

## ISOTOPE GEOCHEMISTRY OF CARBONATE DISSOLUTION AND REPRECIPITATION IN SOILS

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### ABSTRACT

The processes of dissolution and reprecipitation of carbonates in soils developed on carbonate rocks, loess-derived soils, and marine clay soils were studied with the methods of stable isotope geochemistry. Between 10 and 50 percent of the carbonates present in the upper part of soils developed on carbonate rocks are newly formed. In loess-derived soils and in marine clay soils, up to 100 percent of the carbonates present may be newly formed. The efficiency of the dissolution-reprecipitation process varies between 10 and 30 percent. In the salt marsh investigated the dissolution is caused by the action of biogenic carbon dioxide.

### INTRODUCTION

Carbonates are an important constituent of the soil. The processes they are subject to are dissolution followed by (partial) reprecipitation. Reprecipitation can be easily recognized when it results in macroscopic concretions. However, when the newly formed carbonates are finely divided they are difficult to detect by conventional methods.

We have used the methods of stable isotope geochemistry in order to study the processes of dissolution and reprecipitation in a number of soils. Stable isotope geochemistry is based on small differences in the chemical behavior between isotopes of the same element [e.g., oxygen isotopes with mass 18 (<sup>18</sup>O) and 16 (<sup>16</sup>O), and carbon isotopes with mass 13 (<sup>13</sup>C) and 12 (<sup>12</sup>C)], causing variations in their natural abundance ratios. For instance, we will use the large differences in isotopic composition between newly formed freshwater carbonates and those derived from the parent material.

Reviews on the abundances of oxygen and carbon isotopes in nature were presented by Garlick (1969, 1974), Schwarcz (1969), and Hoefs (1973).

### EXPERIMENTAL METHODS

The isotopic analyses are performed on carbon dioxide prepared from the carbonate sam-

ples by treatment with 95 percent orthophosphoric acid. The presence of organic matter in most soil samples analyzed introduces an error in both the carbon and oxygen isotopic composition of less than -0.3‰ (Salomons 1974). Since this small shift has no influence on our conclusions, the time-consuming step of removing the organic matter from the sample prior to analysis was deleted.

Full details on our analytical procedures can be found in Mook (1968) and Mook and Grootes (1973).

The isotopic ratios are given as relative deviations from that of the PDB standard:

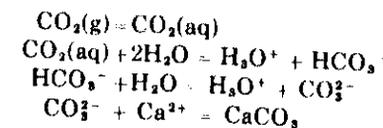
$$\delta(\text{‰}) = \frac{R_s - R_{st}}{R_{st}} \times 1000 \quad \begin{array}{l} R = {}^{13}\text{C}/{}^{12}\text{C}; \\ {}^{18}\text{O}/{}^{16}\text{O} \\ s = \text{sample} \\ st = \text{standard} \end{array}$$

The reproducibility of the analyses on pure carbonates is about  $\pm 0.05\text{‰}$ . Results are primarily based on  $\delta_{\text{PDB}}^{13}\text{C}$  and  $\delta_{\text{PDB}}^{18}\text{O}$  values for NBS-20 of -1.06 and -4.14‰, respectively.

### THEORY

#### 1. The isotopic composition of carbonates

The chemical reactions involved in the inorganic dissolution and reprecipitation of carbonates are:



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Each of these reactions is accompanied by an isotope fractionation (i.e., under equilibrium conditions as during slow reversible processes, the isotopic composition of an element in one compound is not equal to that in another).

In discussing the factors which determine the isotopic composition of calcium carbonate it is practical to use the fractionation between the carbonate mineral and the main reservoirs of oxygen and carbon, water, and dissolved bicarbonate, respectively.

The oxygen isotopic composition of carbonate is related to that of the water by

$$\delta^{18}(\text{CaCO}_3) \approx \delta^{18}(\text{water}) + \epsilon_1 \quad (1)$$

while the relation between the carbon isotopic composition of carbonate and dissolved bicarbonate is presented by

$$\delta^{13}(\text{CaCO}_3) \approx \delta^{13}(\text{HCO}_3^-) + \epsilon_2 \quad (2)$$

Values for  $\epsilon_1$  and  $\epsilon_2$  are tabulated in Table 1. Generally, the fractionation is temperature dependent. Since calcite is the most abundant carbonate species in the soil the respective  $\epsilon_2$  value should be taken from Rubinson and Clayton (1969).

Apart from the temperature during formation, the isotopic composition of carbonates depends on that of the surrounding water and bicarbonate. Large differences in the isotopic composition of water and dissolved bicarbonate in particular exist between fresh and sea water (Mook 1970). These differences are consequently reflected by carbonates formed on the land and in the marine environment.

TABLE 1

*The oxygen isotope fractionation between calcium carbonate and water ( $\epsilon_1$ ) and the carbon isotope fractionation between bicarbonate and calcium carbonate*

T	$\epsilon_1$ *	$\epsilon_2$ †	$\epsilon_2$ ‡
10°	+1.74	+0.10	-0.20
20°	-0.72	+0.85	+0.55
30°	-2.87	+1.50	+1.20

\* After Craig (1965).

† After Emrich et al. (1970); the crystal structure of the carbonate has not been determined.

‡ After Rubinson and Clayton (1969) for calcite at 25°C; the temperature coefficient is taken from Emrich et al. (1970).

## 2. The dissolution of carbonates in soils

The parent material for the carbonates in most soils are ancient marine carbonate rocks. The isotopic composition of these deposits is shown in Fig. 1. The dissolution of carbonates in soils is caused mainly by the action of biogenic carbon dioxide derived from decaying organic matter and root respiration. The dissolution can be presented schematically by the reaction:



The carbon dioxide in the soil atmosphere of temperate climates has a  $\delta^{13}\text{C}_\text{D}$  value varying between -26.5 and -23.5‰ (Galimov 1966). The reaction given above shows that about half of the carbon in the bicarbonate is derived from the carbonates, the remainder from the biogenic carbon dioxide. Therefore, if ancient marine carbonate rocks with a carbon isotopic composition of +1.5‰ are dissolved by biogenic carbon dioxide of -24.5‰, the resulting bicarbonate will have a carbon isotopic composition of -11.5‰. In the Netherlands and other temperate climatic regions the isotopic composition of the groundwater bicarbonate indeed shows values in this range (Mook 1970).

## 3. The reprecipitation of carbonates in the soil

A reprecipitation of carbonates is caused by either of two processes: (1) Movement of the soil solution towards an environment with a lower partial pressure of carbon dioxide. (2) Evaporation of the soil solution.

If relatively small amounts of the dissolved carbonates are reprecipitated (up to 20 percent) it is possible to use Eqs. (1) and (2) to determine the isotopic composition of the reprecipitated carbonates. However, when large amounts are reprecipitated the isotopic composition of the soil solution changes in the course of the process and it is necessary to calculate the isotopic composition of the precipitated carbonates correctly (Salomons 1974; Salomons et al. 1975).

In Fig. 1 the calculated isotopic composition of newly formed freshwater carbonates in a temperate climate is shown together with the composition of ancient marine carbonates. As can be seen it is possible to distinguish between ancient marine carbonate (parent material) and newly formed carbonates in the soil by using the carbon isotopic composition. However, the differences in oxygen isotopic composi-

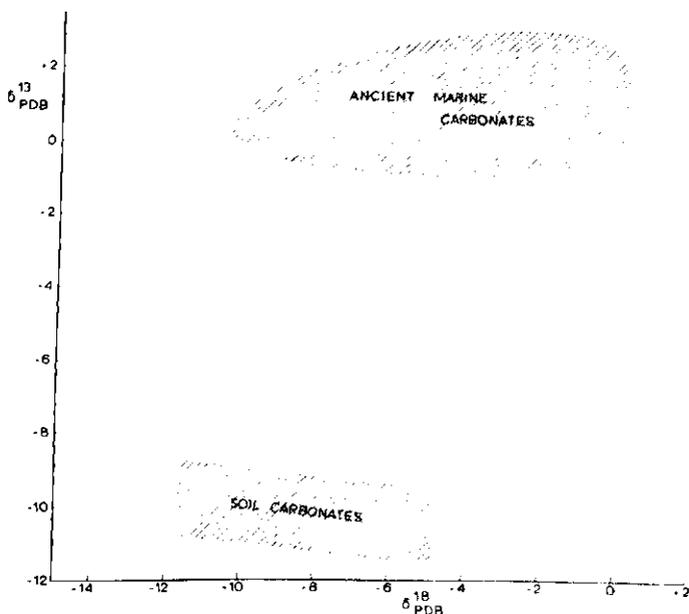


FIG. 1. The stable isotopic composition of ancient marine carbonates (data from Keith and Weber 1964) and the calculated composition of soil carbonates (temperature range  $10^{\circ}$ – $30^{\circ}$ C, oxygen isotopic composition of soil water  $-7.5 \pm 1\%$ , carbon isotopic composition of the dissolved bicarbonate  $12 \pm 1\%$ ).

tion are in most cases small.<sup>2</sup> Therefore, we will restrict our discussions to the carbon isotopic composition of the carbonates.

#### 4. The changes in the isotopic composition of carbonates during the evolution of a soil

The process of dissolution and partial reprecipitation of carbonates is not an occasional process but is being repeated many times in the course of a soil evolution. The question arises what changes are to be expected in the isotopic composition due to such a many-stage process.

The isotopic composition at each stage, depends of course, on the relative amount of newly formed carbonates. This again depends on the efficiency of the reprecipitation process (e.g., the percentage of the dissolved carbonates which become reprecipitated). Zero efficiency means that no reprecipitation takes place so that the isotopic composition of the soil carbonates remains equal to that of the parent material. A high reprecipitation efficiency causes relatively large changes.

<sup>2</sup> Generally, the soil carbonates will have more negative  $\delta^{18}$  values (Fig. 1).

The actual isotope effects due to the dissolution-reprecipitation process were calculated theoretically as a function of the remaining carbonate content of the soil. For the carbon isotopic composition of the parent material (ancient marine carbonates) and the newly formed carbonates we have taken values of 0 and  $-10\%$ , respectively. In order to calculate the changes in carbon isotopic composition the process was divided in a large number of steps. During each step it was assumed that a small amount (1 percent) of the carbonates present was dissolved from which solution carbonate precipitated with varying efficiency. The new isotopic composition of the soil carbonates of the new total carbonate content were then calculated (Fig. 2). In the next section we will use these curves to estimate the efficiency of the reprecipitation process in a number of soils.

#### THE ISOTOPIC COMPOSITION OF CARBONATES IN A NUMBER OF SELECTED SOILS

##### 1. Carbonates in soils developed on carbonate rocks

In France we studied a number of soils formed on a variety of mainly ancient marine carbonate

rocks (Table 2). At one locality it was possible to sample a soil formed on a freshwater carbonate rock (Chateau-London). The thickness of the A-horizon was in most cases about 30-40 cm. To study the isotope-geochemical behavior of the carbonates we sampled the topsoil (0-5 cm) and the parent material. Apart from the stable isotopic composition of the carbonates in

the soil and of the carbonate rocks, the carbonate content of the soil was determined also.

In all cases the isotopic composition of the soil turns out to be different from that of the parent material. As can be seen from Fig. 3 the  $\delta$  values of the soil carbonates are shifted towards more negative values.

As discussed before, such a shift is to be

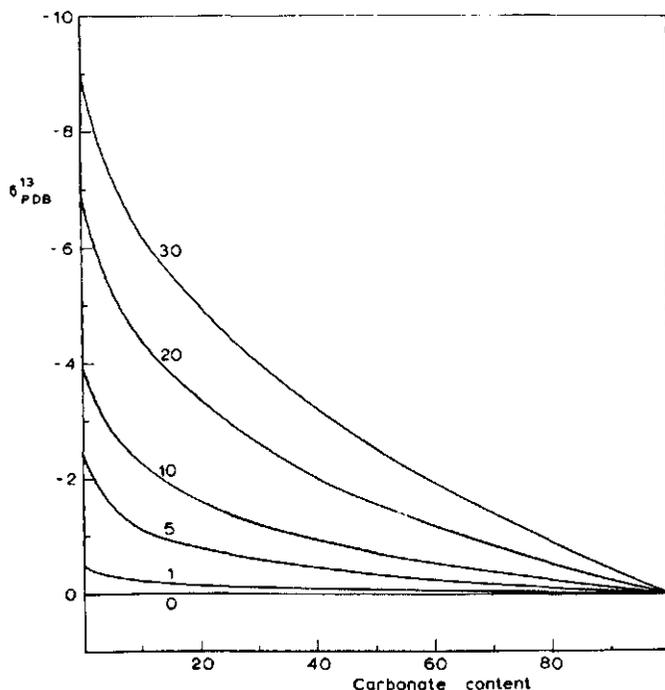


FIG. 2. The calculated isotopic composition of soil carbonates during the evolution of a soil. The efficiency of the reprecipitation process varies between 0 and 30 percent. The initial carbonate content is taken as 100. The carbon isotopic composition of the parent material and of the newly formed carbonates are taken as 0 and  $-10\text{‰}$ , respectively.

TABLE 2

*The isotopic composition (in ‰) of carbonates in soils developed on carbonate rocks*

No.	Locality in France	Age parent material	Rock carbonate		Soil carbonate		Carbonate content soil (%)
			$\delta_{PDB}^{13}$ (‰)	$\delta_{PDB}^{18}$ (‰)	$\delta_{PDB}^{13}$ (‰)	$\delta_{PDB}^{18}$ (‰)	
1	Lérouville	Jurassic	+1.71	-6.05	-0.21	-6.43	39.5
2	Aseraye	Triassic	-0.70	-5.90	-5.93	-7.78	8.8
3	Chaumont	Jurassic	+1.55	-3.87	-3.01	-7.68	11.6
4	Château-Landon	Tertiary	-4.39	-4.17	-8.92	-6.70	24.9
5	Château-Landon	Tertiary	-8.36	-6.26	-10.22	-7.83	20.7
6	Port-St-Nicolas	Cretaceous	+2.12	-1.81	-0.87	-3.72	70.5
7	Berru	Cretaceous	+1.30	-2.63	-0.61	-4.37	14.6
8	Berru	Cretaceous	+1.55	-3.87	-2.86	-4.97	6.2

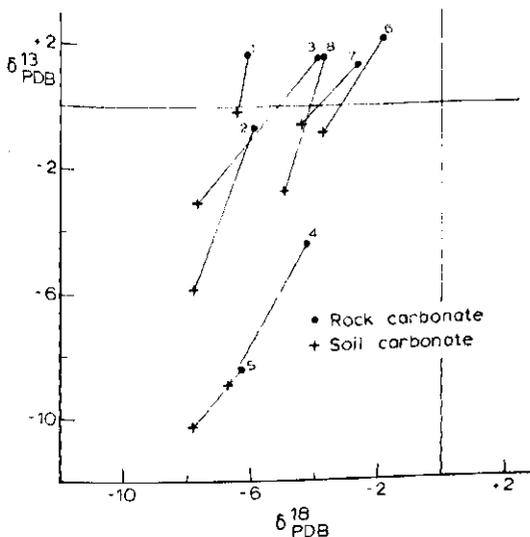


FIG. 3. Isotopic composition of carbonates in the soil, compared with the isotopic composition of the underlying carbonate rock. The numbers refer to the data given in Table 2.

expected when the carbonates are subject to a dissolution-precipitation process.

The amount of newly formed carbonates can be calculated from the carbon isotopic composition. If we assume that the newly formed carbonates are precipitated in equilibrium with the groundwater, their carbon isotopic composition should be about  $-10\text{‰}$ . Using this value  $\delta^{13}(\text{new})$  and the carbon isotopic composition of the parent material  $\delta^{13}(\text{p.m.})$ , we can calculate the amount of newly formed carbonates by using the formula:

$$\% \text{ (newly formed carbonates)} = \frac{\delta^{13}(\text{soil}) - \delta^{13}(\text{p.m.})}{\delta^{13}(\text{new}) - \delta^{13}(\text{p.m.})} \times 100$$

According to this estimation the amount of newly formed carbonates in the soils investigated varies between 10 and 50 percent.

From the carbonate content of these soils and the carbon isotopic composition of the carbonates the efficiency of the dissolution-precipitation process can be estimated (Fig. 2). In the soils discussed above the efficiency turns out to vary between 10 and 30 percent.

## 2. Carbonates in loess

Loess is an eolian sediment which in Europe commonly has been deposited in several stages.

After each deposition soil formation takes place resulting in carbonate losses and in the accumulation of organic matter. The recrystallization of carbonates in loess soils often appears as large concretions. The stable isotopic analyses confirm the fact that these are formed in a freshwater environment (Fig. 4). We further analyzed the isotopic composition of the finely grained carbonates in loess in three profiles. The first was in the southern part of the Netherlands, the second near Dolni Vestonice in Czechoslovakia, and the third near Fellabrunn, Lower Austria (Vogel and Zagwijn 1967).

The Dutch loess profile was sampled to a depth of 6 m. The uppermost 2 m are decalcified; in the remaining profile three ancient soils could be detected. These are indicated by I, II, and III in Fig. 5. The carbonate content of the most complete profile, no. II, increases with depth from about 8 to 16 percent. The  $\delta$  values in the upper part (about 300–400 cm) are shifted toward  $\delta$  values more negative than those in the lower part.

The processes occurring in this soil appear to be the same as in the case of soils developed on carbonate rocks: a dissolution followed by a partial reprecipitation of the carbonates. The isotopic composition of the carbonates in the lower part of the profile falls in the same range as found for ancient marine carbonates. Therefore, it seems likely that loess carbonate in this

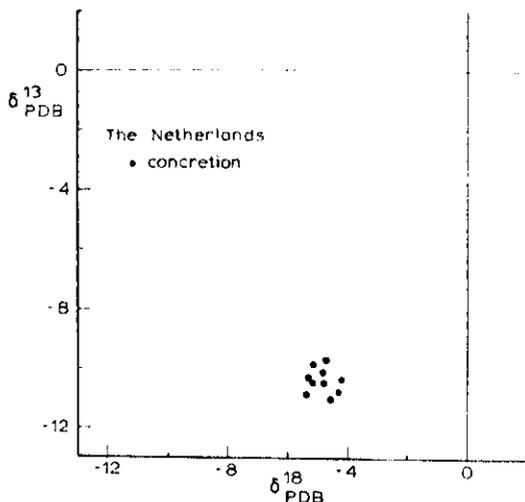


FIG. 4. The isotopic composition of concretions in loess deposits from the southern part of the Netherlands.

TABLE 3

The stable isotopic composition and the apparent C-14 age of the carbonates in less profiles from Dolni Vestonice and Oberfella Brunn. The samples were submitted by B. Klima and by F. Felgenhauer and J. Fink, respectively. The C-14 ages of the organic matter are from Vogel and Zagwijn ((1967). All  $^{14}\text{C}$  ages are conventional

Depth	% carbonates	$\delta_{\text{PDB}}^{13}$ (‰)	$\delta_{\text{PDB}}^{18}$ (‰)	Apparent C-14 age carbonates	C-14 age organic matter
Profile Dolni Vestonice (48°53'N lat., 16°40'E Long.)					
420 cm	8.0	-3.58	-5.53	GrN-6857 25 790 ± 320	GrN-2101 15 350 ± 1000
560 cm	—	—	—	—	GrN-2093 18 400 ± 700
680 cm	0.15	-13.20	-11.18	GrN-6861 10 100 ± 500	GrN-2092 28 300 ± 300
920 cm	10.1	-5.66	-6.61	GrN-6858 32 850 ± 660	GrN-2105 >34 000
1150 cm	—	—	—	—	GrN-2599 >51 800
1200 cm	—	-8.13	-8.13	GrN-6859 27 790 ± 370	—
1390 cm	2.2	-9.86	-10.70	GrN-6860 29 180 ± 460	GrN-2604 >50 000
Profile Oberfella Brunn (48°34'N lat., 16°00'E Long.)					
120 cm	17.1	-6.73	-6.82	GrN-6862 15 680 ± 190	GrN-1911 16 700 ± 800
230 cm	14.0	-6.26	-6.38	GrN-6863 24 275 ± 410	GrN-1901 31 800 ± 500
300 cm	7.9	-8.26	-7.78	GrN-6864 22 425 ± 350	GrN-2610 43 000 ± 700
350 cm	—	—	—	—	GrN-1800 42 300 ± 800*
400 cm	27.9	-3.02	-5.07	—	GrN-1740 42 100 ± 800*

\* According to Vogel and Zagwijn these ages are to be considered as minimum ages because of the presence of contamination from upper layers with higher  $^{14}\text{C}$  content. The pretreatment of GrN-2610 was more rigorous.

case is derived from ancient marine carbonate rocks.

In the loess profile from Dolni Vestonice only the top layers of the ancient soils were analyzed (Table 3). In addition to the stable isotopic composition the carbon-14 content of the carbonates as well as of the organic matter was determined. The carbon-14 activity of the organic matter gives the approximate age of the soil. The  $^{14}\text{C}$  ages above 40,000 years are considered to be minimum ages, because of the difficulties in removing infiltrated humic compounds with higher  $^{14}\text{C}$  activity (Vogel and Zagwijn 1967).

Contrarily, the carbon-14 content of the carbonates generally does not reflect the age of the soil. If no reprecipitation of dissolved carbonates occurs, the soil contains only the ancient carbonates having a  $^{14}\text{C}$  content below the detection limit (older than 50,000 years). However, the dissolution-reprecipitation process introduces carbon-14 into the soil carbonate. The apparent  $^{14}\text{C}$  age of this carbonate may as well be smaller as larger than the actual age of the soil at that level as revealed by the organic matter. The presence of the old parent material

makes the age apparently too large. On the other hand, when a renewed deposition of loess takes place, the formation of the organic matter is halted. A recipitation of carbonates from downward-seeping groundwater may, however, occur. In this case the carbon-14 age of the carbonates may become smaller than that of the organic matter in the same layer.

Comparing the data from the three profiles (Fig. 5 and Table 3) shows that more newly formed carbonates are present in the latter two profiles. In particular the samples taken at 680 and 1390 cm from the profile from Dolni Vestonice contain a very large proportion of newly formed carbonates. The apparent carbon-14 ages of the carbonates in these two soils are smaller than those of the organic matter, indicating that a reprecipitation of carbonates after the renewed deposition of loess has taken place.

### 3. Carbonates in salt marshes and marine clay soils

Along part of the Dutch and West-German coast an extensive accumulation of marine mud takes place. The carbonate content of these sediments varies between 10 and 25 percent

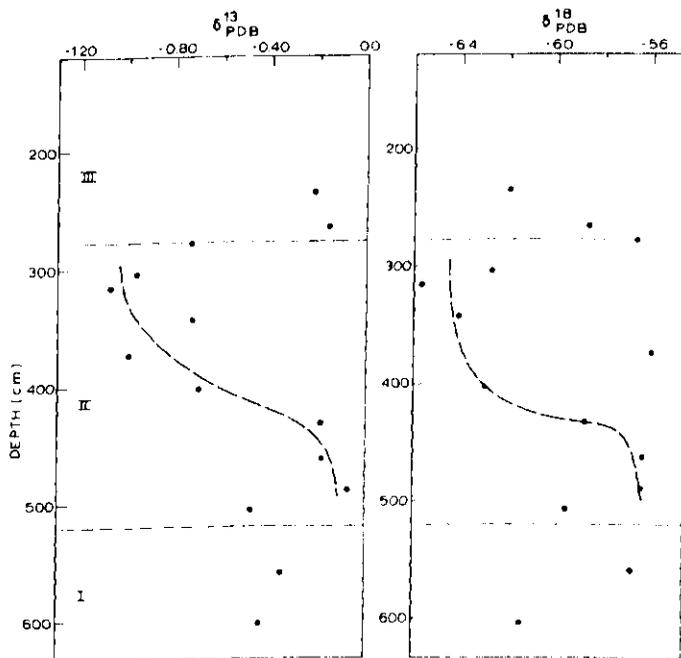


FIG. 5. The stable carbon and oxygen isotopic composition of carbonates in a loess profile. Locality: Schinnen, southern part of the Netherlands.

(Salomons 1975). When the sedimentation has reached the mean high-tide level, it is possible for plants to settle: the tidal flat is turned into a salt marsh. The now starting soil processes continue after embankment. They are particularly suitable for studying the behavior of the carbonates, since the age of the soil is approximately known (date of embankment).

As a region of more detailed investigation we selected the Dollard area in the northern part of the Netherlands. The oldest polder in this area was embanked in 1597. The carbonate content in the topsoil of this polder is 1–2 percent, whereas present-day tidal flat sediments from the same area contain about 11 percent carbonates. The present salt marsh in the Dollard originated after the last embankment in 1924.

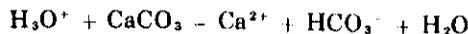
The carbonate content of the surface layers of the salt marsh is about 7 percent. This decalcification is also reflected in the calcium content of the groundwater which is four times the value found for the tidal flat (Salomons 1974).

As stated in the introduction the decalcification of soils is generally caused by the high partial pressure of carbon dioxide in the soil atmosphere, according to the reaction:



We also explained before that in this case the resulting bicarbonate in the groundwater will have a  $\delta^{13}C$  value of about  $-11\text{‰}$ .

However, salt marsh sediments generally contain large amounts of sulfides, the oxidation of which releases sulfuric acid (Brümmer et al. 1969). This also may cause a dissolution of the carbonates according to the reaction:



In this case the carbon in the bicarbonate is derived only from the solid carbonates; the  $\delta$  value will be therefore about  $0\text{‰}$ .

In analyzing the carbon isotopic composition of the bicarbonate it thus is possible to distinguish between these two processes.

We analyzed the carbon isotopic composition of the groundwater bicarbonate in the salt marsh on several occasions: the mean value found is  $-14.3 \pm 0.6\text{‰}$ . This value shows that in the Dollard salt marsh the biogenic carbon dioxide is responsible for the decalcification.

In order to determine whether part of the dissolved carbonates is being reprecipitated, the

carbonates in eleven surface samples of the salt marsh were analyzed isotopically. The result are:  $\delta^{13} = -1.7\text{‰}$  and  $\delta^{18} = -5.6\text{‰}$ . The mean isotopic compositions of the carbonates in the recent tidal flat sediments are  $-0.5$  and  $-4.3\text{‰}$ , respectively (Salomons 1975). Apparently, part of the dissolved carbonates is reprecipitated.

The data from the two profiles (Fig. 6) show that the reprecipitation is restricted to the upper part of the soil.

The same turned out to be true for the polders. The isotopic composition of the carbonates in two profiles from polders embanked in 1924 and 1819, respectively, shows that the

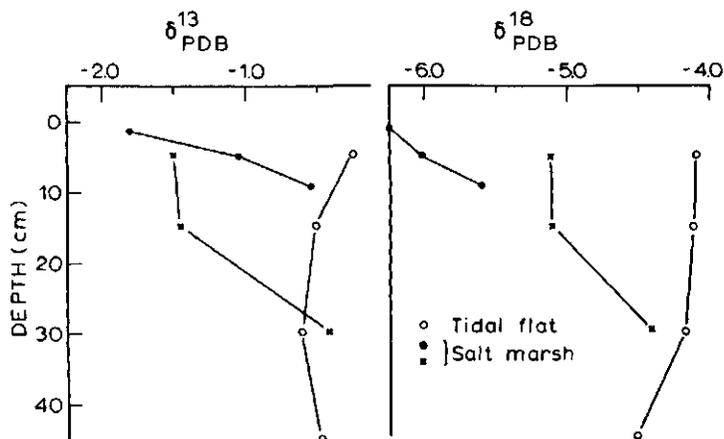


FIG. 6. The isotopic composition of carbonates in two profiles from the Dollard salt marsh and in one profile from the Dollard tidal flat.

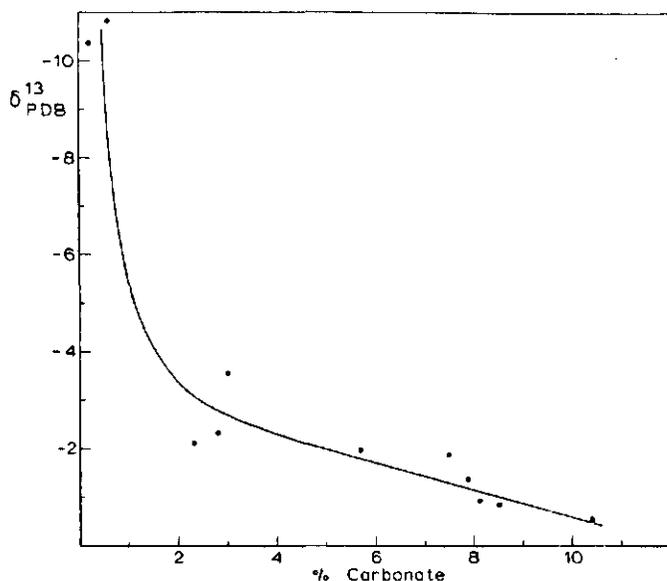


FIG. 7. The relationship between carbonate content and the carbon isotopic composition of the carbonates in marine clay soils.

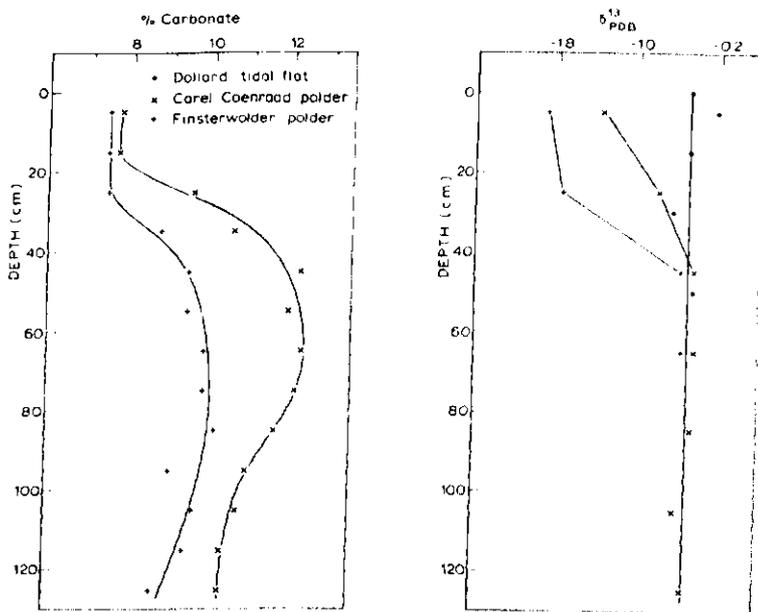


FIG. 8. The isotopic composition of carbonates in two marine soil profiles and in one sediment profile from the recent tidal flat area. The Carel Coenraad polder was embanked in 1924, the Finsterwolderpolder in 1819.

reprecipitation is restricted to the upper 0–50 cm (Fig. 7). Below this depth the  $\delta$  values are similar to those in tidal flat sediments.

To determine the efficiency of the reprecipitation process we analyzed the topsoils (0–10 cm) of polders embanked between 1597 and 1924.

The decalcification processes in the Dollard area result in a decrease of the total carbonate content from about 10 percent to 1–2 percent after 400 years. With increasing age of the polder, decreasing carbonate content, the proportion of freshwater carbonates in the soil increases (Fig. 8). If the carbonate content is about 1–2 percent, most of the carbonates present are newly formed. From a comparison between Figs. 2 and 8 we conclude that the efficiency of the reprecipitation process in the polders investigated is about 20 percent.

#### REFERENCES

- Brümmer, G., H. S. Grunwaldt, and D. Schroeder. 1970. Beiträge zur Genese und Klassifizierung der Marschen. II. Zur Schwefelmetabolik in Schlickten und Salzmarschen. *Z. Pflanzenernähr.* 128: 208–220.
- Craig, H. 1965. The measurement of oxygen paleotemperatures. Spoleto Conf. on Stable Isotopes in Oceanographic Studies and Paleotemperatures. Pisa, 1965.
- Emrich, K., D. H. Ehhalt, and J. C. Vogel. 1970. Carbon isotope fractionation during the precipitation of calcium carbonate. *Earth Planet. Sci. Lett.* 8: 363–371.
- Galimov, E. M. 1966. Carbon isotopes in soil CO<sub>2</sub>. *Geochem. Int.* 3: 889–897.
- Garlick, G. D. 1969. The stable isotopes of oxygen. In K. H. Wedepohl (ed.). *Handbook of geochemistry*, 8B. Springer-Verlag.
- Garlick, G. D. 1974. The stable isotopes of oxygen, carbon and hydrogen in the marine environment. In *The sea*, Vol. 5, Marine chemistry, E. D. Goldberg (ed.). Wiley.
- Hoefs, J. 1973. *Stable isotope geochemistry*. Springer-Verlag.
- Keith, M. L. and J. N. Weber. 1964. Carbon and oxygen isotopic composition of selected limestones and fossils. *Geochim. Cosmochim. Acta* 28: 1787–1816.
- Mook, W. G. 1968. *Geochemistry of the stable carbon and oxygen isotopes of natural waters in the Netherlands*. Diss. Univ. of Groningen.
- Mook, W. G. 1970. Stable carbon and oxygen isotopes in natural waters in the Netherlands. *Proc. I.A.E.A. Conf. Use of Isotopes in Hydrology*. Vienna, 1970: 163–190.
- Mook, W. G. and P. M. Grootes. 1973. The measuring procedure and corrections for the high-precision

- mass spectrometric analysis of isotopic abundance ratios, especially referring to carbon, oxygen and nitrogen. *Int. J. Mass Spect. Ion Phys.* 12: 273-298.
- Rubinson, M. and R. N. Clayton. 1969. Carbon-13 fractionations between aragonite and calcite. *Geochim. Cosmochim. Acta* 33:997-1002.
- Salomons, W. 1974. Chemical and isotopic composition of carbonates during an erosion-sedimentation cycle. Univ. Microfilms, Ann Arbor. Order no. 74-20094.
- Salomons, W. 1975. Chemical and isotopic composition of carbonates in recent sediments and soils from Western Europe. *J. Sediment. Petrol.* 45: 440-449.
- Salomons, W., A. Goudie, and W. G. Mook. 1975. The isotopic composition of calcrete deposits and soil carbonates from Europe Africa and India. In preparation.
- Schwarcz, A. P. 1969. The stable isotopes of carbon. In K. H. Wedepohl (ed.), *Handbook of geochemistry*, 6-B-I. Springer-Verlag.
- Vogel, J. C. and W. H. Zagwijn. 1967. Groningen radiocarbon dates VI. *Radiocarbon* 9: 63-106.