to the atmosphere (Michaelis, Usdowski & Menschel 1985). We numerically simulated the precipitation process in a similar way to outgassing the solution, described above. The calculation started from outgassed, supersaturated solution with defined chemical and

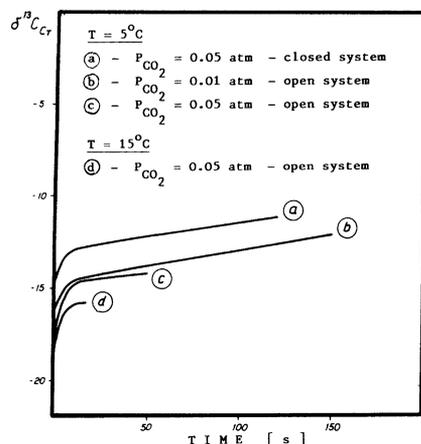


Fig 3. Evolution of  $\delta^{13}\text{C}$  values of the TDIC in solution during initial outgassing without precipitation of  $\text{CaCO}_3$ . The activity of  $\text{CO}_3^{2-}$  ions in solution, corresponding to final points of the curves, equals ca  $2.2 \cdot 10^{-5}$  mol/L.

isotopic composition. The time evolution of  $\delta^{13}\text{C}_{\text{TDIC}}$  was computed by an iterative method, using the isotope mass balance formula

$$\delta^{13}\text{C}_{\text{TDIC}}^{i+1} = \delta^{13}\text{C}_{\text{TDIC}}^i \frac{c_{\text{TDIC}}^i}{c_{\text{TDIC}}^{i+1}} - \delta^{13}\text{C}_{\text{F}}^i \frac{\Delta c_{\text{TDIC}}}{2 c_{\text{TDIC}}^{i+1}} - \delta^{13}\text{C}_{\text{CaCO}_3}^i \frac{\Delta c_{\text{TDIC}}}{2 c_{\text{TDIC}}^{i+1}} \quad (11)$$

where  $\delta^{13}\text{C}_{\text{TDIC}}^{i+1}$  represents the carbon isotopic composition of the precipitated portion of  $\text{CaCO}_3$ , corresponding to the change in the total carbon content of the solution  $c_{\text{TDIC}}^i$  by  $\Delta c_{\text{TDIC}}$ . Isotopic equilibrium between  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  ions in the solution was assumed (high rate of  $\text{HCO}_3^- \rightarrow \text{CO}_2 + \text{H}^+$  reaction). The isotopic composition of total precipitated calcite ( $\delta^{13}\text{C}_{\text{CaCO}_3}^{\text{TOT}}$ ) was calculated as a weighted mean of the  $\delta^{13}\text{C}_{\text{CaCO}_3}^i$  values. Results of the calculations are summarized in Figure 4, from which several interesting conclusions about the dynamics of the precipitation process can be drawn:

1) The  $^{13}\text{C}$  content of individual portions of  $\text{CaCO}_3$  increases strongly during the initial stages of precipitation. This is mainly due to an ongoing outgassing process accompanied by a relatively large isotope fractionation factor for the  $\text{HCO}_3^- \rightarrow \text{CO}_2$  reaction which should be compared with the small value of  $\epsilon_{\text{CaCO}_3-\text{HCO}_3^-}$  (cf Table 1). This “two-sink,” Rayleigh-type process results in values which, for a certain interval, may be even higher than equilibrium values with atmospheric  $\text{CO}_2$ . Such an “inertia” effect can be seen especially well in the  $\delta^{13}\text{C}_{\text{CaCO}_3}^i$  curve calculated for  $15^\circ\text{C}$ . In later stages of precipitation, when the  $\text{P}_{\text{CO}_2}$  in solution is only 10–20% higher than in the bulk atmosphere, the influence of atmospheric  $\text{CO}_2$  becomes noticeable, bending the  $\delta^{13}\text{C}_{\text{CaCO}_3}^i$  curve towards the equilibrium value.

2) Carbonate solutions formed under lower partial pressures of  $\text{CO}_2$  (open or closed system) precipitate  $\text{CaCO}_3$  more slowly and with higher  $\delta^{13}\text{C}_{\text{CaCO}_3}^i$  values than the solutions formed under higher  $\text{P}_{\text{CO}_2}$  values.

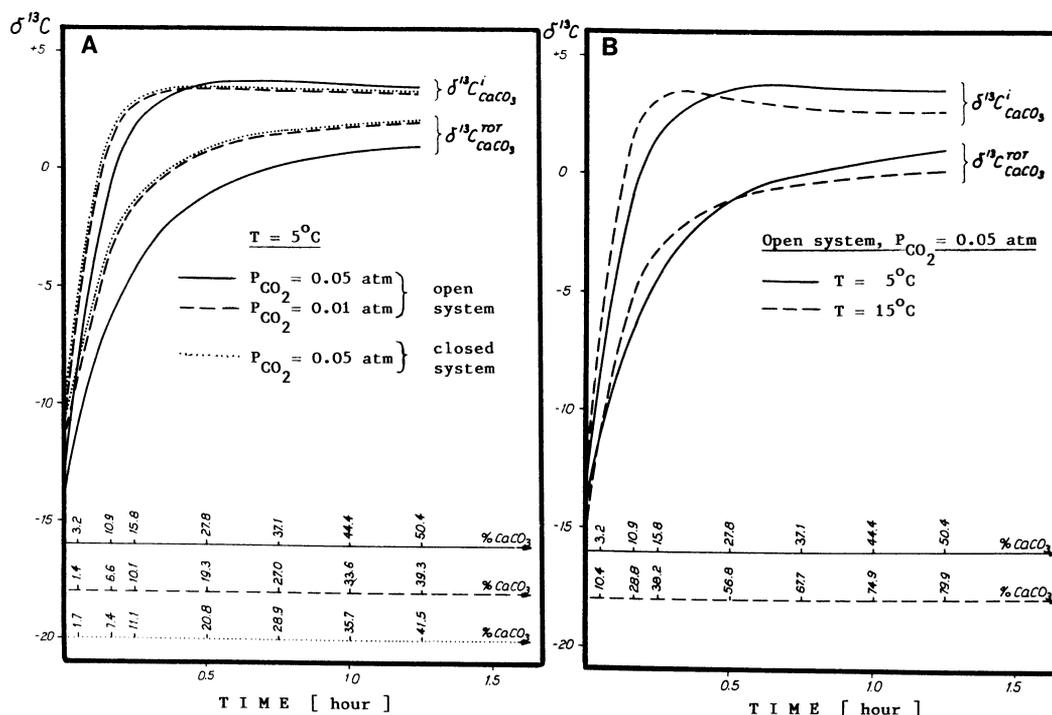


Fig 4A. Changes in  $\delta^{13}\text{C}$  values of individual portions ( $\delta^{13}\text{C}_{\text{CaCO}_3}^i$ ) and total precipitated ( $\delta^{13}\text{C}_{\text{CaCO}_3}^{\text{TOT}}$ ) calcite as a function of time elapsed since the beginning of the precipitation process, under different conditions of carbonate solution formation. Percentage of the  $\text{CaCO}_3$  precipitated from the beginning of the process is also indicated. B. Temperature influence on  $\delta^{13}\text{C}_{\text{CaCO}_3}^i$  and  $\delta^{13}\text{C}_{\text{CaCO}_3}^{\text{TOT}}$  values during precipitation.

3) The influence of the temperature on the precipitation rate of  $\text{CaCO}_3$  is noticeable. The change from 5–15°C results in an increased precipitation rate by a factor of 2–3, depending on the actual stage of the precipitation process. This is due to the temperature dependence of the rate constants  $k_{-1}$  and  $k_{-2}$ .

#### *Influence of $\delta^{13}\text{C}$ of Soil $\text{CO}_2$*

In order to examine the influence of different  $\delta^{13}\text{C}$  values of soil  $\text{CO}_2$  on isotopic composition of precipitating calcite, the necessary numerical calculation was made according to the procedure described previously. The values of soil  $\text{CO}_2$  in the order of –30, –20 and –16‰ vs PDB was assumed.

In general, the time dependence of  $\delta^{13}\text{C}_{\text{CaCO}_3}^{\text{TOT}}$  and  $\delta^{13}\text{C}_{\text{CaCO}_3}^{\text{i}}$  of the precipitating calcite is similar to that presented on Figure 4. However, starting points of the  $\delta^{13}\text{C}_{\text{CaCO}_3}^{\text{i}}$  and  $\delta^{13}\text{C}_{\text{CaCO}_3}^{\text{TOT}}$  curves are shifted with respect to analogous points on Figure 4 calculated per  $\delta^{13}\text{C}$  of the soil  $\text{CO}_2$  equal to –25‰. For extreme values of  $\delta^{13}\text{C}$  of the soil  $\text{CO}_2$ , *ie.*, –30 and –16‰, the  $\delta^{13}\text{C}_{\text{CaCO}_3}^{\text{i}}$  in open-system conditions reaches the following values respectively:

- 22.0 and –6.3‰ for  $P_{\text{CO}_2} = 0.05$  atm at 5°C
- 17.5 and –5.4‰ for  $P_{\text{CO}_2} = 0.01$  atm at 5°C
- 21.1 and –7.1‰ for  $P_{\text{CO}_2} = 0.05$  atm at 15°C

For the closed system with  $P_{\text{CO}_2} = 0.05$  atm at  $t = 5^\circ\text{C}$ , the corresponding values are –13.8‰ and –6.6‰. Both  $\delta^{13}\text{C}_{\text{CaCO}_3}^{\text{TOT}}$  and  $\delta^{13}\text{C}_{\text{CaCO}_3}^{\text{i}}$  approach equilibrium with atm  $\text{CO}_2$  as the rate of precipitation approaches zero. The higher the  $\delta^{13}\text{C}$  of soil  $\text{CO}_2$ , the more rapidly  $\delta^{13}\text{C}_{\text{CaCO}_3}^{\text{TOT}}$  and  $\delta^{13}\text{C}_{\text{CaCO}_3}^{\text{i}}$  increase at the initial stages of the precipitation process.

#### CONCLUDING REMARKS

Our model can be regarded as an up-to-date approach towards better understanding of the physical and chemical parameters controlling the isotopic composition of carbonate deposits formed in a cave environment. In numerical calculations, the most recent values of the equilibrium and kinetic chemical reaction constants were used together with the widely accepted values of carbon isotope fractionation factors. Supersaturation of the solution as a prerequisite for the initiation of precipitation was introduced in accordance with recent experimental data. The precipitation rates of  $\text{CaCO}_3$  obtained in the model ( $10^{-7}$ – $10^{-8}$  mol/L s) are in satisfactory agreement with the values quoted in literature (Dreybrodt 1985).

For a temperature close to +5°C, which is typical for most mid-latitude caves, the model predicts values of  $\delta^{13}\text{C}$  of precipitated calcite in the range of ca –16 to +3‰, depending on particular conditions of the precipitation process. The majority of  $\delta^{13}\text{C}$  values measured in speleothems are in the range of –11 to –5‰. This, with model predictions, suggests that only several percent of the total carbon in the solution is precipitated. It is worth noting that 100% yield of the precipitation would lead to yearly growth layers of speleothems up to two orders of magnitude larger than observed in nature.

Although the agreement between measured and calculated  $\delta^{13}\text{C}$  values of speleothems argues for the validity of the model, we should not forget the simplified assumptions on isotopic equilibrium between  $\text{HCO}_3^-$  and  $\text{CO}_{2\text{w}}$  reservoirs in solution, the absence of backward reaction  $\text{CO}_{2\text{w}} \rightarrow \text{HCO}_3^-$  and of concentration gradients for  $\text{H}^+$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  ions in solution.

#### REFERENCES

- Buhmann, B and Dreybrodt, W 1985 The kinetics of calcite dissolution and precipitation in geologically relevant situations of karst areas. *Chem Geol* 48:189–211.
- Dandurand, J.L, Gourt, R, Hoefs, J, Menschel, G, Schott, J and Usdowski, E 1982 Kinetically controlled variations of major components and carbon and oxygen isotopes in a calcite-precipitating spring. *Chem Geol* 36:299–315.
- Dreybrodt, W 1980 Deposition of calcite from thin films of natural calcareous solutions and the growth of speleothems. *Chem Geol* 29:89–105.

- Dreybrodt, W 1982 A possible mechanism for growth of calcite speleothems without participation of biogenic carbon dioxide. *Earth & Planetary Sci Letters* 58:293–299.
- Garrels, RM 1960 *Mineral equilibria*. New York, Harper & Row:21–42.
- Geyh, MA, Franke, HW and Dreybrodt, W 1983 Anormal grosse  $\delta^{13}\text{C}$ -Werte von Hochgebirgssinter, Vergeblicher Versuch einer palaeoklimatischen Bedeutung. *Bodmerenalp/SZ*:49–61.
- Hendy, CH 1971 The isotopic geochemistry of speleothems – I. The calculation of the effects of different modes of formation on the isotopic composition of speleothems and their applicability as palaeoclimatic indicators. *Geochim et Cosmochim Acta* 35:801–824.
- Hoover, TE and Berkshire, DC 1969 Effects of hydration on carbon dioxide exchange across an air-water interface. *Jour Geophys Research* 74:456–464.
- Langmuir, D 1984 Physical and chemical characteristics of carbonate water. *In Guide to the hydrology of carbonate rocks. UNESCO Studies and reports in hydrology ser*:69-131.
- Michaelis, J, Usdowski, E and Menschel G 1985 Partitioning of  $^{13}\text{C}$  and  $^{12}\text{C}$  on the degassing of  $\text{CO}_2$  and the precipitation of calcite — Rayleigh-type fractionation and a kinetic model. *Am Jour Sci* 285:318–327.
- Mook, WG, Bommerson, JC and Staverman, WH 1974 Carbon isotope fractionation between dissolved bicarbonate and gaseous carbon dioxide. *Earth & Planetary Sci Letters* 22:169–176.
- Salomons, W and Mook, WG 1986 Isotope geochemistry of carbonates in the weathering zone. *In Fritz, P and Fontes, J Ch, eds, Handbook of environmental isotope geochemistry 2. The terrestrial environment* B. Amsterdam, Elsevier:239–269.
- Siegenthaler, U and Münnich, KO 1981  $^{13}\text{C}/^{12}\text{C}$  fractionation during  $\text{CO}_2$  transfer from air to sea. *In Bolin, B, ed, Carbon cycle modelling*. Chichester, John Wiley & Sons:249–257.
- Thode, HG, Shima, M, Rees, CE and Krishnamurthy, KV 1965 Carbon-13 isotope effects in systems containing carbon dioxide bicarbonate, carbonate and metal ions. *Can Jour Chem* 43:582–595.
- Usdowski, E, Hoefs, J and Menschel, G 1979 Relationship between  $\text{C}^{13}$  and  $^{18}\text{O}$  fractionation and changes in major element composition in a recent calcite-depositing spring—a model of chemical variations with inorganic  $\text{CaCO}_3$  precipitation. *Earth & Planetary Sci Letters* 42:267–276.
- Vogel, JC, Grootes, PM and Mook, WG 1970 Isotopic fractionation between gaseous and dissolved carbon dioxide. *Zeitschr Physics* 230:225–238.