

ISOTOPIC APPROACH TO CALCITE DISSOLUTION AND PRECIPITATION IN SOILS UNDER SEMI-ARID CONDITIONS

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(Received September 22, 1986; revised and accepted June 15, 1987)

Abstract

Dever, L., Fontes, J.Ch. and Riché, G., 1987. Isotopic approach to calcite dissolution and precipitation in soils under semi-arid conditions. *Chem. Geol. (Isot. Geosci. Sect.)*, 66: 307-314

Two phases of crystallization of secondary calcite are identified in shallow soil horizons from northeastern Brazil where present-day climatic conditions are semi-arid. The ¹⁴C and ¹³C contents of the total dissolved inorganic carbon (TDIC) from soil solutions are compatible with open-system conditions. In the deeper part of the profile (1.5-3-m depth) the precipitation of secondary calcite is attributed to the degassing of solutions under wet climatic conditions. Interpretation of the radiocarbon activities leads to ages between 22,000 and 17,000 yr. for the pure secondary calcite. In the upper part (0.3-1.5-m depth) of the profile, active formation of calcite through dissolution-precipitation cycles is occurring. In this zone the precipitation is controlled mainly by the evaporation of soil solution as shown by the progressive enrichment in ¹⁸O of secondary carbonates.

The accretion of calcite occurs at the surface and at 1.5-m depth due to changes in the position of the evaporation front.

1. Introduction

Dissolution and precipitation processes usually lead to a change in the carbon isotope composition of the secondary carbonate formed (e.g., Magaritz, 1973; Wallick, 1976; Salomons et al., 1978; Hillaire-Marcel, 1979; Magaritz and Amiel, 1980; Magaritz et al., 1981; Dever et al., 1983; Gardner, 1984). This variation occurs through the addition of biogenic carbon into the solid phase. The dating of secondary calcite for palaeoclimatic and/or palaeohydrologic purposes requires a knowledge of the isotopic geochemistry of the system which prevailed during the dissolution and precipitation of the calcite. The carbon ratio between gaseous and liquid

phases determines whether or not the system is open or closed with respect to carbon dioxide during dissolution (Wigley, 1975). The precipitation of secondary calcite is caused mainly by degassing and/or evaporation of the soil solution. Taking into account the palaeoclimatic conditions which lead to dissolution and precipitation, the isotopic composition of the secondary calcite may then be related to climatic changes during the late Pleistocene and Holocene.

2. Profiles

Weathering of the limestone of late Proterozoic age in northeast Brazil can reach up to 3 m

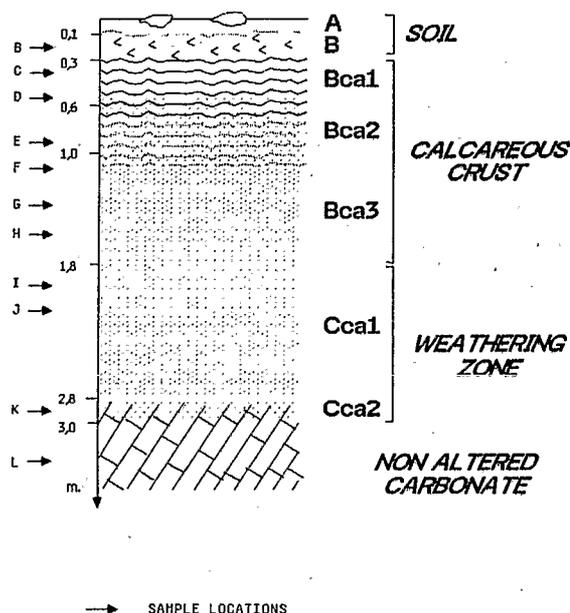


Fig. 1. Alteration profile lying on Proterozoic carbonate from Irecê (NE Brazil).

in depth (Riché et al., 1982). At the top of the sequence the soil (0–0.3 m) represents a decarbonation zone. It contains some relics of the undissolved original matrix. The soil overlies a subhorizontal lime crust (0.3–1.5 m) which is hard at the top and poorly cemented at the bottom. Beneath this crust isovolumetric weathering is observed (1.5–3 m). The decrease in weathering with depth correlates with a change in the colour from white to black. The original subvertical dip of the limestone is preserved in the vicinity of the unaltered matrix (Fig. 1).

Because the unaltered matrix has a very low microporosity, water percolation occurs mainly in fissures. Due to the in situ recrystallization of the calcite crystals the microporosity increases with weathering but it decreases in the lime crust owing to the precipitation of secondary calcite (needles).

3. Sampling

The matrix was sampled from surface to the bottom of the weathering zone (Fig. 1) where

secondary calcite had been isolated. From the gaseous phase samples of volume sufficient to contain 1–2 cm³ STP CO₂ were collected in previously evacuated glass vessels, connected to hollow needles driven to different depths. Soil water was extracted by distillation under vacuum for ¹⁸O analysis and groundwater was taken from two boreholes (Z₁ and Z₂) in the same area for chemical and isotope analyses (Table I). ¹³C and ¹⁴C measurements were performed on aliquots of the TDIC precipitated with BaCl₂·2H₂O at high (9–10) pH obtained by addition of pure (carbonate free) NaOH solution.

4. Gas–solution–solid interactions

In the gaseous phase the ¹³C contents vary with depth, being –15.53, –15.42, –15.13, –14.60 and –14.27‰ at 0.1, 0.3, 0.5, 0.6 and 0.7 m, respectively, in profile 1. This range of high values can be attributed to the changes in vegetal cover (castor oil plant to corn) in the last few years, castor oil, a C₃ plant, releases a lighter CO₂ than corn which is a C₄ plant. The ¹³C content of the soil CO₂ thus reflects a mixture of the two origins (observed values for corn plant and for humus layer –12.0 and –24.5‰, respectively). The slight enrichment with depth is attributed to partial isotopic equilibration between the gas and the solid phase. This process could occur via the aqueous phase through calcite dissolution–precipitation. If the mineralization of the soil CO₂ takes place under isotopic equilibrium with the gas phase being renewed continuously (open-system conditions) the ¹³C and ¹⁴C contents of the TDIC (Table I) at isotopic equilibrium can be calculated according to Deines et al. (1974), Wigley et al. (1978) and Dever et al. (1982):

$$\delta_{\text{TDIC}} = \delta_g + K_0 p_{\text{CO}_2} [\text{TDIC}]^{-1} [\epsilon_{\text{a-g}} + K_1 \epsilon_{\text{b-g}} (a_{\text{H}^+})^{-1} + K_1 K_2 \epsilon_{\text{c-g}} (a_{\text{H}^+})^{-2}] \quad (1)$$

TABLE I

Chemical and isotopic results

(a) Chemical analyses and calculated thermodynamic conditions of the calco-carbonic system

T	pH	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ ⁻	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	$\alpha_{\text{H}_2\text{CO}_3}$	$\alpha_{\text{HCO}_3^-}$	$\alpha_{\text{CO}_3^{2-}}$	SI _{calcite}	f_{CO_2}	
(°C)										($\times 10^{-5}$)	($\times 10^{-3}$)	($\times 10^{10-5}$)		($\times 10^{-2.5}$)	
Z ₁	25	7.2	8.45	4.61	3.22	0.07	1.92	3.40	1.56	10.54	9.3	1.6	0.3	0.25	0.9
Z ₂	25	7.2	5.30	4.12	3.04	0.08	2.16	2.33	0.77	7.24	8.5	1.9	0.4	0.21	0.8

(b) Isotopic composition of the TDIC for groundwater; measured and calculated values at equilibrium

	$\delta^{13}\text{C}$ (‰ vs. PDB)		$A^{14}\text{C}$ (pmC)		$\delta^{18}\text{O}$ (‰ vs. SMOW)	$\delta^2\text{H}$ (‰ vs. SMOW)
	calculated	measured	calculated	measured		
Z ₁	-13.57	-10.82	101.7	94.1	-4.52	-31.3
Z ₂	-13.47	-11.38	101.7	95.4	-5.53	-38.0

α = chemical activity; SI_{calcite} = saturation index of calcite; f_{CO_2} = CO₂ fugacity ($10^{-2.5}$ atm.); ionic contents in meq l⁻¹.

$$A_{\text{TDIC}} = \left(A_g K_0 P_{\text{CO}_2} \left[\{ 1 + (2.3 \epsilon_{a-g} \cdot 10^{-3}) \} \right. \right. \\ \left. \left. + \{ 1 + (2.3 \epsilon_{b-g} \cdot 10^{-3}) \} K_1 (a_{\text{H}^+})^{-1} \right. \right. \\ \left. \left. + \{ 1 + (2.3 \epsilon_{c-g} \cdot 10^{-3}) \} \right. \right. \\ \left. \left. \times K_1 K_2 (a_{\text{H}^+})^{-2} \right] \right) [\text{TDIC}]^{-1} \quad (2)$$

where K_0 , K_1 , K_2 are the constants of dissociation for CO₂ dissolution, and first and second dissociation of H₂CO₃ ($10^{-1.46}$, $10^{-6.35}$ and $10^{-10.33}$ at 25°C), respectively [Plummer et al. (1978) give the temperature dependence of these]; ϵ_{a-g} , ϵ_{b-g} , ϵ_{c-g} are ¹³C isotope fractionation factors (in ‰) for dissolved CO₂, HCO₃⁻ and CO₃²⁻ with respect to gaseous CO₂; (-1.06‰, +7.91‰, +7.58‰ at 25°C), respectively [their temperature dependence is given in Mook (1980)]; TDIC is the chemical activity of the total dissolved inorganic carbon; δ_g , A_g are the ¹³C (in ‰) and ¹⁴C contents (in pmC) of the gaseous CO₂, respectively; 2.3 is the ratio between isotope enrichment factors: $\epsilon^{14}\text{C} = 2.3 \epsilon^{13}\text{C}$ (experimental data from Saliège and Fontes, 1984); and a_{H^+} is the chemical activity of H⁺

Values of δ_{TDIC} are calculated using eq. 1 assuming that values of δ_g are derived from the

organic matter of the C₃ photosynthetic cycle (where the ¹³C of the gas phase is ~ -21 ‰ (e.g., Galimov, 1966; Lerman, 1972; Fritz et al., 1978; Rightmire, 1978; Dörr and Munnich, 1979; Reardon et al., 1979; Dever et al., 1983; Haas et al., 1983). Table I indicates that calculated values are close to -13 ‰ for the TDIC in groundwater. The difference between this and the measured values (~ -11 ‰) is related to a minor supply of carbon from the matrix according to:

$$\delta_{\text{TDIC}} = (1-x) \delta_{\text{TDIC calc.}} \\ + x (\delta_{\text{solid carb.}} + \epsilon_{\text{TDIC-solid carb.}}) \quad (3)$$

Using the observed value of $\delta_{\text{solid carb.}} = +11$ ‰, it follows that a fraction $x \doteq 9\%$ of the TDIC has been obtained through calcite dissolution. Since the solution is saturated with respect to the calcite (Table I), this admixture of carbon into the aqueous phase must occur through a process of dissolution and precipitation under non-steady-state conditions (steady state would imply that the ¹³C content of the TDIC would be in equilibrium with the surface layers of the solid phase).

Using the same value of x for the ¹⁴C balance it follows that A_g calculated from an analogous equation to eq. 3 is 104%. This value is reasonably compatible with the average activity of the

TABLE II

Radiocarbon and stable isotopes contents of solid carbonates from the alteration profiles

No.	Depth (cm)	$\delta^{13}\text{C}$ (‰ vs. PDB)	$\delta^{18}\text{O}$ (‰ vs. PDB)	$A^{14}\text{C}$ (pmC)
<i>Profile 1:</i>				
C	30	-7.42	-4.32	—
D	55	-7.67	-4.05	11.2
E	80	-8.06	-4.15	15.2
F	105	-7.90	-4.40	—
G	130	-7.62	-4.87	12.8
H	155	-7.00	-4.83	—
I	190	-6.79	-4.82	9.2
J	205	-6.83	-5.26	4.1
K	255	+0.23	-6.14	6.7
L	300	+6.43	-7.05	2.6
<i>Profile 2:</i>				
1	15	-10.03	-7.66	20.5
2	45	-8.18	-4.41	25.5
3	80	-7.98	-4.05	16.9
4	210	-8.19	-4.90	5.0
5	280	-8.02	-5.39	11.0
6	300	+3.46	-4.72	1.6
7	320	+11.16	-3.73	0.0
8	350	+11.03	-3.79	—

atmospheric CO_2 in the years preceding the nuclear tests (Nydal and Lövseth, 1983).

5. Solid phase (Table II)

The unusually high $\delta^{13}\text{C}$ -values (+11 and +6.4‰) measured for the original limestone in the profile are related to a reducing environment where methanogenesis took place, giving rise to cogenetic CO_2 highly enriched in ^{13}C (Fritz et al., 1971).

The solid carbonate in the upper part of the unsaturated zone, weathering zone and lime crust, shows fairly constant ^{13}C contents: $-7.61 \pm 0.37\text{‰}$ in profile 1 and $-8.09 \pm 0.11\text{‰}$ in profile 2 (Table II). These values are higher than expected for calculated values at equilibrium (at 20°C) with the aquifer TDIC (-13.5 and -14.0‰). If dissolution occurs under open-system conditions (i.e. the isotopic composition of the TDIC is derived from the gas one) and the precipitation is driven by degassing of the solution, then the corresponding en-

richment in ^{13}C of the TDIC is given by (Dever et al., 1983):

$$\delta_1 - \delta_2 \doteq \frac{1}{2} [\epsilon_{b-g} + \epsilon_{b-s}] [(b_1 - b_2/b_1)] \quad (4)$$

or if a "Rayleigh-type" process occurs (Michaelis et al., 1985) then:

$$\delta_1 - \delta_2 \doteq \frac{1}{2} [\epsilon_{b-g} + \epsilon_{b-s}] \ln b_2/b_1 \quad (5)$$

where δ_1, δ_2 are the isotopic compositions of the liquid phase (TDIC) before and after degassing, respectively; $\epsilon_{b-g}, \epsilon_{b-s}$ are the isotopic enrichment factors between HCO_3^- , CO_2 gas and CaCO_3 , respectively [values of ϵ are equilibrium ones since the chemical reaction is rate limiting. Any kinetic fractionation would thus take place at the liquid-gas interface between dissolved (a) and gaseous (g) CO_2 when CO_2 is degassing and would probably be limited since the equilibrium value of ϵ_{a-g} is low]; and b_1, b_2 are the HCO_3^- concentrations in the solution before (1) and after (2) degassing, respectively.

This treatment assumes that: (1) H_2CO_3 and CO_3^{2-} can be neglected when pH is between 7 and 8; and (2) equimolar quantities of carbon are lost from the solution by degassing, and by precipitation of solid carbonate, i.e. the solution cannot become supersaturated (this may be a crude approximation).

Considering an enrichment in ^{13}C of $\sim 5\text{--}6\text{‰}$ between calculated and measured values for the secondary calcite, eq. 5 leads to a bicarbonate ratio b_2/b_1 close to 0.3. In an open system this ratio could be related to the ratio of p_{CO_2} -values by the relation:

$$b_2/b_1 = [K_0 K_1 (a_{\text{H}^+})^{-1} p_{\text{CO}_2}]_{(2)} / [K_0 K_1 (a_{\text{H}^+})^{-1} p_{\text{CO}_2}]_{(1)} = 0.3 \quad (6)$$

If it is assumed that there are no significant temperature variations and pH is stable (pH at saturation with respect to the calcite), the variation in p_{CO_2} required for such enrichment is less than one order of magnitude. Such p_{CO_2} variations have often been observed in the unsaturated zone (e.g., Fritz et al., 1978; Rightmire, 1978; Dörr and Munnich, 1979; Reardon

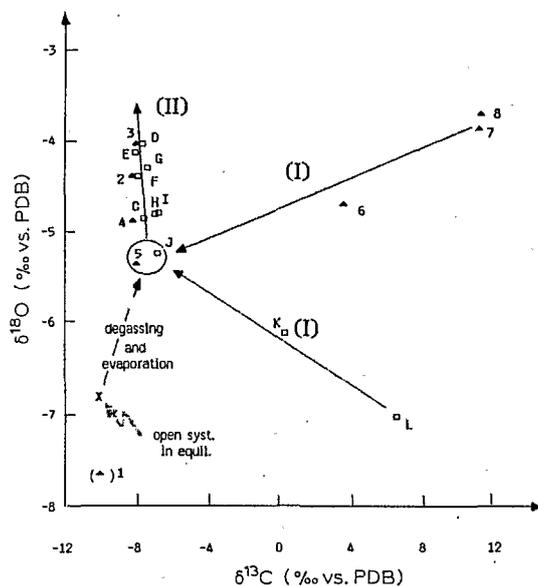


Fig. 2. Evolution of the stable isotope contents in the solid phase during the two pedogenetic phases (*squares*=profile 1; *triangles*=profile 2; X: calcite in equilibrium with water and TDIC in the saturated zone).

et al., 1979; Dever et al., 1983; Haas et al., 1983).

The carbonates of the rock matrix show large differences in stable-isotope composition between the two profiles (sample L in profile 1 and samples 7 and 8 in profile 2 in Table II). Weathering processes acting on the matrix lead to ^{13}C and ^{18}O contents of -7 , -8‰ and -5.3 , -5.4‰ , respectively, towards the upper part of the weathering zone (1.8–2.0-m depth). In this zone, secondary calcite has been isolated and has isotope contents of -5.4‰ for both ^{13}C and ^{18}O . Corresponding values for $\delta^{13}\text{C}$ and ^{18}O contents of CO_2 gas and water in equilibrium (20°C) with this calcite are -16 and -8‰ , respectively. Points 5 and J (Fig. 2) represent the late evolution of a first type of alteration process (lines I in Fig. 2). Such evolutions could account for the observed mixture of two types of calcite in the profile. The secondary calcite is formed in equilibrium with present-day groundwater, slightly enriched in ^{13}C and ^{18}O through degassing and evaporation (true equilibrium with deep groundwater is marked as X in Fig. 2). The primary calcite, which is the

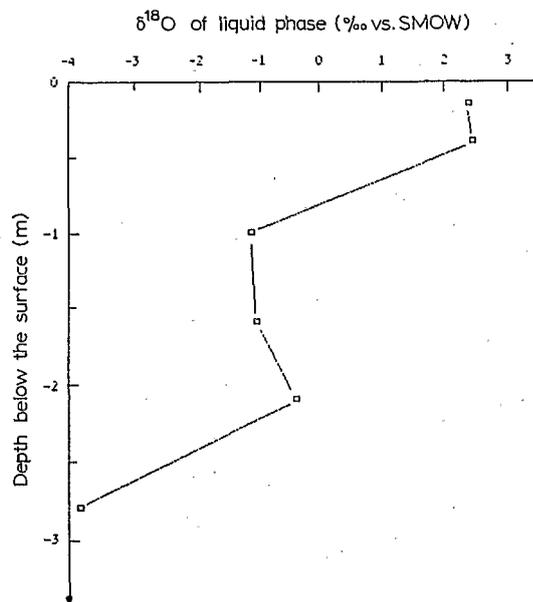


Fig. 3. Variation of the ^{18}O content in the liquid phase with depth.

other end-member of evolutions I, was formed from a water enriched in ^{18}O in a reducing environment. The gradual change of colour of the matrix from black to white can be related to the change in the ratio of the mixture of the two types of calcite.

From this solid carbonate, a second alteration process occurs (line II in Fig. 2). The progressive enrichment in ^{18}O from the bottom to the top of the lime crust indicates that precipitation is caused by the evaporation of the soil solution during capillary rise. Such an increase in heavy isotopes towards the surface is presently observed for the water (Fig. 3).

As precipitation of the secondary calcite reduces the porosity of the lime crust, the development of the process of alteration can be correlated with the amount and the intensity of rain. For a small amount of rain, the percolation of water will be limited to the topmost part of the profile (above the crust). In this zone, p_{CO_2} is high because of root activity and this induces calcite dissolution. During dry periods calcite precipitation is driven by evaporation of water and CO_2 losses from the soil solution. Therefore, the crust will grow from the top. For

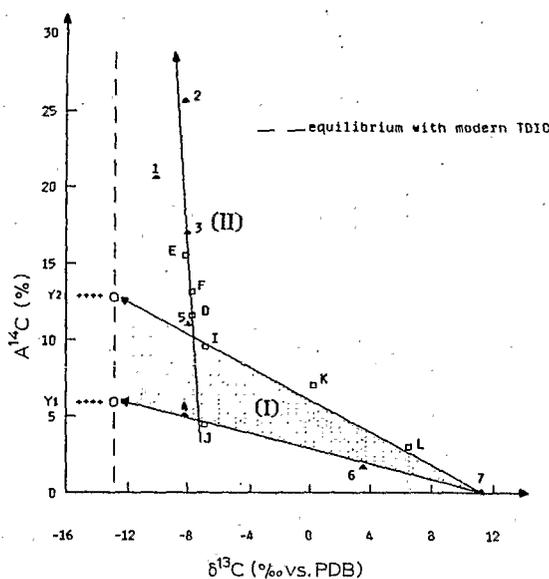


Fig. 4. Carbon isotope contents of the carbonates in the weathering zone (I) and calcareous crust (II); their evolutions during the alteration process.

heavy rains, the water will move downward through the lime crust to the weathering zone where dissolution may occur. In this case the lime crust will grow from the bottom with calcite precipitation induced by the evaporation of part of the soil solution after capillary rise.

6. Dating of the pedogenetic processes

Radiocarbon activities (in pmC) of the solid phase vary from zero at the bottom of the weathering zone to 20–25% at the top of the lime crust. The high radiocarbon activities of subsurface layers are due to biogenic carbon input during the dissolution and precipitation processes.

In a diagram $\delta^{13}\text{C}$ vs. $A^{14}\text{C}$ (Fig. 4) the two previously defined pedogenetic phases can be identified. The first one (evolution I) includes all the data from the weathering zone. The solid lines account for the mixing between the original carbonate, sample 7 ($A^{14}\text{C}=0\%$), and the secondary calcites. Assuming that the interactions between TDIC and the outside layers of the crystals can be neglected, the radiocarbon

activities of the secondary calcites will reflect radioactive decay since their crystallization. The open circles in Fig. 4 represent the calculated values of the secondary calcites precipitated in equilibrium with respect to the ^{13}C content of present-day TDIC in an open system (dashed line). The corresponding ^{14}C values, Y_1 and Y_2 , give radiocarbon activities of the end-members and represent pure secondary calcite. From these values one can calculate "radiocarbon ages" of 22,000 to 17,000 BP, respectively. It is not possible to decide whether this time range corresponds to one or two phases of weathering as suggested by the stable-isotope diagram.

A second pedogenetic phase takes place in the upper part of the profile (II). The carbonates from the weathering zone are partially dissolved and contribute to the accretion of the lime crust by precipitation of "tertiary" (third generation) calcites. The precipitation is induced by evaporation (cf. ^{18}O contents). The radiocarbon activities measured for these mixtures of carbonates from the bottom to the top of the lime crust indicate a post-Würm development. An extrapolation to ^{13}C equilibrium with present-day TDIC gives a ^{14}C activity of ~96% for a pure "tertiary" calcite. This value is close to the measured activity of the TDIC. Despite the large uncertainty on this extrapolation, this is in agreement with the concept of a still active crust accretion (Riché et al., 1982).

7. Conclusions

The stable-isotope compositions measured on the secondary calcite show that two main conditions led to calcite supersaturation of the solution causing precipitation of secondary carbonates:

- (1) the degassing of the solution which gives a higher $\delta^{13}\text{C}$ -values in the crystal than equilibrium ones; and
- (2) the evaporation of the solution which leads to an ^{18}O enrichment with respect to equilibrium with groundwater.

The isotopic disequilibrium during precipitation has a minor effect on the radiocarbon activities. Then, under open-system conditions, the ^{14}C contents of the secondary component of the mixing can be considered as indicators of "radiocarbon ages". At least two main pedogenetic phases have been identified. A first one took place under humid conditions between 22,000 and 17,000 B.P., where calcite precipitation was driven by degassing. These dates are in agreement with those measured on peat (32,000–16,000 B.P.) in Bolivia (Servant et al., 1981). A second one, giving rise to a calcareous crust, was developed by evaporation of the soil solution. The accretion of the crust is still active and the stable-isotope contents and the radiocarbon activities of the solid phase can be used for reconstructing palaeoclimatic conditions.

Acknowledgments

The authors thank G. Faure and G.B. Allison for their careful reading.

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