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natural stable isotopes for sediment transport studies

W. Salomons and W.G. Mook

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NATURAL STABLE ISOTOPES FOR SEDIMENT TRANSPORT STUDIES

ISOTOPE GEOCHEMISTRY

0. INTRODUCTION

Isotope geochemistry is the study and application of the natural abundance and behaviour of the isotopes of those elements participating in geochemical cycles. This concerns radioactive as well as stable isotopes. The elements of primary importance are hydrogen, carbon and oxygen.

The modern isotopic research is based on the discovery by W.F. Libby (1946) of the natural abundance of carbon-14 and tritium -the radioactive isotopes of carbon and hydrogen- on the one hand, and on the experimental and theoretical work by H.C. Urey (1947) concerning the fractionation effects for stable isotopes on the other.

The chemical properties of an element are determined by the number of (negative) electrons that an atom of that element contains. This number equals the number of (positive) protons in the atomic nucleus. Apart from protons the nucleus contains a number of neutrons, having the same mass but no electric charge. To a first approximation the neutrons have no influence on the chemical properties of the element.

As repulsive (electric) forces exist between the protons, the presence of neutrons is required to stabilize the nucleus. For the light elements the numbers of protons and neutrons are equal. Examples of stable nuclei are $^4_2He_2$, $^{12}_6C_6$, $^{14}_7N_7$, $^{16}_8O_8$, while also the single proton ($^1_1H_0$ = hydrogen) is stable.

Instabilities are considered to be caused by an excess of protons or neutrons. Examples of the latter are the unstable or radioactive nuclei: $^3_1H_2$, $^{14}_6C_8$. A slight excess of neutrons does not necessarily result in unstable nuclei: $^2_1H_1$, $^{13}_6C_7$, $^{15}_7N_8$, $^{17}_8O_9$, $^{18}_8O_{10}$ are stable nuclei. A consequence of the neutron excess, however, is that the probability of formation during the nucleosynthesis has been smaller, resulting in smaller natural concentrations for these nuclei.

Atomic nuclei of an element containing different numbers of neutrons are called *isotopes* (ισο τοπος = at the same place in the periodic system of the elements). The earlier statement, that (to a first approximation) the chemical properties of the isotopes of an element are equal, needs revision if we look into detail. The fact is that in nature variable relative concentrations of isotopes are observed because of slight differences in physical and chemical properties.

The differences in physical and chemical properties of isotopic compounds (i.e. chemical compounds consisting of molecules containing different isotopes of the same element) are caused by mass differences of the atomic nuclei. The consequence of the mass difference is two-fold:

1. The heavier isotopic molecules have a lower mobility. The kinetic energy of the molecules is solely determined by temperature: $kT = \frac{1}{2}mv^2$ (k = Boltzman constant, T = absolute tempetature, m = molecular mass, v = average molecular velocity). Therefore, isotopic molecules have also the same $\frac{1}{2}mv^2$. This means that the molecules with larger m necessarily have a smaller v. Some practical consequences are:

a. heavier molecules have a lower diffusion velocity.

b. the collision frequency with other molecules -the primary condition for chemical reaction- is smaller for heavier molecules; this is one of the reasons why, as a rule, the lighter molecules react faster.

2. The heavier molecules generally have higher binding energies.

These phenomena are observed in several examples:

a. $^1H_2^{18}O$ and $^1H^2H^{16}O$ evaporate less easy than does $^1H_2^{16}O$ (lower vapour pressure);

b. $^{13}CO_2$ dissolves more slowly in an alkali solution and assimilates less easy than $^{12}CO_2$;

c. in most chemical reactions the light isotopic species reacts faster than the heavy: $Ca^{12}CO_3$ dissolves faster in an acid solution than does $Ca^{13}CO_3$.

In an isotopic equilibrium between two chemical compounds generally the heavy isotope is concentrated in that compound which has the largest molecular weight.

1. KINETIC FRACTIONATION AND EQUILIBRIUM FRACTIONATION

With the transition of an element from one chemical compound to an other, or with the transition of a compound from one phase to an other, isotope fractionation occurs. This is the phenomenon that with these transitions the isotopic abundance ratio of the element changes. For instance, water vapour contains relatively less $^1H_2{}^{18}O$ and $^1H^2H^{16}O$ than the original water; $^{12}CO_2$ is preferentially taken up by plants with respect to $^{13}CO_2$; by bacterial decomposition of plants methane (CH_4, marsh-gas) arises containing considerably less ^{13}C than the decaying plant material; marine limestone has a higher $^{18}O/^{16}O$ abundance ratio than the water from which it precipitated.

We should emphasize the distinction between two kinds of isotope fractionation: kinetic fractionation and equilibrium fractionation. *Kinetic fractionation* deals with irreversible physical or chemical processes. Examples are presented by the evaporation of water where the vapour is immediately withdrawn from further contact with the water, absorption and diffusion of gasses, and irriversible chemical reactions as the bacterial decay of plants and a rapid calcite precipitation. Here the fractionation effect is exclusively determined by the binding energies of the original compounds: in physical processes the isotopically lighter molecules have higher velocities and smaller binding energies (heat of evaporation), in chemical processes the light molecules react more rapidly than the heavy.

Before we are able to give a quantitative treatment of isotope fractionation, we have to define an expression for isotopic concentrations. These are generally expressed as *isotopic (abundance = concentration) ratios:*

$$R = \frac{\text{abundance of rare isotope}}{\text{abundance of abundant isotope}} \tag{1.1}$$

The ratio R generally carries a superscript referring to the isotope under consideration. For instance:

$$R^{13}(CO_2) = \frac{\left[^{13}CO_2\right]}{\left[^{12}CO_2\right]}$$

$$R^{18}(CaCO_3) = \frac{\left[CaC^{18}O^{16}O_2\right]}{\left[CaC^{16}O_2\right]}$$

$$R^2(H_2O) = \frac{\left[^1H^2HO\right]}{\left[^1H_2O\right]}$$

One should clearly distinguish between an *isotopic ratio* and an *isotopic concentration*. The latter is defined by (for instance in the case of CO_2):

$$\frac{\left[^{13}CO_2\right]}{\left[^{13}CO_2\right] + \left[^{12}CO_2\right]} = \frac{R^{13}}{1+R^{13}} \qquad (1.2)$$

The general definition of an *isotopic fractionation factor* is:

$$\alpha_A(B) = \frac{R_B}{R_A} \qquad (1.3)$$

in other words, the isotopic ratio in the phase or compound B relative to that in A. The factor α consequently is the *enrichment* ($\alpha<1$) or the depletion ($\alpha<1$) of the rare isotope in B with respect to A.

In general the isotope effects are small and unrecognizable in classical chemistry: $\alpha \approx 1$. Therefore, the deviation of α from 1 is widely used rather than the fractionation factor. This quantity, referred to as the *fractionation*, is defined by:

$$\varepsilon = \alpha - 1 \quad (x \ 10^3 \ ^0/_{00}) \qquad (1.4)$$

Also here, the fractionation of B with respect to A is denoted by $\varepsilon_A(B)$. From the definition of (1.3) we simply derive:

$$\varepsilon_A(B) = -\varepsilon_B(A)/(1+\varepsilon_B(A)) \simeq -\varepsilon_B(A) \qquad (1.5)$$

The second type of fractionation is the *equilibrium (or thermodynamic) fractionation*. This is essentially the isotope effect involved in a (thermodynamic) equilibrium reaction. As a formal example we choose the *isotopic exchange reaction:*

$$A* + B \overset{\rightarrow}{\underset{\leftarrow}{}} A + B* \tag{1.6}$$

where the asterisk points to the presence of the rare isotope. The fractionation factor for this equilibrium between phases or compounds A and B essentially is the equilibrium constant for the exchange reaction 1.6:

$$K = \frac{[A] \, [B*]}{[A*] \, [B]} = \frac{[B*]/[B]}{[A*]/[A]} = \frac{R_B}{R_A} = \alpha_A(B) \tag{1.7}$$

If sufficient information about the binding energies of atoms and molecules is available, the fractionation effect can be calculated, the kinetic (Bigeleisen, 1952) as well as the equilibrium (Urey, 1947) effects. In reality, however, these data are often not sufficiently known in detail. With kinetic isotope effects we are confronted with an additional difficulty. This arises from the fact that natural processes almost never deal with purely kinetic effects. Moreover, kinetic fractionation does not lend itself to a laboratory measurement, because (1) a complete irreversibility can not be guanranteed (part of the water vapour will return to the liquid), while the degree of irreversibility can not be quantified, (2) the vanishing phase or compound will have a non-homogeneous and often immeasurable isotopic composition, because the isotopic effect primarily refers to the surface of the compound (the surface layer of evaporating water will become enriched in ^{18}O and ^2H as the water mixes not rapidly enough.

Equilibrium fractionation, on the other hand, can well be determined by laboratory experiments. In several cases a reasonable agreement has been shown between experimental data and thermodynamic calculations.

The general condition for the occurrence of an isotopic equilibrium between two compounds is the availability of an isotopic exchange mechanism. This can be a reversible chemical equilibrium as:

$$H_2{}^{16}O + C^{16}O^{18}O \underset{\rightleftarrows}{} H_2C^{16}O_2{}^{18}O \underset{\rightleftarrows}{} H_2{}^{18}O + C^{16}O_2$$
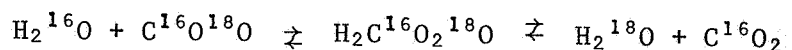
or a reversible physical process as, for instance, evaporation/condensation. The reaction rates of exchange processes and, consequently, the periods of time required to reach isotopic equilibrium, vary greatly. The exchange, for instance, of $H_2O \rightleftarrows CO_2$ proceeds rapidly, that of $H_2O \rightleftarrows CaCO_3$ slowly.

In a kinetic isotope effect the resulting fractionation generally exceeds that in an equilibrium process. Moreover, in a kinetic process the

rare isotope might be enriched in the phase, where it becomes depleted in the equivalent equilibrium process. This can be understood by comparing the fractionation factor in a reversible equilibrium with the kinetic fractionation factores involved in the two opposed single reactions.

As an example we take the carbonic acid equilibrium:

$$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-$$
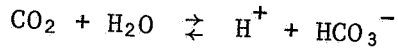
For the single reactions

$$^{12}CO_2 + H_2O \xrightarrow{k_{12}} H^+ + H^{12}CO_3^-$$

and

$$^{13}CO_2 + H_2O \xrightarrow{k_{13}} H^+ + H^{13}CO_3^-$$
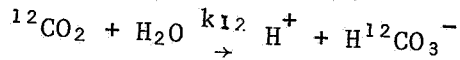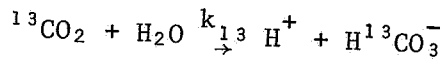
the reaction rates are:

$$r_{12} = k_{12} \left[^{12}CO_2 \right] \quad \text{and} \quad r_{13} = k_{13} \left[^{13}CO_2 \right]$$

where k_{12} and k_{13} are the respective reaction constants. The isotopic ratio of the thus formed bicarbonate is:

$$R^{13}(\Delta HCO_3^-) = \frac{r_{13}}{r_{12}} = \frac{k_{13} \left[^{13}CO_2 \right]}{k_{12} \left[^{12}CO_2 \right]} = \alpha_k \, R^{13}(CO_2)$$

where α_k is the kinetic fractionation factor for this reaction. Reversely, for

$$H^{12}CO_3^- + H^+ \xrightarrow{k'_{12}} {}^{12}CO_2 + H_2O$$

and

$$H^{13}CO_3^- + H^+ \xrightarrow{k'_{13}} {}^{13}CO_2 + H_2O$$
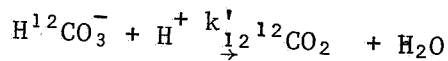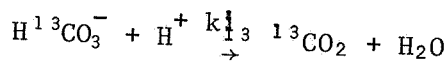
the reaction rates are:

$$r'_{12} = k'_{12} \left[H^{12}CO_3^- \right] \quad \text{and} \quad r'_{13} = k'_{13} \left[H^{13}CO_3^- \right]$$

The carbon dioxide thus formed has an isotopic ratio:

$$R^{13}(\Delta CO_2) \;=\; \frac{r^{\downarrow}_{13}}{r^{\downarrow}_{12}} \;\; \frac{k^{\downarrow}_{13}}{k^{\downarrow}_{12}} \;\; \frac{[H^{13}CO_3^-]}{[H^{12}CO_3^-]} \;=\; \alpha_k' \; R^{13}(HCO_3^-)$$

In a state of isotopic equilibrium the isotope effects balance:

$$R^{13}(\Delta HCO_3^-) \;=\; R^{13}(\Delta CO_2)$$

so that

$$\frac{\alpha'_k}{\alpha_k} \;=\; \frac{R^{13}(CO_2)}{R^{13}(HCO_3^-)} \;=\; \frac{[^{13}CO_2]\;[H^{12}CO_3^-]}{[^{12}CO_2]\;[H^{13}CO_3^-]} \;=\; \alpha_e \qquad\qquad (1.8)$$

where the equilibrium fractionation factor α_e appears to be equivalent to the equilibrium constant of the exchange reaction:

$$H^{13}CO_3^- \;+\; {}^{12}CO_2 \;\rightleftarrows\; H^{12}CO_3^- \;+\; {}^{13}CO_2$$
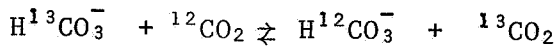
In many cases α_k and α'_k appreciably differ from 1 (several per cent, mostly <1), their ratio less (in the order of per mil). In chapter 3 we will see that a rapid evaporation of water might cause the water vapour to be about twice as depleted in ^{18}O as the vapour in equilibrium with water. The reason for this is, that $H_2^{16}O$ is favoured also in the condensation process.

From eq. 1.8 it is obvious that, while α_k for a certain phase transition is smaller than 1, α_e might be larger than 1. An example is to be found in the system: dissolved/gaseous CO_2 : the ^{13}C content of CO_2 rapidly (α_k) withdrawn from an aqueous CO_2 solution will be smaller than that of the dissolved CO_2; under equilibrium conditions (α_e) the gaseous CO_2 contains relatively more ^{13}C.

2. THE NATURAL ABUNDANCE OF ENVIRONMENTAL ISOTOPES

2.0 INTRODUCTION

This chapter is concerned with the natural concentrations of the stable isotopes of carbon and oxygen. We will successively treat for each isotope separately matters as the natural abundance, internationally agreed definitions and the natural fractionation effect. A general view is presented in table 2.1. The variations in the natural isotopic abundances will be treated in detail in the next chapters.

2.1. THE STABLE ISOTOPES

2.1.0. *DEFINITIONS*

For practical reasons the isotopic abundance ratios

$$R^{13} = \frac{^{13}C}{^{12}C}, \quad R^{2} = \frac{^{2}H}{^{1}H}, \quad R^{18} = \frac{^{18}O}{^{16}O} \tag{2.1}$$

are never reported as absolute numbers. The main reasons are:
(i) the mass spectrometers having sufficient sensitivity for isotope work are not suitable for obtaining reliable absolute ratios; (ii) the necessity of an international comparison of results introduces the use of standards to which the samples can be related as well; (iii) the use of isotopic ratios would lead to reporting results as numbers consisting of a large (5 or 6) amount of figures; (iv) absolute ratios are in principle less relevant than the changes in ratios occurring during transitions between phases or molecules.

Instead isotopic abundances are generally reported as a *deviation* of the isotopic ratio of the sample A *relative* to that of a standard S:

$$\delta_S(A) = \frac{R_A - R_S}{R_S} \quad (\times 10^3 \ {}^o\!/\!{oo}) \tag{2.2}$$

Table 2.1. Practical data about the natural abundances, properties and analytical techniques concerning the natural isotopes of hydrogen, carbon and oxygen. The precisions quoted are those commonly obtained by most laboratories.

	HYDROGEN			CARBON			OXYGEN		
	^1H	^2H (D)	^3H (T)	^{12}C	^{13}C	^{14}C	^{16}O	^{17}O	^{18}O
Natural abundance	0.99985	0.00015	$\leqslant 10^{-17}$	0.989	0.011	$\leqslant 10^{-12}$	0.99765	0.00035	0.0020
Abundance in hydrological cycle as	H_2O	H_2O	H_2O	$CO_2 - HCO_3^- - CO_3^{2-} - CaCO_3$			$H_2O - CaCO_3$		
Natural spec. activity	-	-	$\leqslant 36 dpm/1H_2O$	-	-	$\leqslant 14 dpm/gC$	-	-	-
Half-life	stab.	stab.	12.35 yr	stab.	stab.	5730 yr	stab.	stab.	stab.
Max.beta energy			18keV			156keV			
Variations in hydrological cycle		200 $^o/oo$	$0-10^{-16}$	stab.	30 $\%oo$	$0-10^{-12}$		10 $^o/oo$	30 $^o/oo$
International standard		V-SMOW	VIENNA-T		PDB	0.95xNBS oxalic acid I			V-SMOW
Unit		$\delta^2_{SMOW}(^o/oo)$	TU=3.24pC/1H_2O		$\delta^{13}_{PDB}(^o/oo)$	a^{14} (%)			$\delta^{18}_{V-SMOW}(^o/oo)$
Measuring instrument		MS	PGC, LSS		MS	PGC, LSS			MS
Measured as		H_2	C_2H_6 or H_2O		CO_2	CO_2,C_2H_2 CH_4,C_6H_6			CO_2
Standard deviation σ		1 $^o/oo$	$\geqslant 1$ %		0.05 $^o/oo$	$\geqslant 4$ $^o/oo$			0.05 $^o/oo$

MS = mass spectrometer

PGC = proportional gas counter
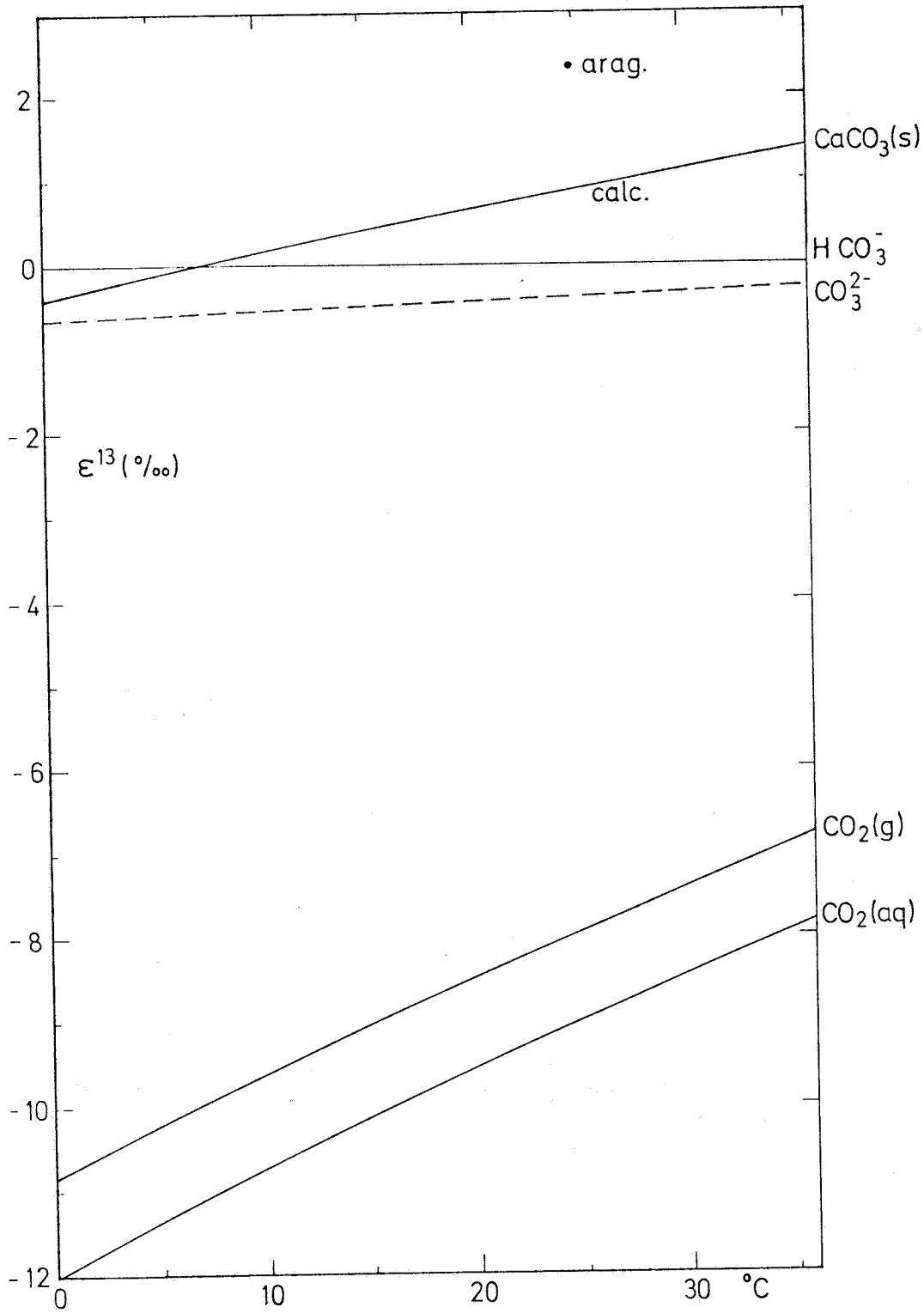
LSS = liquid scintillation spectrometer

Fig. 2.1. Equilibrium fractionations for carbon isotopes between gaseous CO_2 (g), dissolved CO_2(aq), dissolved CO_3^{2-} ions and solid $CaCO_3$(s) with respect to dissolved HCO_3^- as functions of temperature; arag = δ_b (aragonite) at 25.0°C.

where the δ values are given in per mil (‰). The $\delta^{13}C$ value of a sample of which $^{13}C/^{12}C = 0.0112380$ $(R_S^{13} = 0.0112372)$ thus is +0.07 ‰; a δ^{18} value of -15 ‰$(R_S^{18} = 0.0020790)$ means that $^{18}O/^{16}O = 0.0020478$.

Although the symbols δ^2H (or δD), $\delta^{13}C$, $\delta^{18}O$, are the usual for reporting $^2H/^1H$, $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios respectively, we will for convenience restrict ourselves to δ^2, δ^{13} and δ^{18}.

The fractionation ε, similarly defined as δ by eq. 1.4 and indicating the difference in isotopic ratio between two phases, can be expressed in the δ values of these phases:

$$\delta_S(B) - \delta_S(A) = \varepsilon_A(B) \left[1 + \delta_S(A) \times 10^{-3}\right] \simeq \varepsilon_A(B) \quad (\times 10^3 \text{ ‰}) \qquad (2.3.)$$

The product of ε and δ, both small numbers, can be neglected to a first approximation.

2.1.1. CARBON-13

2.1.1.0. The natural abundance of ^{13}C

The chemical element carbon consists of two stable isotopes, ^{12}C and ^{13}C, with an abundance of about 98.8% and 1.1%: $^{13}C/^{12}C = 0.011$ (Nier, 1950). As a result of several fractionation processes the isotopic ratio shows a natural variation of almost 100 ‰ . In bacterial methane (marsh-gas). the ^{13}C content is very low, while on the other hand the bicarbonate fraction of groundwater occasionally showed a high ^{13}C concentration. In the carbonic acid system, to which our interest will be restricted, variations up to 30 ‰ are observed.

2.1.1.1. Carbon isotope fractionations

We will restrict ourselves to the isotope effects dealing with the carbonic acid system: $CO_2 - H_2O - H_2CO_3 - CaCO_3$.
Values for the fractionation effects between these phases under equilibrium conditions are obtained from laboratory experiments.
A survey is presented in fig. 2.1 and table 2.2.

Table 2.2. Carbon isotope fractionation in the equilibrium system $CO_2-H_2O-HCO_3-CaCO_3$. $\varepsilon_x(y)$ represents the fractionation of compound y relative to compound x. Values for intermediate temperatures may be calculated by linear interpolation (see also fig. 2.1).
$T = t+273.15$; g = gaseous CO_2, a = dissolved CO_2, b = dissolved HCO_3^- ions, c = dissolved CO_3^{2-} ions, s = solid $CaCO_3$.

t (°C)	$\varepsilon_b(g)$[1] (°/oo)	$\varepsilon_g(a)$[2] (°/oo)	$\varepsilon_b(a)$[3] (°/oo)	$\varepsilon_b(c)$[4] (°/oo)	$\varepsilon_b(s)$[5] (°/oo)
0	-10.83	- 1.18	-12.00	- 0.65	- 0.39
5	-10.20	- 1.15	-11.35	- 0.60	- 0.11
10	- 9.60	- 1.13	-10.72	- 0.54	+ 0.15
15	- 9.02	- 1.10	-10.12	- 0.49	+ 0.41
20	- 8.46	- 1.08	- 9.54	- 0.44	+ 0.66
25	- 7.92	- 1.06	- 8.97	- 0.39	+ 0.91
30	- 7.39	- 1.04	- 8.42	- 0.34	+ 1.14
35	- 6.88	- 1.02	- 7.90	- 0.29	+ 1.37

[1] Mook et al., 1974 : $\varepsilon_b(g) = - 9.483 \times 10^3/T + 23.89$ °/oo

[2] Vogel et al., 1970 : $\varepsilon_g(a) = - 0.373 \times 10^3/T + 0.19$ °/oo

[3] [1] en [2] : $\varepsilon_b(a) = - 9.866 \times 10^3/T + 24.12$ °/oo

[4] Thode et al.,1965 and [1]: $\varepsilon_b(c) = - 0.867 \times 10^3/T + 2.52$ °/oo

[5] Our critical evaluation : $\varepsilon_b(s) = - 4.232 \times 10^3/T + 15.10$ °/oo
using original data from: (calcite)
Rubinson & Clayton, 1969;
Emrich et al., 1970
and foregoing relations

In nature these equilibrium effects do occur. The kinetic fractionation of specific interest is that during carbon dioxide assimilation, i.o.w. the CO_2 uptake by plants. The relatively large fractionation (up to about -18 ‰) is comparable to the effect observed during absorption of atmospheric CO_2 by an alkaline solution (Baertschi, 1951; 1953). A quantitative estimate shows that the isotope effect as a result of diffusion of CO_2 through air can not explain the fractionation (Craig, 1954):

$$\alpha = \left[\frac{M_{44} + M_a}{M_{44} \times M_a} \quad \frac{M_{45} \times M_a}{M_{45} + M_a} \right]^{\frac{1}{2}} \tag{2.4}$$

where M_{44} and M_{45} refer to the mass numbers of the isotopic CO_2 molecules, while M_a is the hypothetical mass number of air ($\simeq 29$). The resulting value of α is 1.0044, so that only 4.4 ‰ of the total assimilation fractionation can be explained by the diffusion. The remaining part, therefore, has to be found in the surface of the liquid phase.

2.1.1.2. The ^{13}C standard

According to the definition of δ in eq. 2.2, isotopic ratios are related to that of a specific standard. By international agreement PDB is used as the reference standard. PDB is the (marine) carbonate from a certain belemnite found in the North-American Pee Dee formation. Because this material is not available any more, the US National Bureau of Standards distributes an other marine limestone of which the δ^{13} value is accurately established with respect to PDB. This reference standard, Solnhofener limestone NBS20, is defined by (Craig, 1957):

$$\delta^{13}_{PDB} \text{ (NBS20)} = -1.06 \text{ ‰} \tag{2.5}$$

As a secondary reference standard spectrographically pure graphite , NBS21, is available. According to our measurements (Mook, 1968) the δ^{13} is:

$$\delta^{13}_{PDB} \text{(NBS21)} = - 28.22 \text{ ‰}$$

(cf. Craig, 1957, later increased by 1‰, pers. comm.).
Henceforth all δ^{13} values are reported relative to PDB, unless stated otherwise.
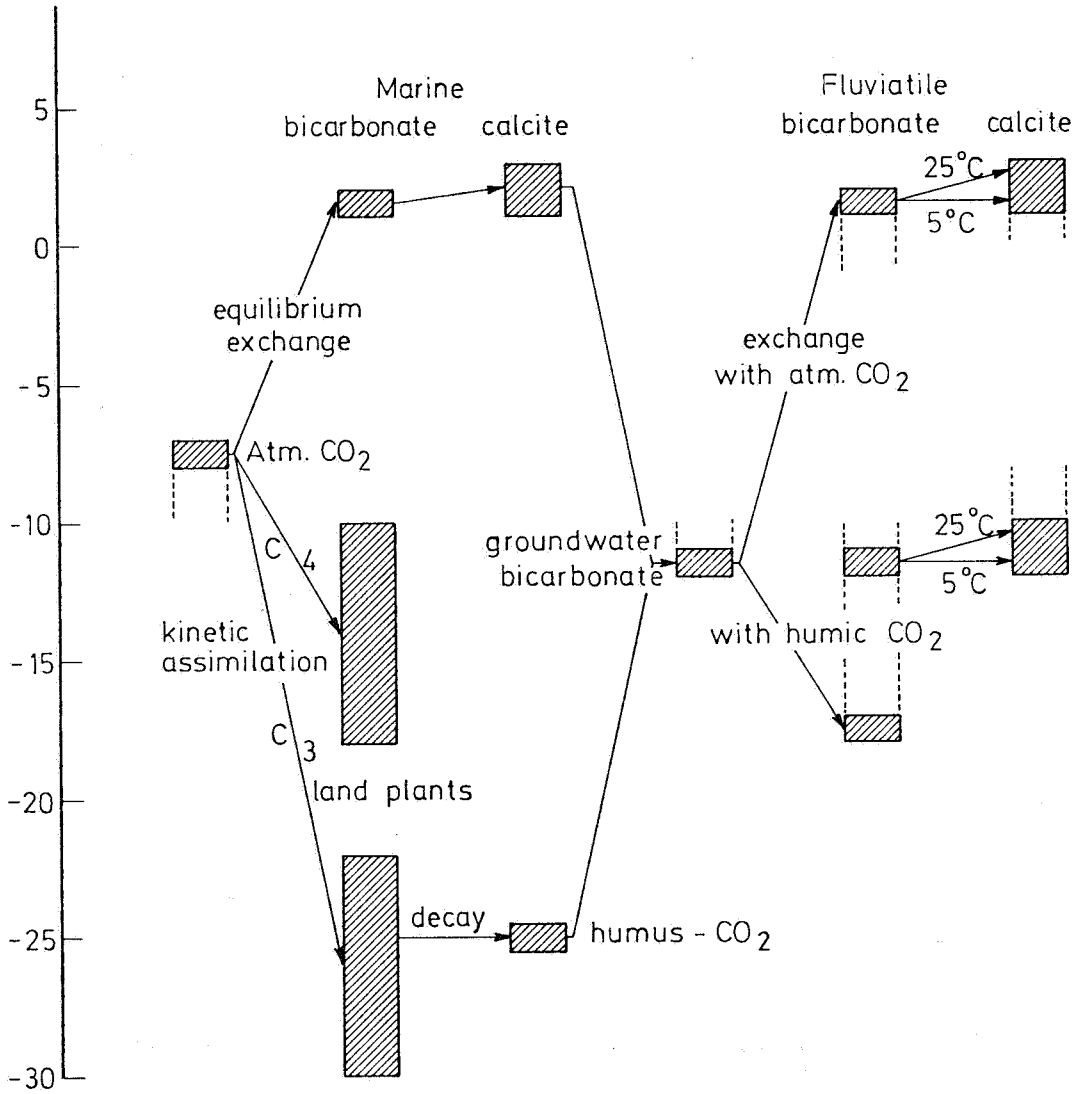
Fig. 2.2. Schematic survey of the natural δ^{13} variations relative to PDB.

2.1.1.3. *A survey of natural* δ^{13} *variations*

We will restrict ourselves to a general survey (fig 2.2) (cf. Vogel & Ehhalt, 1963; Mook, 1970).

A maximal δ^{13} of the atmospheric CO_2 in combination with a minimal CO_2 concentration was observed in oceanic air far removed from continental influences. The lower (more negative) values in continental air are due to the admixture of CO_2 from organic origin ($\sim - 25$ ‰), i.e. from decay of plant material and, primarily, from the combustion of fossil fuel (coal, oil, gas) by man (Keeling, 1958; 1961). Keeling et al.(1979) observed a lineair relation between δ^{13} and the partial pressure of the atmospheric CO_2 (p_{CO_2} in ppm) (number are valid for jan. 1,1978):

$$\delta^{13}(CO_2) = -7.24 - \frac{p_{CO_2} - 334.2}{p_{CO_2}} (26.54 - 7.24 \tag{2.6}$$

In cities and industrial areas δ^{13} values are occasionally observed of $- 16$ ‰ at a CO_2 concentration double the natural. On a global scale the avarage CO_2 content in "pure" air has increased by 20.1 ppm, in combination with a δ^{13} change of 0.55 ‰ since jan 1, 1956 (Keeling et al., 1979)

Plant carbon has a lower ^{13}C content than the atmospheric CO_2 from which it has been assimilated. As is mentioned in sect. 2.1.1.1., during CO_2 uptake a selection is made in favour of ^{12}C, depending on the type of plant and the climatic and ecological conditions. Two extreme modes of assimilation processes show strongly differing degrees of fractionation. The Hatch-Slack photosynthetic pathway results in δ^{13} figures around -12 ‰ and is primarily represented by certain grains or desert grasses. In moderate climate the large majority of plants is subjected to the Calvin type mechanism, producing δ^{13} values between -20 and -30 ‰ . The CO_2 formed by decay of plant remains in these climates consequently show δ^{13} values of -25 ± 1 ‰.

It has turned out that the atmospheric CO_2 is in isotopic equilibrium with the oceanic dissolved bicarbonate. The δ^{13} (HCO_3^-) values in the ocean are about $+1$ to $+1.5$ ‰ , in agreement with the equilibrium fractionation $\varepsilon_b(g)$ at temperatures between 15 and 20 ^{o}C (table 2.2). According to the fractionation $\varepsilon_b(s)$ we may expect a α^{13} value for the calcite slowly precipitating and thus in equilibrium with the bicarbonate of $+2$ to $+2.5$ ‰. This is indeed the normal range observed for recent marine carbonates (fig. 2.2).

The CO_2 of human origin, generated by plant decay, plays an important role in constituting the dissolved inorganic carbon content of groundwater. After dissolution of this CO_2 the infiltrating rain water is able to dissolve the soil limestone:

$$CO_2 + H_2O + CaCO_3 \rightarrow Ca^{2+} + 2HCO_3^- \qquad (2.7)$$
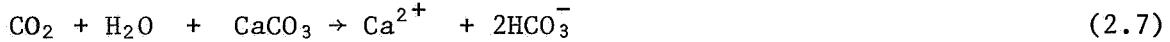
Because this limestone generally is of marine origin ($\delta^{13} \simeq +2\%_0$), this process results in a δ^{13} value of the dissolved bicarbonate of about -11 to -12 $\%_0$ (in moderate climates). This range of δ^{13} values is indeed generally found in groundwater and in the closely related river waters.

In nature δ^{13} (HCO_3^-) values are, however, observed which significantly differ from this range, in the soil as well as in fresh surface water as in lakes. The latter is caused by isotopic exchange with the excess of atmospheric CO_2 (-7.2 $\%_0$), ultimately resulting in δ^{13} values identical to oceanic values. Consequently, also fresh water carbonates can be met with having "marine" δ^{13} values. In these cases the marine character of the carbonate has to be confirmed by the δ^{18} value (sect. 2.1.2.3.).

2.1.2. OXYGEN-18

2.1.2.0. The natural abundance of ^{18}O

The chemical element oxygen consists of three stable isotopes, ^{16}O, ^{17}O and ^{18}O, with an abundance of 99.76, 0.035 and 0.20% respectively (Nier, 1950). The observation of ^{17}O concentrations apart from the more abundant and, consequently, more accurately measurable ^{18}O variations is only in some cases interesting. We shall, therefore, focus our attention to the $^{18}O/^{16}O$ ratio ($\simeq 0.0020$). This ratio shows a natural variation of about 100 $\%_0$. In some (saline) lakes subjected to a high degree of evaporation high ^{18}O contents are found, while especially the antarctic precipitation is low in ^{18}O. Generally in the hydrological cycle we are confronted with a range of δ^{13} values not exceeding 20 $\%_0$.

2.1.2.1. Oxygen isotope fractionations

The isotope effects to be discussed are related to the system H_2O (vapour) - H_2O (liquid) - $CaCO_3$. The isotope fractionations have been determined by laboratory experiments. Fig 2.3. presents a survey of the temperature dependent equilibrium effects.

The laboratory fractionations are as well found under natural circumstances,

Table 2.3. Oxygen isotope fractionation in the equilibrium system CO_2- H_2O - $CaCO_3$. $\varepsilon_x(y)$ represents the fractionation of compound y relative to compound x. Values for intermediate temperatures may be calculated by linear interpolation (see also fig. 2.3). $T = t + 273.15$; ℓ = liquid water, v = water vapour, i = ice^x , g = gaseous CO_2, ℓg = $CO_2 \underset{\leftarrow}{\rightarrow} H_2O$ at 25 ^oC, s = solid $CaCO_3$, sg = CO_2 from $CaCO_3$ by 100 $^o/oo$ H_3PO_4 treatment at 25 ^oC (see also: Friedman & O'Neil, 1977).

t (°C)	$\varepsilon_\ell(v)^{1)}$ (°/oo)	$\varepsilon_{\ell g}(g)^{2)}$ (°/oo)	$\varepsilon_{\ell g}(sg)^{3)}$ (°/oo)	$\varepsilon_\ell(g)^{4)}$ (°/oo)	$\varepsilon_\ell(s)^{5)}$ (°/oo)
0	-11.58	+ 5.12	+ 3.91	+46.51	+35.13
5	-11.09	+ 4.02	+ 2.67	+45.37	+33.86
10	-10.62	+ 2.96	+ 1.48	+44.28	+32.63
15	-10.17	+ 1.94	+ 0.33	+43.22	+31.44
20	- 9.74	+ 0.96	- 0.78	+42.19	+30.30
25	- 9.32	0	- 1.85	+41.20	+29.19
30	- 8.91	- 0.92	- 2.89	+40.24	+28.12
35	- 8.51	- 1.81	- 3.89	+39.32	+27.09

[1] Majoube, 1971; 1/T adjustment from original:

$$10^3 \ln \alpha = -1.137(10^6/T^2) + 0.4156(10^3/T) + 2.0667):$$

$$\varepsilon_\ell(v) = - 7.363 \times 10^3/T + 15.38 \; ^o/oo$$

[2] Vogel et al., 1970 (adjusted): $\varepsilon_{\ell g}(g) = 16.670 \times 10^3/T - 55.91 \; ^o/oo$

[3] Epstein, 1976 (1/T adjustment to PDB resp. V-SMOW scale from original data: $t = 16.2 - 4.3 (\delta_s - \delta_w) + 0.14 (\delta_s - \delta_w)^2$ (δ_w is δ^{18} of ocean water vs. V-SMOW):

$$\varepsilon_{\ell g}(sg) = 18.765 \times 10^3/T - 64.79 \; ^o/oo$$

[4] O'Neil et al, 1975 : $\varepsilon_\ell(g) = 17.302 \times 10^3/T - 16.83 \; ^o/oo$

[5] [3] [4] and Sharma & Clayton, 1965:

$$\varepsilon_\ell(s) = 19.333 \times 10^3/T - 35.53 \; ^o/oo$$

ε_{CaCO_3} (CO_2 from $CaCO_3$, H_3PO_4, 25 ^oC) = + 10.08 $^o/oo$

$\varepsilon_{V-SMOW-CO_2}$ (PDB - CO_2) = + 0.29 $^o/oo$; $\delta^{18}_{V-SMOW} = 1.0412 \; \delta^{18}_{PDB-CO_2} + 41.61 \; ^o/oo$

^{x} $\varepsilon_\ell(i) \sim + 2 \; ^o/oo$ at 0 ^oC (Craig & Gordon, 1965).
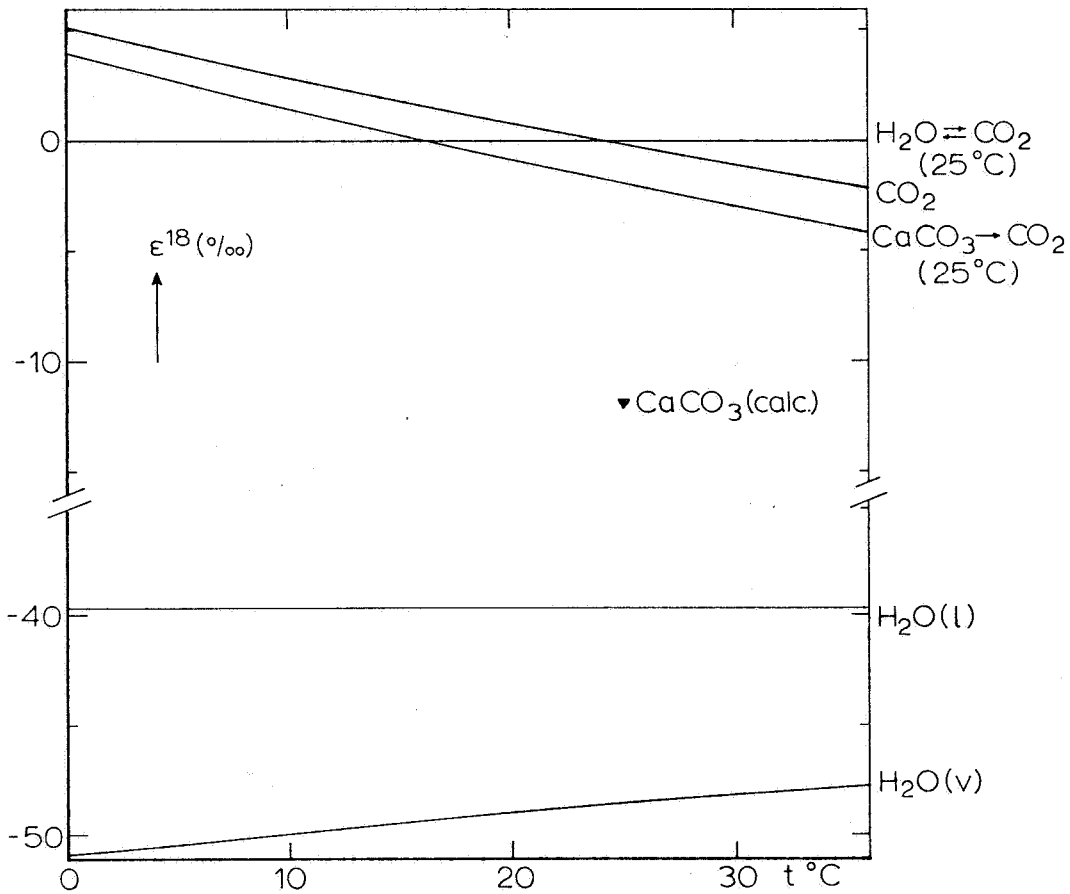
Fig. 2.3 Equilibrium fractionations for oxygen isotopes between $H_2O(l)$, water vapour (v), gaseous CO_2, solid $CaCO_3$ (s) and $CaCO_3 \rightarrow CO_2$ (CO_2 prepared from $CaCO_3$ by treatment with 100 % ortho-phosphoric acid at 25 $^\circ$C) with respect to $H_2O \rightleftarrows CO_2$ (CO_2 in isotopic equilibrium with water at 25 $^\circ$C) as a function of temperature.

as was the case for the carbon isotopes. The most striking fact is that, concerning the δ^{18} values, many mollusks appear to form their shell carbonate in agreement with thermodynamic laws. The palaeo-temperature scale presented by Epstein et al. (1953) (δ^{18} values in $\%_0$):

$$t = 16.5 - 4.3\delta^{18} + 0.14(\delta^{18})^2 \tag{2.8}$$

is deduced from ^{18}O measurements on carbonate layed down by shell animals at known temperature and known δ^{18} of the water. In eq. 2.8 δ^{18} applies to the $^{18}O/^{16}O$ ratio of the carbonate with respect to the water.

Kinetic effects are observed during the evaporation of ocean water. The oceanic vapour has turned out to be isotopically lighter than would follow from equilibrium fractionation. In the case of lakes the evidence for kinetic fractionation is indirect.

2.1.2.2. *The ^{18}O standards*

For reporting δ^{18} values two primary reference standards are available, one for carbonates, one for water samples.
This historically grown situation complicates this matter considerably. It arises from the practical fact that the isotopic ratios of carbonates as well as of water are actually measured on CO_3 which has some relation to the original sample, rather than on the material itselfs.

(a) *V-SMOW* (Vienna - Standard Mean Ocean Water)

The International Atomic Energy Agency, section Isotope Hydrology, has available for distribution a batch of well preserved "standard mean ocean water" which applies for ^{18}O as well for ^2H. This primary reference standard V-SMOW replaces the original SMOW standard, in fixing the zero point of the δ^{18}_{V-SMOW} scale. All *water*samples are to be referred to this standard.

The laboratory analysis of $^{18}O/^{16}O$ in water implies the equilibrium of a water sample with CO_2 of known isotopic composition at $25^{\circ}C$ and the mass spectrometric analysis of this equilibrated CO_2 (sect. 6.1.3.). The fractionation between CO_2 and H_2O (table 2.3) is irrelevant because this procedure is applied to all water samples (x) as well as the standard, while

$$\delta^{18}_{V-SMOW} (x) = \delta^{18}_{CO_2} \xleftarrow{} V-SMOW (CO_2 \xleftarrow{} x) \tag{2.9}$$

Before september 1976, when it was decided to use V-SMOW as the primary standard, a SMOW standard sample was not available.

SMOW was defined by means of the standard sample NBS1 (Craig, 1961a) available from the US National Bureau of Standards:

$$\delta^{18}_{SMOW} \ (NBS1) = - \ 7.94 \ \text{\textperthousand}$$

From an extensive laboratory intercomparison it became obvious that the difference between the early SMOW and the present V-SMOW is very small (Gonfiantini, 1978):

$$\delta^{18}_{V-SMOW} \ (SMOW) \simeq \ + \ 0.07 \ \text{\textperthousand} \tag{2.10}$$

As a secundary standard sample SLAP (Standard Light Arctic Precipitation) is introduced, also distributed by the IAEA:

$$\delta^{18}_{V-SMOW} \ (SLAP) \simeq \ - \ 55.5 \ \text{\textperthousand} \tag{2.11}$$

In order to avoid the influence of small instrumental errors, some laboratories prefer to have the V-SMOW scale defined by two extreme points. To this end the sample δ^{18} is interpolated between V-SMOW (0 \text{\textperthousand}) and SLAP (-55.5 \text{\textperthousand}) according to:

$$\delta^{18}_{V-SMOW} \ (x) = \frac{\delta^{18}_{m}(x) - \delta^{18}_{m}(V-SMOW)}{\delta^{18}_{m}(SLAP) - \delta^{18}_{m}(V-SMOW)} \cdot \delta^{18}_{V-SMOW} \ (SLAP) \tag{2.12}$$

where m refers to the marine (= working) standard and δ^{18}_{V-SMOW} (SLAP) is given by eq. 2.11, or directly from instrumental reading.

(b) *PDB (Pee Dee Belemnite)*

Carbonates are compared with a non-existent calcite sample, PDB carbonate. The zero point of this PDB scale is fixed (Craig, 1957) by means of the NBS20 reference sample (Solenhofener limestone) which is defined as:

$$\delta^{18}_{PDB} \ (NBS20) = - \ 4.14 \ \text{\textperthousand} \tag{2.13}$$
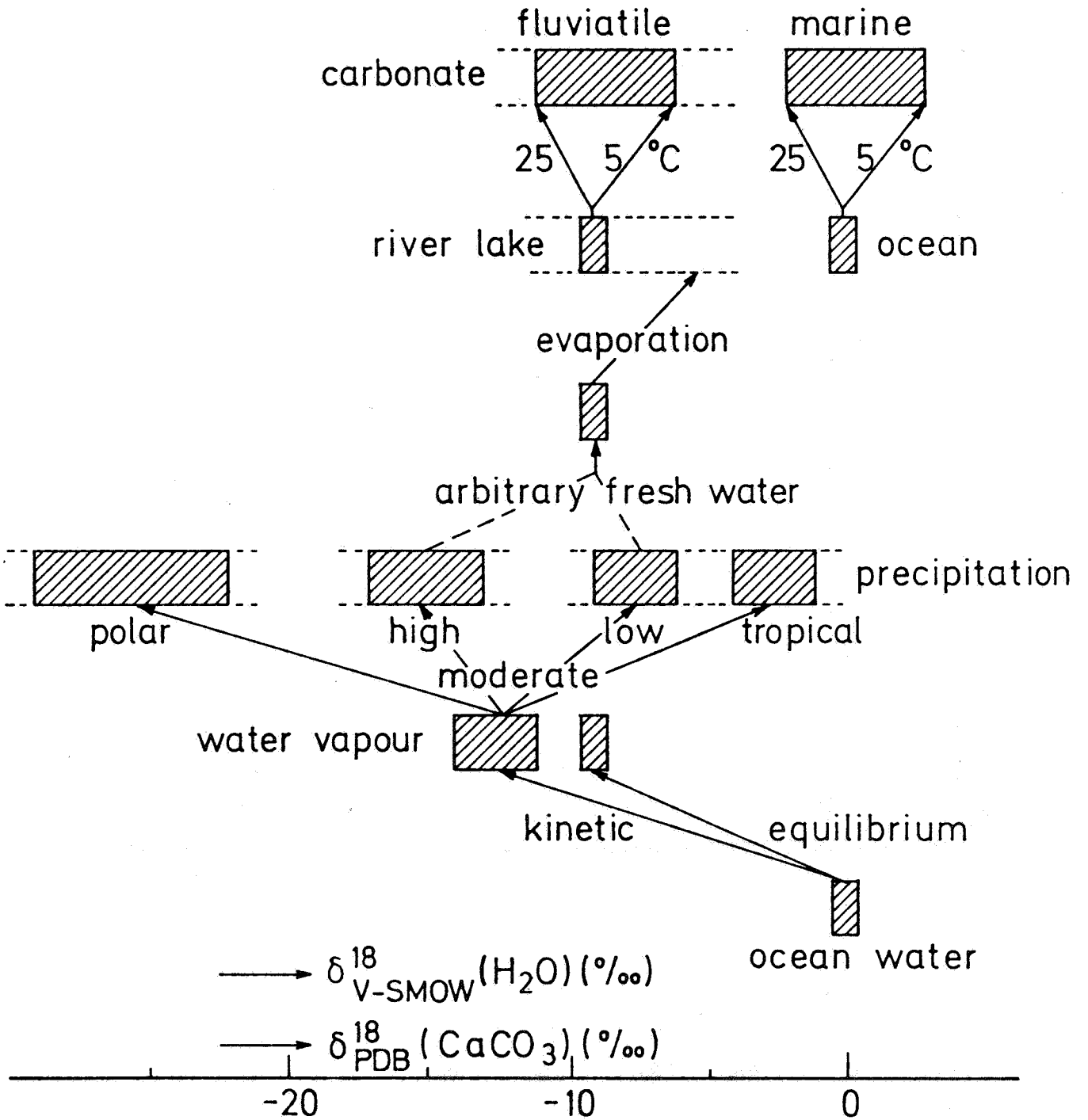
Fig. 2.4 Schematic survey of the natural δ^{18} variations relative to V-SMOW or PDB.

In reality not the carbonate itself is analysed for the $^{18}O/^{16}O$ ratio but rather the CO_2 prepared according to a standard procedure: treatment in vacuo with 100% (or 95%) orthophosphoric acid at 25°C. However:

$$\delta_{PDB}^{18} (x) = \delta_{PDB \to CO_2}^{18} (x \to CO_2) \qquad (2.14)$$

because samples and standard are treated similarly, so that the fractionation between the carbonate and the CO_2 prepared from it (table 2.3) is not relevant.

The relations between the PDB, PDB-CO_2 , V-SMOW-CO_2 scales are given in table 2.3. These are only of interest in isotope studies on silicates, oxydes, carbonates, water and their correlations.

Henceforth all δ^{18} values of carbonates are reported relative to PDB (-CO₂), all δ^{18} values of water relative to V-SMOW (-CO₂), unless stated otherwise.

2.1.2.3. *A survey of natural δ^{18} variations*

The ^{18}O content in the surface layer of the world oceans, forming the largest global water reservoir, has been found to be very much uniform, varying between + 0.5 and − 0.5 ‰ (Epstein & Mayeda, 1953; GEOSECS-reports, priv. comm.). Only in tropical and polar regions larger deviations are observed. In the first case the more positive values are caused by strong evaporation, in the second more negative values orginate from isotopically light meltwater.

If ocean water would evaporate under equilibrium conditions, the water vapour would be 8 to 10 ‰ depleted in ^{18}O, depending on temperature. However, the oceanic vapour appears to have an average δ^{18} value of −12 to − 13 ‰ , due to the partly kinetic fractionation. Essential parameters in this process are the relative humidity of the air and the wind speed.

The transition of atmospheric water vapour to precipitation depends on so many climatological and local factors, that the δ^{18} variations in precipitation are very large. As a general rule the figures are smaller (more negative) the further the rain is removed from the main origin of the vapour: the equatorial regions.

Earlier we paid attention to the fact that the slow precipitation of carbonate is a process during which there is an isotopic equilibrium between the carbonate and the water. The ^{18}O content of the carbonate thus is primarily determined by that of the water. In the second instance it
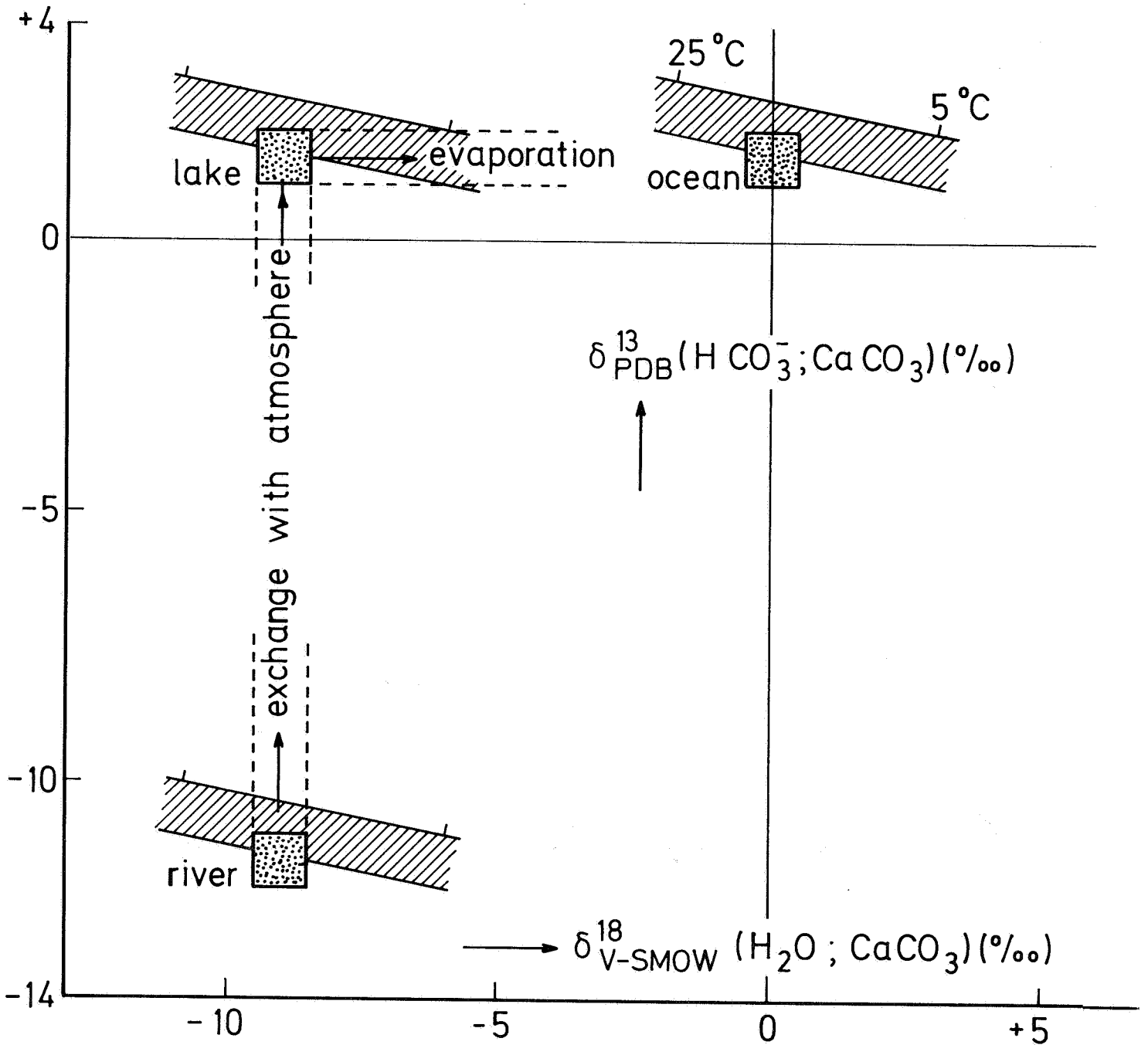
Fig. 2.5 Relation between the natural variations in $\delta^{13}(HCO_3^-,$ $CaCO_3)$ and $\delta^{18}(H_2O, CaCO_3)$. The graph is essentially a combination of the figures 2.2 and 2.4

depends on the temperature as is indicated in the upper part of fig. 2.4. Conversily, from the δ^{18} of marine carbonates we can in principle deduce the temperature of the water, provided the δ^{18} (water) is known ($\simeq$ 0 $^0/_{00}$). This is the original basis of the ^{18}O palaeothermometry of fossil marine shells (review by Bowen, 1966).

2.1.3. *RELATION BETWEEN δ^{13} AND δ^{18} VARIATIONS*

The differences and the relations between the various natural water-carbonate systems become more obvious and more complete by considering both the δ^{18} of the water and δ^{13} of the dissolved bicarbonate. Fig. 2.5 is a schematic representation of three isotopically typical waters, each provided with the temperature dependent range of calcites precipitated under equilibrium conditions. This figure essentially is a combined graph of figs 2. and 2.4.

The three typical waters are:

(1) *Ocean water*, having δ^{18} values around 0 $^0/_{00}$ (by definition) at present; the carbonate range refers to recent marine carbonates. During interchanging glacial and interglacial periods in the past δ^{13} of ocean water has been subjected to variation.

Moreover, δ^{18} values of marine limestone have increased in the course of geological times, while the δ^{13} values have essentially remained the same. (Keith et al., 1964; Veizer & Hoefs, 1976).

(2) *Ground and river water*, for which in fig 2.5 an arbitrary value of δ^{18} has been chosen. In fresh water bicarbonate δ^{13} generally is around -11 to - 12 $^0/_{00}$.The isotopic composition of the fluviatile carbonates derived from this water simply result from the known equilibrium fractionations (tables 2.1 and 2.3)

(3)*Stagnant or lake water* can be subjected to processes altering the isotopic composition. Provided the water has a sufficient residence time in the basin,isotopic exchange can change the ^{13}C content until an equilibrium situation with the atmospheric CO_2. Then δ^{13} equals that in the ocean. The dutch lake IJsselmeer is a good example. In warmer climates the oxygen isotopic composition may change due to evaporation in the direction of less negative values.

Obviously intermediate values of δ^{13} and δ^{18} can be found: in estuaries between (1) and (2), in lakes between (2) and (3) or between (1), (2) and (3) depending on the degrees of exchange and evaporation respectively.

REFERENCES

Baertschi, P. 1952. Die Fraktionierung der Kohlenstoffisotopen bei der
   Absorption von Kohlendioxyd. Helv. Chim. Acta 35, 1030

Baertschi, P. 1953. Die Fraktionierung der natürlichen Kohlenstoffisotopen
   im Kohlendioxydstoffwechsel grüner Pflanzen. Helv. Chim. Acta 36, 773

Bigeleisen, J. 1952. The effects of isotopic substitutions on the rates of
   chemical reactions. J. Phys. Chem. 56, 823-828

Bowen, R. 1966. Paleotemperature Analysis. Elsevier Publ. Comp., 265 pp

Craig, H. 1954. Carbon 13 in plants and the relationships between carbon 13
   and carbon 14 variations in nature. J. Geol. 62, 115

Craig, H. 1957. Isotopic standards for carbon and oxygen and correction factors
   for mass-spectrometric analysis of carbon dioxyde. Geochim. Cosmochim.
   Acta 12, 133-149

Craig, H. 1961. Standards for reporting concentrations of deuterium and oxygen-
   18 in natural waters. Science 133, 1833-1834

Craig, H. and Gordon, L.I. 1965. Deuterium and oxygen-18 variations in the
   ocean and the marine atmosphere. In: Stable Isotopes in Oceanographic Stu-
   dies and Paleotemperatures, Spoleto 1-122

Emrich, K., Ehhalt, D. and Vogel, J.C. 1970. Carbon isotope fractionation du-
   ring the precipitation of Calcium carbonate. Earth. Planet. Sci. Lett. 8,
   363-371

Epstein, S., Buchsbaum, R., Lowenstam, H.A. and Urey, H.C. 1953. Revised car-
   bonate-water isotopic temperature scale. Bull. Geol. Soc. Am. 64, 1315-1325

Epstein, S. and Mayeda, T. 1953. Variations of O^{18} content of waters from na-
   tural sources. Geochim. Cosmochim. Acta 4, 213-224

Epstein, S. 1976. A revised oxygen paleotemperature scale. Geol. Soc. Amer.
   Bull.

Friedman, I. and O'Neil, J.R. 1977. Compilation of stable isotope fractionation
   factors of geochemical interest. USGS Prof. Paper 440-KK

Gonfiantini, R. 1978. Standards for stable isotope standards in natural compounds.
   Nature 271, 534-536

Keeling, C.D. 1958. The concentration and isotopic abundances of atmospheric
   carbon dioxide in rural areas. Geochim. Cosmochim. Acta 13, 322

Keeling, C.D. 1961. The concentration and isotopic abundances of atmospheric
   carbon dioxide in rural and marine air. Geochim. Cosmochim. Acta 24, 277

Keeling, C.D., Mook, W.G. and Tans, P.P. 1979. Recent trend in the $^{13}C/^{12}C$ ratio
   of atmospheric carbon dioxide. Nature 277, 121-123

Keith, M.L., Anderson, G.M. and Eichler, R. 1964. Carbon and oxygen isotopic composition of mollusk shells from marine and fresh-water environments. Geochim. et Cosmochim. Acta 28, 1757

Libby, W.F. 1946. Atmospheric helium three and radiocarbon from cosmic radiation. Phys. Rev. 69, 671-672

Majzoub, M. 1971. Fractionnement en oxygen-18 et en deuterium entre l'eau et sa vapeur. J. Chim. Phys. 68, 1423-1436

Mook, W.G. 1968. Geochemistry of the stable carbon and oxygen isotopes of natural waters in the Netherlands. Thesis Univ. Groningen, 157 pp

Mook, W.G. 1970. Stable carbon and oxygen isotopes of natural waters in the Netherlands. In: Isotope Hydrology, IAEA, Vienna, 163-189

Mook, W.G., Bommerson, J.C. and Staverman, W.H. 1974. Carbon isotope fractionation between dissolved bicarbonate and gaseous carbon dioxide. Earth. Planet. Sci. Lett. 22, 169-176

Nier, A.O. 1950. A redetermination for the relative abundances of the isotopes of carbon, nitrogen, oxygen, argon and potassium. Phys. Rev. 74, 789

O'Neil, J.R., Landford, H., Adami, L.H. and Epstein, S. 1975. Revised value for the O^{18} fractionation between CO_2 and H_2O at 25 ^0C. Jour. Research. U.S. Geol. Survey 3, 623-624

Rubinson, M. and Clayton, R.N. 1969. Carbon-13 fractionation between aragonite and calcite. Geochim. Cosmochim. Acta 33, 997-1002

Sharma, T. and Clayton, R.N. 1965. Measurement of O^{18}/O^{16} ratios of total oxygen of carbonates. Geochim. Cosmochim. Acta 29, 1347

Thode, H.G., Shima, M., Rees, C.F. and Krishnamurty, K.V. 1965. Carbon-13 isotope effects in systems containing carbon dioxide, bicarbonate, carbonate and metal ions. Canad. J. Chem. 43, 582

Urey, H.C. 1947. The thermo dynamic properties of isotopic substances. J. Am. Chem. Soc., 562-581

Veizer, J. and Hoefs, J. 1976. The nature of O^{18}/O^{16} and C^{12}/C^{13} secular trends in sedimentary carbonate rocks. Geochim. Cosmochim. Acta 40, 1387-1396

Vogel, J.C. and Ehhalt, D. 1963. The use of carbon isotopes in groundwater studies. In: Radioisotopes in Hydrology, IAEA, Vienna, 383-396

Vogel, J.C., Grootes, P.M. and Mook, W.G. 1970. Isotopic fractionation between gaseous and dissolved carbon dioxide. Z. Phys. 230, 225-238

Letter Section

FIELD OBSERVATIONS OF THE ISOTOPIC COMPOSITION OF PARTICULATE ORGANIC CARBON IN THE SOUTHERN NORTH SEA AND ADJACENT ESTUARIES

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ABSTRACT

Salomons, W. and Mook, W.G., 1981. Field observations of the isotopic composition of particulate organic carbon in the southern North Sea and adjacent estuaries. Mar. Geol., 41: M11—M20.

The carbon isotopic composition of the organic matter in fluvial sediments and in fluvial suspended matter falls in the range valid for continental organic matter (-25 to $-28^o/_{oo}$). The $\delta^{13}C$ values in sediments from marine sedimentation areas and in marine suspended matter varies between -20 and $-25^o/_{oo}$. The rather low mean values for the deposited sediments of $-13.2^o/_{oo}$ suggest the presence of relatively large amounts of continental organic matter. This may be a direct supply by the present-day rivers and/or organic matter derived from the erosion of peat layers, even in the marine environment. A distinction between these two sources of detrital continental organic matter is not possible with stable isotopes studies.

In the estuaries studied the organic matter contents decrease and the $\delta^{13}C$ values of the organic matter increase in the seaward direction. These changes are primarily caused by the mixing of fluvial and marine sediments.

INTRODUCTION

Recent argillaceous sediments from Western Europe (Fig. 1) are composed of quartz, clay minerals, feldspars, carbonates and organic matter in varying proportions. The main sources for the marine sediments in the southern North Sea are (1) material carried by the net sea current from the English Channel in a northerly direction along the Belgian and Dutch coast, (2) material eroded from coastal and shallow-water clay deposits, and (3) suspended matter transported by the various rivers (McCave, 1973). The overall transport of suspended matter in the coastal areas of Belgium and The Netherlands is directed to the north. The origins of the carbonates, clay minerals and trace metals in these sediments have been discussed in a number of recent publications (Salomons, 1975; Salomons et al., 1975;
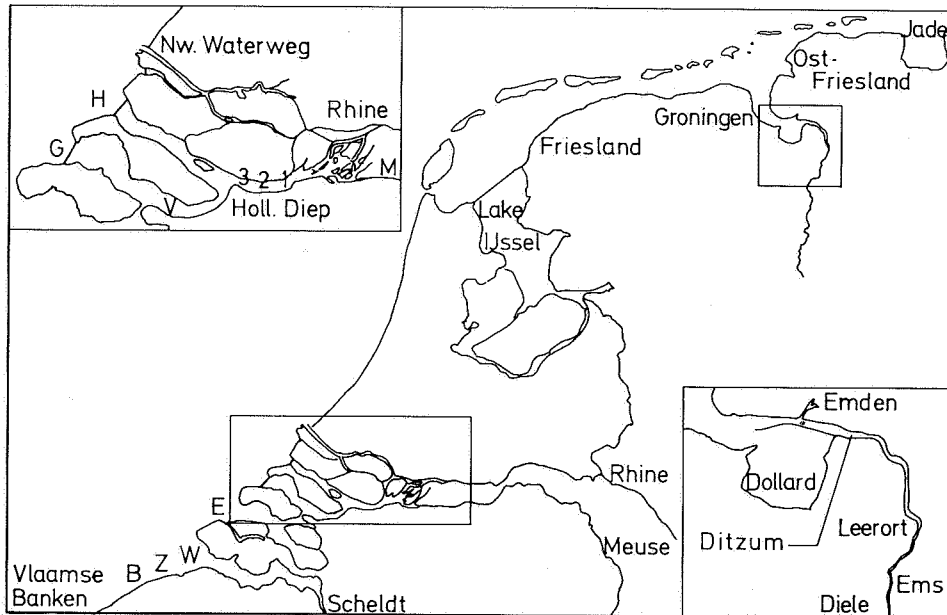
M12

Fig. 1. Map of the Netherlands showing the sampling localities.

Salomons and Mook, 1977; Salomons and De Groot, 1978). It was found that the carbonates and clay minerals of Wadden Sea sediments are for less than 20% derived from the rivers Rhine and Meuse. A mixing process was observed of marine and fluvial sediments in the estuaries of the rivers Rhine and Ems. The origin of organic carbon in sediments is more difficult to determine; organic carbon is partly of detrital, partly of authigenous origin. Furthermore, the terminology used in the literature is often not consistent (e.g. there is a difference between organic matter found in marine sediments and marine organic matter). In Table I an attempt has been made to differentiate between various sources of organic matter in sediments found in the marine and fluvial environments.

According to Postma (1973), the primary production in the southern North Sea exceeds the fluvial input of organic carbon by a factor of 14. Other sources for detrital organic matter are the ancient peat deposits at present being eroded in the marine environment. However, direct information on the ratio of marine to continental (source) organic matter in sediments and suspended matter is not available.

A number of studies demonstrated the value of stable isotope geochemistry to differentiate between marine- and land-derived (continental) organic carbon in sediments (Nissenbaum and Kaplan, 1972; Newman et al., 1973; Aizenstat et al., 1973; Schultz and Calder, 1976; Gearing et al., 1977; Tan and Strain, 1979). To obtain a first overall picture on the origin of organic matter in Recent sediments and relate its origin to other sedimentary com-

TABLE I

Sources of organic matter found in fluvial and in marine sediments

	Sources	$\delta^{13}C$ (‰)
Organic matter found in fluvial sediments	Autochthonous organic matter (e.g. algal production in the river system)	-31 ± 2
	Detrital organic matter (e.g. erosion of soils)	-27.5 ± 1
Organic matter found in marine sediments	Fluvial organic matter	-27 ± 2
	Eroded ancient peat deposits	-27.5 ± 1
	Autochthonous organic matter (e.g. derived from organic products in the marine environment	-19 ± 2

ponents (e.g. clays and carbonates) studied in two earlier investigations (Salomons, 1975; Salomons et al., 1975) we have determined the isotopic composition of the organic carbon in a large number of sediments from the southern North Sea and in fluvial and estuarine deposits (Fig. 1).

It should be noted, however, that from stable carbon isotopes it is not possible to distinguish between different sources of continental organic matter (e.g., fluvial organic matter and peat being eroded in the marine environment).

EXPERIMENTAL METHODS

The dry sediment samples were first treated with dilute hydrochloric acid to remove carbonates. After washing and drying, the residues were combusted to CO_2 in a small combustion system (Mook, 1968). The carbon dioxide samples were analysed for $^{13}C/^{12}C$ with a Varian M86 mass spectrometer. The results are reported relative to the PDB standard as:

$$\delta^{13}C_{PDB} = (^{13}C/^{12}C)_{sample}/(^{13}C/^{12}C)_{PDB} - 1 \; (\times \; 10^3 \; ‰)$$

The calibration is based on $\delta^{13}C_{PDB}(NBS20) = -1.06‰$ and on well-calibrated laboratory standards [$\delta^{13}C_{PDB}(NBS21) = -28.19‰$].

RESULTS

Content and isotopic composition of organic carbon in sediment samples from one locality

The organic carbon content of sediment samples from one locality varies

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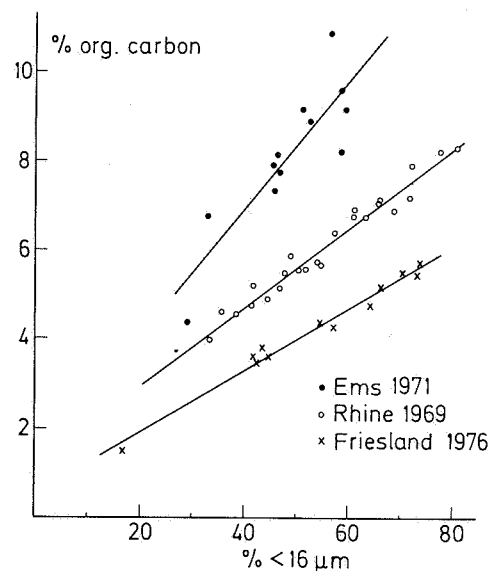
Fig. 2. Correlation between the organic carbon contents and the % < 16 μm in sediment samples from the same locality.

TABLE II

Isotopic composition of organic carbon in sediment samples from the same locality along the Ems estuary, with differences in grain size distribution (% < 16 μm)

Sample nr.	% < 16 μm	Organic carbon (%)	$\delta^{13}C_{PDB}$ (⁰/₀₀)
Diele			
63(1971)	29.3	4.4	−26.1
66(1971)	33.1	6.7	−27.4
70(1971)	58.9	8.2	−28.0
71(1971)	45.9	7.3	−28.0
73(1971)	58.9	9.6	−27.3
Leerort			
88(1971)	57.9	5.2	−26.6
90(1971)	68.5	6.0	−26.6
92(1971)	32.7	3.5	−26.9
93(1971)	45.4	4.6	−26.8
97(1971)	19.9	2.7	−27.0
Ditzum			
75(1971)	84.2	5.7	−25.2
78(1971)	83.0	5.5	−24.8
79(1971)	75.7	4.8	−26.0
81(1971)	80.7	5.2	−25.0
83(1971)	40.4	4.8	−25.0

widely. The content correlates positively with the amount of finely grained particles, as expressed by the percentage of particles less than 16 microns in diameter (Salomons and De Groot, 1978; Fig. 2).

Organic carbon contents are high in clay-rich samples and low in sandy samples. In order to compare the composition of sediments from different sedimentation areas, the concentrations at 50% < 16 μm will be used. These values are obtained by analysing a large number of samples from each separate locality and constructing curves as shown in Figure 2. In order to determine whether also the isotopic composition of the organic carbon depends on the grain-size distribution, samples from the Ems-estuary and from some marine sedimentation areas have been analysed (Table II). Although differences in the isotopic composition of sediment samples from one locality do occur, these appear not to be related to the grain-size distribution. In most cases the spread in these values is rather small. Therefore, we did not analyse individual samples, but made representative averages by mixing a large number of samples. These were analysed in duplicate for the isotopic composition of the organic carbon. A number of localities have been sampled repeatedly. The largest difference in δ^{13}C of sediments from the river Rhine taken over the period 1957—1973 is about 1°/$_{00}$; similar variations are found in the Dutch Wadden Sea area. Our conclusion thus is that the temporal differences in δ^{13}C for sediments from one locality are small. Apparently the sources of the organic matter have a relatively constant composition.

Organic carbon in fluvial sediments

Fluvial sediments of the rivers Rhine, Meuse, Ems and Scheldt have been sampled in the fresh-water tidal areas. The organic carbon contents (at 50% < 16 μm) as well as the δ^{13}C values are given in Table III. The organic carbon content of the fluvial sediments varies between 5.5% (Scheldt) and 8.4% (Ems). The δ^{13}C values vary between −28 and −25°/$_{00}$, which is the range valid for land-derived material, where δ^{13}C values of peat generally are −27 ± 1°/$_{00}$.

The relatively low carbon-14-content of 65% (equivalent to an age of 3560 years) of a sediment sample from the river Rhine (1958) points to the presence of old and stable organic components in the sediment.

Organic carbon in coastal marine sediments

Coastal marine sediments have been sampled off the Belgian, the Dutch and the German coast (Fig. 1). Results of the analyses of the organic carbon contents and their stable isotopic composition are given in Table IV, some carbon-14 data are presented in Table VII.

Organic carbon varies between 2.3% (Vlaamse Banken) and 4.3% (Wadden Sea). Compared with the fluvial sediments, the organic carbon con-

M16

TABLE III

The isotopic composition of organic carbon in fluvial sediments
The % organic carbon refers to the calculated value at 50% < 16 μm (e.g. each value represents about 10—15 analyses from one locality)

	Organic carbon (%)	$\delta^{13}C_{PDB}$ (‰)
Rhine 1958	7.0	−25.4
Rhine 1969 (june)	5.9	−25.3
Rhine 1969 (november)	6.3	−25.9
Rhine 1970 (october)	7.0	−25.6
Rhine 1971 (october)	7.4	−25.5
Rhine 1973 (may)	8.6	−25.0
Rhine 1973 (october)	7.9	−25.4
Meuse 1958	7.9	−25.2
Meuse 1969	6.5	−26.0
Ems 1971	8.4	−27.4
Scheldt 1973	5.5	−28.0

TABLE IV

The isotopic composition of organic carbon in marine sediments
The organic carbon contents refer to the values at 50% < 16 μm

		Organic carbon (%)	$\delta^{13}C_{PDB}$ (‰)
Vlaamse Banken	1960	2.3	−23.2
Blankenberghe	1959	2.4	−23.8
Zwarte Polder	1959	2.8	−22.2
Westerschelde	1974	2.7	−25.4
Oosterschelde	1973	3.0	−24.0
Grevelingen	1959	3.8	−22.7
IJmuiden	1960	3.8	−23.4
Friesland	1957	3.7	−24.6
Friesland	1970	4.3	−24.2
Friesland	1976	4.0	−23.2
Groningen	1957	3.3	−22.8
Groningen	1975	3.6	−22.3
Groningen	1976	3.9	−21.7
Dollard	1958	3.8	−25.3
Ost-Friesland	1969	3.8	−21.3
Jade	1969	3.0	−20.1

tent is considerably lower. The Wadden Sea sediments are richer in organic carbon than the marine sediments south of the Rhine—Meuse estuary.

The $\delta^{13}C$ values of the organic matter vary between −20.1‰ (Jade) and −25.3‰ (Dollard), comprising the whole range of values for continental (−25‰) to marine organic matter (around −20‰). The mean value for

the organic matter in the marine sediments studied is $-23.2^o/_{oo}$. This rather low (negative) value suggests the presence of relatively (about 50% or more) large fractions of continental organic matter.

The contribution of relatively stable continental organic matter is further supported by the carbon-14 results, varying between 48 and 84% (Table VII). The high ^{14}C values in the Wadden Sea are observed for those sediments that have high (less negative) $\delta^{13}C$ values. Marine organic matter apparently is younger and less stable compared to continental organic matter.

Organic carbon in estuarine sediments

Estuarine sediment samples from the Rhine—Meuse estuary have been collected in 1957 and in 1958 before the closure of the Haringvliet and the Grevelingen. The Ems estuary was sampled in 1971. The sampling localities are shown in Fig. 1.

The main mud discharge in the Rhine—Meuse estuary was through the Haringvliet, whereas not more than 10% was discharged through the Volkerak (Terwindt, 1967). The freshwater boundary was located in the Hollands Diep. In the Ems estuary the limit of salt intrusion is located between Leerort and Ditzum.

In both estuaries the sedimentary organic carbon content decreases, the $\delta^{13}C$ values increase in the seaward direction. This is a consequence of the mixing of marine and fluvial sediments. The organic carbon content (12%) as well as the carbon isotopic composition (about $-25.4^o/_{oo}$) in the Hollands Diep sediments (Rhine—Meuse estuary) are similar to those ob-

TABLE V

The isotopic composition of organic carbon, inorganic carbon and clay minerals in the estuaries of the rivers Rhine—Meuse and of the Ems

Locality	Salinity ($^o/_{oo}$)	Organic carbon		Inorganic carbon	Clay fraction $\delta^{18}O_{PDB}$ ($^o/_{oo}$)
		%	$\delta^{13}C_{PDB}$ ($^o/_{oo}$)	$\delta^{13}C_{PDB}$ ($^o/_{oo}$)	
Rhine—Meuse					
Rhine	0.2	7.0	−25.5	−3.6	+16.6
Meuse	0.2	7.9	−25.8	−3.3	+15.8
Hollands Diep 1	0.2—4	7.1	−25.7	−2.0	+16.6
Hollands Diep 2	0.2—8	7.1	−25.4	−1.3	+17.2
Hollands Diep 3	0.2—12	7.1	−25.0	−1.2	+19.1
Haringvliet	2.0—25	4.8	−24.7	−0.6	+19.1
Ems					
Diele	0.2	8.4	−27.4	−5.0	+19.8
Leerort	0.2	4.9	−26.8	−0.6	+19.3
Ditzum	3	3.7	−25.2	−0.5	+19.3
Dollard	5—20	3.8	−25.3	−0.5	+19.5

served in the Rhine and Meuse sediments. Apparently the organic carbon is of continental origin.

The isotopic composition of the carbonates ($\delta^{13}C$, $\delta^{18}O$) and clay minerals ($\delta^{18}O$), on the other hand, differ from those shown by the fluvial sediments (Table V). From the latter data we conclude that between 35 and 45% of these sedimentary components are derived from the North Sea. In the Ems estuary the carbonates and clay minerals collected at Leerort are mainly of marine origin (about 90%) (Salomons and Mook, 1977) whereas the organic carbon is mainly of continental origin.

Organic carbon in suspended matter

The last obvious step was to collect suspended matter from the North Sea and the Nieuwe Waterweg (October 1971) (Fig. 3). The samples have been taken at various depths. In some cases the amount of material allowed to determine both the isotopic composition of the organic and the inorganic carbon as well as the grain-size composition (% < 16 μm). However, in a few cases it was necessary to combine two samples from one locality taken at different depths. In these cases, both depths are given in Table VI.

The grain-size distribution (% < 16 μm) generally is close to the value used for characterizing the deposited sediments. Therefore, organic carbon contents from both the sediments and the suspended matter (Tables IV and VI) may be directly compared. The organic carbon content of marine suspended matter is higher compared to that in estuaries (compare localities A and B with E and G), contrary to the deposited sediments. The high $\delta^{13}C$
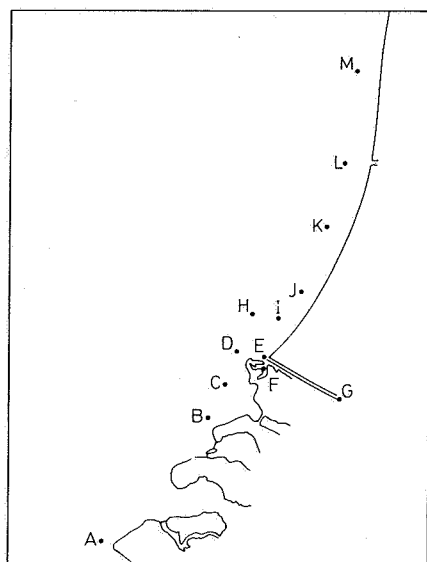

Fig. 3. The sampling localities for suspended matter along the Dutch North Sea coast.

TABLE VI

Isotopic composition of organic and inorganic carbon in suspended matter from the North sea and the Nieuwe Waterweg (Rotterdam Harbour)

Locality	Depth (m)	% < 16 μm	Organic carbon		Inorganic carbon		
			%	$\delta^{13}C_{PDB}$ ($^o/_{oo}$)	%	$\delta^{13}C_{PDB}$ ($^o/_{oo}$)	$\delta^{18}O_{PDB}$ ($^o/_{oo}$)
A	0	—	6.6	−21.9	—	—	—
	2+4	44.5	6.4	—	—	—	—
	6+8	—	6.6	−22.2	17.8	−0.2	−3.2
B	0	—	7.8	−21.0	—	—	—
	2+4		8.7	−21.0	11.4	−0.5	−4.4
	6+8	43.1	6.0	−22.0	—	—	—
C	0+2	—	7.6	−24.2	—	—	—
	4+6		6.6	−24.6	22.2	−0.2	−3.4
E	0	51.5	5.5	−26.4	21.5	−0.8	−4.3
	4	51.4	5.9	−26.6	18.3	−0.8	−5.0
	8	50.5	5.0	−26.4	19.5	−0.6	−4.6
	10	48.9	5.4	−26.3	19.6	−0.7	−4.6
	14	50.9	5.0	−25.8	20.5	−0.7	−4.4
G	0	43.2	5.9	−27.2	18.3	−1.0	−5.3
	8	32.7	4.6	−27.0	15.3	−0.9	−5.2
	12	48.0	6.8	−26.8	16.6	−1.1	−5.6
	16	34.2	4.7	−27.1	16.1	−0.8	−4.7
I	0	—	9.2	−15.2	16.7	−0.6	−4.0
J	0+4	—	12.6	−20.6	—	—	—
K	0	—	9.8	−20.1	—	—	—

E = Europoort and G = Botlek.

values at the localities A, B, J and K show that the high organic carbon contents are caused by the presence of marine organic matter. In general, the amount of marine organic carbon in the suspended matter is higher than that in the sediments. It should be noted, however, that the marine contribution to the suspended matter is seasonally dependent; a survey in February showed much less variation in $\delta^{13}C$ (−22 to −24$^o/_{oo}$). The mean values of 16 samples was −23.2 ± 0.6$^o/_{oo}$.

The organic carbon in the Nieuwe Waterweg, Europoort and Botlek is mainly continental: the $\delta^{13}C$ values vary between −26 and 27$^o/_{oo}$ (Table VI). The $\delta^{13}C$ values of the suspended inorganic carbonate vary between −1.1 and −0.2$^o/_{oo}$. The estuarine values (−1$^o/_{oo}$) differ from those observed in fluvial sediments (−2.6$^o/_{oo}$). This can be explained by a mixing of marine and fluvial carbonates in the estuaries, as has been described for the deposited sediments (Salomons, 1975).

The influence of fluvial carbonates on the composition of the carbonates in marine suspended matter is rather limited. Only close to the mouth of the river Rhine (locality I) can the presence of fluvial carbonates be detected. Apparently, the amount of suspended matter transported by the Rhine to the North Sea is small as compared to the amount of suspended matter already present. These data, therefore, confirm the conclusions derived from an earlier examination of the isotopic composition of carbonates and clay minerals (Salomons, 1975; Salomons et al., 1975) in the deposited sediments.

M20

TABLE VII

The carbon-14 content of the organic carbon in a number of marine (m), fluvial (f) and estuarine (e) sediment samples
The ^{14}C content is given in percentages of modern carbon (0.95 × spec. act. of NBS oxalic acid)

Number	Locality	Carbon-14 (pmc)	
GrN	Ost-Friesland	83.9 ± 0.7	m
GrN-6754	Friesland	48.0 ± 0.6	m
GrN-6797	Groningen	66.6 ± 1.2	m
GrN-7046	Grevelingen	55.9 ± 1.0	m
GrN-5669	Biesbosch (Rhine) 1958	65.1 ± 0.6	f
GrN-7047	Biesbosch (Rhine) 1969	91.4 ± 1.3	f
GrN-7045	Europoort	66.9 ± 0.8	m
GrN-7048	Rijnhaven (Rotterdam Harbour)	58.2 ± 0.7	e

REFERENCES

Aizenstat, Z., Baedecker, M.J. and Kaplan, I.R., 1973. Distribution and diagenesis of organic compounds in Joides sediments from Gulf of Mexico and Western Atlantic. Geochim. Cosmochim. Acta, 40: 1881—1898.
Gearing, P., Plucker, F.E. and Parker, P.L., 1977. Organic carbon stable isotope ratios of continental marine sediments. Mar. Chem., 5: 251—266.
McCave, I.N., 1973. Mud in the North Sea. In: E.D. Goldberg (Editor), North Sea Science. M.I.T. Press, pp. 75—100.
Mook, W.G., 1968. Geochemistry of Stable Carbon and Oxygen Isotopes of Natural Waters in the Netherlands. Thesis, University of Groningen.
Newman, J.W., Parker, P.L. and Gehrends, E.W., 1973. Organic carbon isotope ratios in Quaternary cores from the Gulf of Mexico. Geochim. Cosmochim. Acta, 37: 225—238.
Nissenbaum, A, and Kaplan, I.R., 1972. Chemical and isotopic evidence for the in situ origin of marine humic substances. Limnol. Oceanogr., 17: 570—582.
Postma, H., 1973. Transport and budget of organic matter in the North Sea. In: E.D. Goldberg (Editor), North Sea Science. M.I.T. Press, pp. 326—334.
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. and De Groot, A.J., 1978. Pollution history of trace metals in sediments, as affected by the Rhine river. In: W.E. Krumbein (Editor), Environmental Biogeochemistry and Geomicrobiology. Ann Arbor Science, Volume 1: 149—162.
Salomons, W. and Mook, W.G., 1977. Trace element concentrations in estuarine sediments: mobilization, mixing or precipitation. Neth. J. Sea Res., 11: 119—129.
Salomons, W., Hofman, P., Boelens, R. and Mook, W.G., 1975. The oxygen isotopic composition of the fraction less than 2 microns (clay fraction) in Recent sediments from Western Europe. Mar. Geol., 18: M23—M28.
Schultz, D.J. and Calder, J.A., 1976. Organic carbon $^{13}C/^{12}C$ variations in estuarine sediments. Geochim. Cosmochim. Acta, 40: 381—385.
Tan, F.C. and Strain, P.M., 1979. Organic carbon isotope ratios in Recent sediments in the St. Lawrence estuary and the Gulf of St. Lawrence. Est. Coastal Mar. Sci., 8: 213—225.
Terwindt, J.H.J., 1967. Mud transport in the Dutch delta area and along the adjacent coast line. Neth. J. Sea Res., 3: 505—531.

Letter Section

THE OXYGEN ISOTOPIC COMPOSITION OF THE FRACTION LESS THAN 2 MICRONS (CLAY FRACTION) IN RECENT SEDIMENTS FROM WESTERN EUROPE

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ABSTRACT

Salomons, W., Hofman, P., Boelens, R. and Mook, W.G., 1975. The oxygen isotopic composition of the fraction less than 2 microns (clay fraction) in Recent sediments from western Europe. Mar. Geol., 18: M23—M28.

The oxygen isotopic composition of the clay fraction in Recent argillaceous sediments in western Europe shows regional differences, the δ^{18}_{SMOW} values varying between + 15.8 and + 21.7‰. This phenomenon is used for sediment-transport studies. In the Rhine—Meuse estuary a landward transport of marine sediments is observed. The clay fraction of the sediments in the Wadden Sea is only for a minor part derived from the rivers Rhine and Meuse.

INTRODUCTION

Large amounts of mud have been deposited in The Netherlands and adjacent areas. The deposition takes place mainly in the estuaries, the harbours and along the coast. An important sedimentation area is the northern part of The Netherlands and West Germany. It is estimated that in the Dollard area alone (Fig.1) about $884 \cdot 10^6$ tons of mud have been deposited since the 17th century (De Smet and Wiggers, 1960).

The mud deposits found at the localities shown in Fig.1, are composed mainly of quartz, clay minerals, feldspars, organic matter and carbonates. Especially the carbonate and the organic-matter content show large regional variations (Salomons, 1974). The organic-matter content of fluvial mud is about 15%, values for marine mud vary between 4 and 6%. The carbonate content varies between 2% for the river Ems to 40% for the Somme. The carbonate content of the marine mud deposits decreases in a northerly direction along the coast from about 27% for the Belgian coast to 11% for the coast of West Germany. In a former study we presented our results on the

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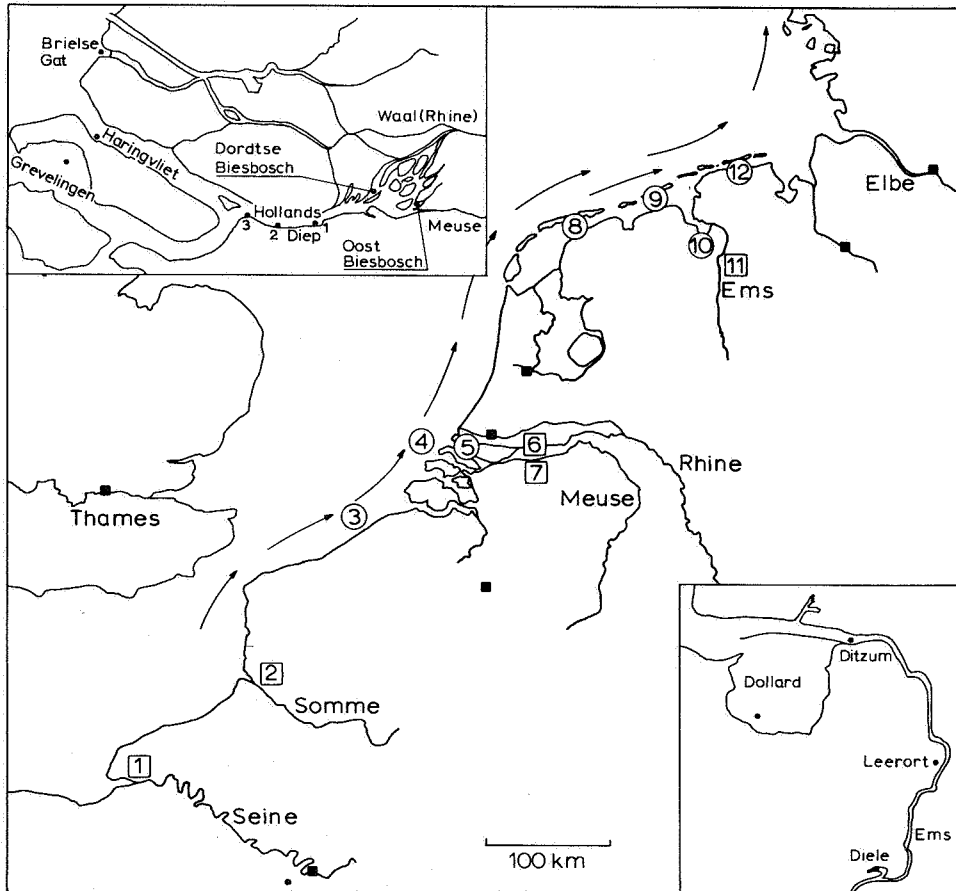
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Fig.1. The area studied and location of samples. The Rhine—Meuse estuary is pictured in the NW-corner, the Ems estuary in the SE-corner. 1 = Seine; 2 = Somme; 3 = Vlaamse Banken; 4 = Grevelingen; 5 = Haringvliet; 6 = Rhine; 7 = Meuse; 8 = Friesland; 9 = Groningen; 10 = Dollard; 11 = Ems; 12 = Ostfriesland.

origin of the carbonates, which occur in the silt-sized fraction of these sediments (Salomons, 1974). In this paper we will discuss the stable oxygen isotopic composition of the smaller-grained clay fraction.

The oxygen isotopes in clay minerals of ocean sediments have been the subject of studies by Savin and Epstein (1970), whereas the clay minerals in soils were discussed by Lawrence and Taylor (1972). The oxygen isotopic composition of clay minerals is determined by that of the surrounding water during their formation. The regional differences in the ^{18}O content of precipitation are thus reflected in the clay minerals in soils. In the estuarine or coastal environment to which the clay minerals are transported and where they become part of the sediments, the ^{18}O content of the water is generally

higher by several ‰. The processes of isotopic equilibration, however, are ex-
tremely slow, so that the sedimentary clay minerals do not attain isotopic
equilibrium with the surrounding water. The oxygen isotopic composition,
especially that of kaolinite, illite and smectite, in ocean sediments is hardly
affected (Savin and Epstein, 1970).

Therefore, it is possible in principle to use the isotopic composition as a
natural tracer for sediment-transport studies.

EXPERIMENTAL METHODS

All samples were prepared by the BrF_5 method as described by Clayton and
Mayeda (1963). The isotopic analyses were performed using a Varian-Mat M-86
mass spectrometer according to the procedures given by Mook and Grootes
(1973). Results are based on the values for NBS-20 of -1.06 and -4.14‰ for
respectively δ_{PDB}^{13} and δ_{PDB}^{18} and they are presented relative to the SMOW
standard using: $\delta_{SMOW}^{18} = 1.0305\ \delta_{PDB}^{18} + 30.5$ ‰. The analytical reproducibility
is better than $\pm\ 0.25$‰.

SAMPLING

All sediment samples were collected from the uppermost, recently depos-
ited material. Portions of about twenty samples from each locality were taken
to compose a representative sample. In this sample the clay fraction ($< 2\ \mu$m)
was separated. Part of the material was used for the semi-quantitative X-ray
analysis, the other part was analysed for oxygen isotopes.

RESULTS AND DISCUSSIONS

The localities sampled are given in Fig.1. The mineralogical composition of
the clay minerals in the sediment samples is rather homogeneous. The domi-
nant clay mineral is illite, while montmorillonite, vermiculite and kandite occur
in smaller amounts. The same dominance (more than 80%) has been observed

TABLE I

The oxygen isotopic composition of the fraction $< 2\ \mu$m in argillaceous fluvial sediments

River	δ_{SMOW}^{18} (‰)	σ	N
Rhine	+ 16.6	0.3	8
Meuse	+ 15.8	0.4	5
Ems	+ 19.8	1.0	5
Seine	+ 20.7	0.2	2
Somme	+ 21.7	0.2	2

σ refers to the average deviation, N to the number of analyses.

M26

by Favejee (1960). Due to the fact that the differences in the mineralogical composition between the sedimentation areas are small, it is difficult to apply the mineralogical composition to study the origin of the clays.

The *oxygen isotopic composition* of the fluviatile sediments (Table I) varies between 16.0 and 21.7‰. If the clay minerals were formed during the *Quaternary* we might expect a difference between the sediments from the river Rhine on the one hand and the rivers Seine, Somme, Ems and Meuse on the other. The latter have drainage areas not far from the coast where the isotopic composition of the precipitation at present is around —8‰. The precipitation in the drainage area of the Rhine has partly undergone both the continental and altitude effect, causing a shift to more negative values (—9 to —11°/$_{00}$). The isotopic composition of the river Meuse varies between —7 and —8‰. These differences are not reflected in the isotopic composition of the clay fraction. Apparently a large part of the clay minerals found in these river sediments was partly derived from ancient eroded argillaceous sediments in their respective drainage areas.

The isotopic data for the *marine* samples (Fig.1) are given in Table II. The main sources for the sediments in this area are the rivers Rhine and Meuse

TABLE II

The oxygen isotopic composition of the fraction < 2 μm in argillaceous sediments from western Europe

Locality	δ^{18}_{SMOW} (‰)	σ	N
Southern areas:			
Vlaamse Banken	20.0	0.4	7
Grevelingen	19.2	0.4	9
Rhine—Meuse estuary:			
Oost Biesbosch (Meuse)	15.8	0.4	5
Dortse Biesbosch (Rhine)	16.6	0.3	8
Hollands Diep 1	16.6	0.4	6
Hollands Diep 2	17.2	0.5	5
Hollands Diep 3	19.1	0.1	3
Haringvliet	19.1	0.3	6
Brielse Gat	19.7	0.8	6
Wadden Sea area:			
Friesland	19.8	1.0	6
Groningen	19.2	0.5	5
Dollard	19.5	0.5	8
Ostfriesland	20.5	0.4	3
Ems estuary:			
Diele	19.8	1.0	5
Leerort	19.2	0.4	3
Petkum	19.3	0.4	4

σ refers to the average deviation, N to the number of analyses.

TABLE III

The amount of suspended matter transported annually by a number of sources

Source	Supply (10⁶ ton/year)
Rhine—Waal[1]	3.20
Meuse[1]	0.70
English Channel[2]	5.10
Scheldt[2]	0.40
Ems[2]	0.14

[1] After Terwindt, 1967.
[2] After McCave, 1973.

and the northward current through the English Channel (Table III). The over-all transport of the suspended matter in the coastal areas of Belgium and The Netherlands is directed to the north. The material coming through the English Channel is partly deposited at the Vlaamse Banken and in the Grevelingen.

The difference in the oxygen isotopic composition of the clay minerals from the two main sources presents the possibility of determining their relative influence on the sediments deposited north of the large river estuaries. The oxygen isotopic composition of the clay material from the river Ems on the contrary, is nearly equal to that of nearby marine sediments. Therefore, it is not possible to determine the contribution of the river Ems to the clay fraction in Wadden-Sea sediments.

Considering the overall stream pattern of the North Sea, the Wadden-Sea sediments are derived from material transported from the south. From the δ^{18} figures in the clay minerals (Table II) we must conclude, however, that the contribution of the river Rhine is very small (about 10—20%). The same conclusion was drawn from the isotopic composition of the carbonates (Salomons, 1974).

The *estuarine* samples were also collected between 1958 and 1960, that is, before the closure of the Haringvliet and the Grevelingen. The situation at that time, together with the sample localities is presented in Fig.1. The fresh-water boundary in this estuary lies in the Hollands Diep. About 90% of the suspended matter is discharged through the Haringvliet, the remainder through the Volkerak to the North Sea (Terwindt, 1967).

The oxygen isotopic composition of the clay fraction changes progressively in a seaward direction (Table II). This cannot be attributed to isotopic exchange as stated before. Therefore, the sediments in this estuary do not originate from one source. At the locality Hollands Diep 1 the δ^{18} is still close to those found in the fluviatile samples. At Hollands Diep 3 it is very close to values found for the marine sediments. Consequently, we arrive at the conclusion that in this estuary a mixing of marine and fluviatile clay material occurs. Using the value of + 16.3‰ for the latter and + 19.6‰ for the marine clay, it can be calculated

M28

that about 50% of the clay material in the Hollands Diep is of a marine origin although the average chlorinity of the water is only 2‰. The same discrepancy between the chlorinity of the water and the composition of the sediments was found for the carbonate fraction of the sediments (Salomons, 1974). This landward transport of marine material in estuaries has also been observed by Meade (1969), Postma (1967) and many others.

CONCLUSIONS

(1) The fraction less than 2 μm of the clay sediments in the Rhine—Meuse estuary is mainly derived from the marine environment, according to the δ^{18} of the clay minerals.

(2) Only a minor part of the fraction less than 2 μm in the sediments from the Wadden Sea area is derived from the rivers Rhine and Meuse.

ACKNOWLEDGEMENTS

REFERENCES

Clayton, R.N. and Mayeda, T.K., 1963. The use of bromine pentafluoride in the extraction of oxygen from oxides and silicates for isotopic analyses. Geochim. Cosmochim. Acta, 27: 43—52.
De Smet, L.A.H. and Wiggers, A.J., 1960. Einige Bemerkungen über die Herkunft und die Sedimentationsgeschwindigkeit der Dollartablagerungen. Verh. K. Ned. Geol. Mijnbouwk. Genoot., 19: 129—133.
Favejee, J.C.L., 1960. On the origin of the mud deposits in the Ems-estuary. In: J.H. van Voorthuyzen and P.H. Kuenen (Editors), Das Ems Estuarium (Nordsee). Verh. K. Ned. Geol. Mijnbouwk. Genoot., 19: 147—152.
Lawrence, J.R. and Taylor, H.P., 1972. Hydrogen and oxygen isotope systematics in weathering profiles. Geochim. Cosmochim. Acta, 36: 1377—1393.
McCave, I.N., 1973. Mud in the North Sea. In: E.D. Goldberg (Editor), North Sea Science, pp.75—99.
Meade, R.H., 1969. Landward transport of bottom sediments in estuaries of the Atlantic coastal plain. J. Sediment. Petrol., 39: 222—234.
Mook, W.G. and Grootes, P.M., 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 Spectrom. Ion Phys., 12: 273—298.
Postma, H., 1967. Sediment transport and sedimentation in the marine environment. In: American Association for the Advancement of Science, Estuaries, Washington, Publ. No. 83, pp.158—179.
Salomons, W., 1974. Chemical and isotopic composition of carbonates during an erosion— sedimentation cycle. University micro films, Ann Arbor, Order No. 74-20094.
Savin, S.M. and Epstein, S., 1970. The oxygen and hydrogen isotope-geochemistry of ocean sediments and shales. Geochim. Cosmochim. Acta, 34: 43—63.

CHEMICAL AND ISOTOPIC COMPOSITION OF CARBONATES IN RECENT SEDIMENTS AND SOILS FROM WESTERN EUROPE[1]

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ABSTRACT: The sediments and soils constitute an erosion-sedimentation cycle composed of: Solid carbonate rock → Soil → Fluviatile sediment → Estuarine sediment → Marine sediment → Salt marsh. Determinations were made of the total carbonate and dolomite contents of the sediments as well as the strontium and carbon-14 content of the carbonates and their stable carbon and oxygen isotopic composition. In soils the isotopic composition of the carbonates was studied. The soils analysed are from the Netherlands and France. The sediments are from the rivers Rhine, Meuse, Ems, Seine, Somme and Rhône, from the estuaries of the Rhine, Meuse and the Ems and from the coastal areas of Belgium, the Netherlands and Western Germany.

The isotopic composition of the carbonates in soils is different from that of the parent material. This difference is due to the presence of newly formed carbonates. The amount varies between 10 and 50% of the carbonates present. The rivers Rhine, Meuse and Seine contain both soil-derived carbonates and carbonates from eroded carbonate rocks. The carbonates in the river Somme originate mainly from carbonate rocks. The carbonates in the estuaries of the Rhine, Meuse and Ems are predominantly derived from the marine environment. The carbonates are transported up to the freshwater boundary in these estuaries. The carbonates in marine sediments from the Wadden area are derived for about one fifth from the rivers Rhine and Meuse.

INTRODUCTION

Carbonate rocks occur rather abundantly on the continent of Western Europe. Carbonate particles are washed away from the soils developed on these rocks and added to the sediment load of the rivers. The carbonate content of the river deposits investigated varies between 2 and 40%. The bulk of this material is transported by way of the estuaries to the North Sea. There the fluviatile carbonates are added to carbonates derived from skeletal material and from eroded carbonate formations along the coast.

The marine sediments are transported by the prevailing currents to the various areas of deposition. An important depositional area is the Wadden Sea in the Northern part of the Netherlands and Western Germany (localities 9–13 in Fig. 1). When the accumulation of the tidal sediments has reached the mean high water

level, it is possible for plants to settle and the tidal flat is turned into a salt marsh. The sediments and soils discussed are all part of the same erosion-sedimentation cycle.

The object of this investigation was to study the origin of the carbonates in this cycle by means of mineralogical, chemical and isotope analysis. Weathering processes were studied in soils on carbonate rocks and salt marshes. More than 1,200 sediment samples were collected at the localities shown in Figure 1. Samples are partly from the same set as used by de Groot (1964) for his manganese study, additional samples have been taken in the course of this investigation.

EXPERIMENTAL METHODS

The Total Carbonate Content of the Sediments and Soils

The total carbonate content was measured by treating the sample with dilute hydrochloric acid solution and the carbon dioxide evolved is measured by gas volumetry. This amount is converted to the percentage calcium carbonate in the sample.
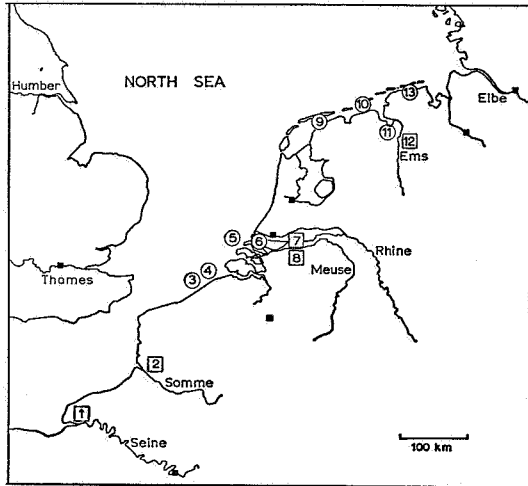
FIG. 1.—The area studied. Detailed maps of the Rhine-Meuse estuary and the Ems estuary are given in Figures 7 and 9.

1 = Seine	8 = Meuse
2 = Somme	9 = Friesland
3 = Vlaamse Banken	10 = Groningen
4 = Zwarte Polder	11 = Dollard
5 = Grevelingen	12 = Ems
6 = Haringvliet	13 = Ost-Friesland
7 = Rhine	

FIG. 2.—Relationship between the total carbonate content and the percentage of particles less than 20 μm in sediment samples from the Hollands Diep, Dordtsche Biesbosch and Haringvliet. For comparison the carbonate content at 50% < μm is used.

The Carbonate Content of Samples at Separate Localities

The carbonates in the investigated sediments occur mainly in the silt-sized fraction. The carbonate content of sediment samples from the same locality may show a wide range of values. In sandy samples the carbonate content is lower compared to that of the clay-rich samples. Therefore, in comparing different sedimentation areas, samples with the same grain-size distribution have to be compared. As a measure of the grain-size distribution in these finely grained sediments, we use the percentage of particles with a diameter less than 20 μM. To compare the carbonate content between different areas we use the carbonate content at 50% less than 20 μM (Fig. 2). These values are obtained by analysing from each separate locality a large number of samples and constructing curves as shown in Figure 2.

Mineralogy

The mineralogy was determined by X-ray diffraction analysis. Use was made of a Philips diffractometer, CuKα radiation was employed. A monochromator was mounted in front of the counter; this eliminated background radiation
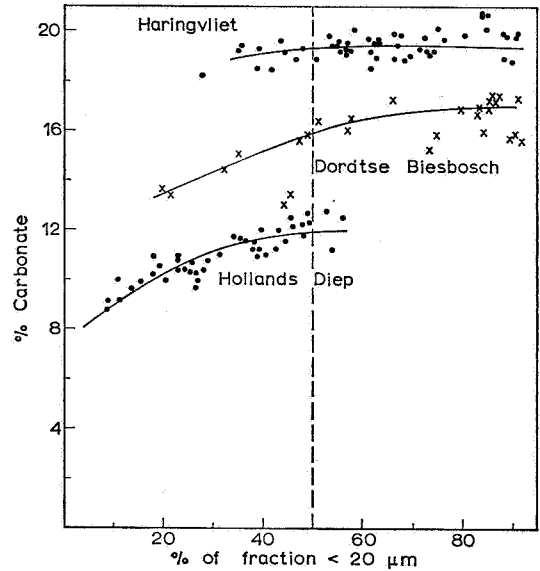
due to the fluorescence of iron present in the sediment samples.

The magnesium content of calcite was estimated from the position of the 104 reflection (Goldschmidt et al., 1961). Fluorite was used as an internal standard. In a few cases the magnesium content of individual calcite grains in the samples was determined directly with microprobe analysis, which confirmed the data obtained with X-ray diffraction.

Dolomite Content

The dolomite content was determined with quantitative X-ray diffraction. As a measure for the dolomite content the area of the 104 reflection was used. A calibration curve was established by adding known amounts of dolomite to a sediment sample. The reproducibility of the analysis varies between 10 and 20%, depending on the dolomite content.

Strontium Content

The total strontium content of the sediment samples was determined as part of a study on the occurrence of magnesium, calcium and strontium in argillaceous sediments. The analyses were performed by activation analysis at the RCN (Reactor Centrum Nederland) by Dr. H. A. Das. Additional analyses for this study
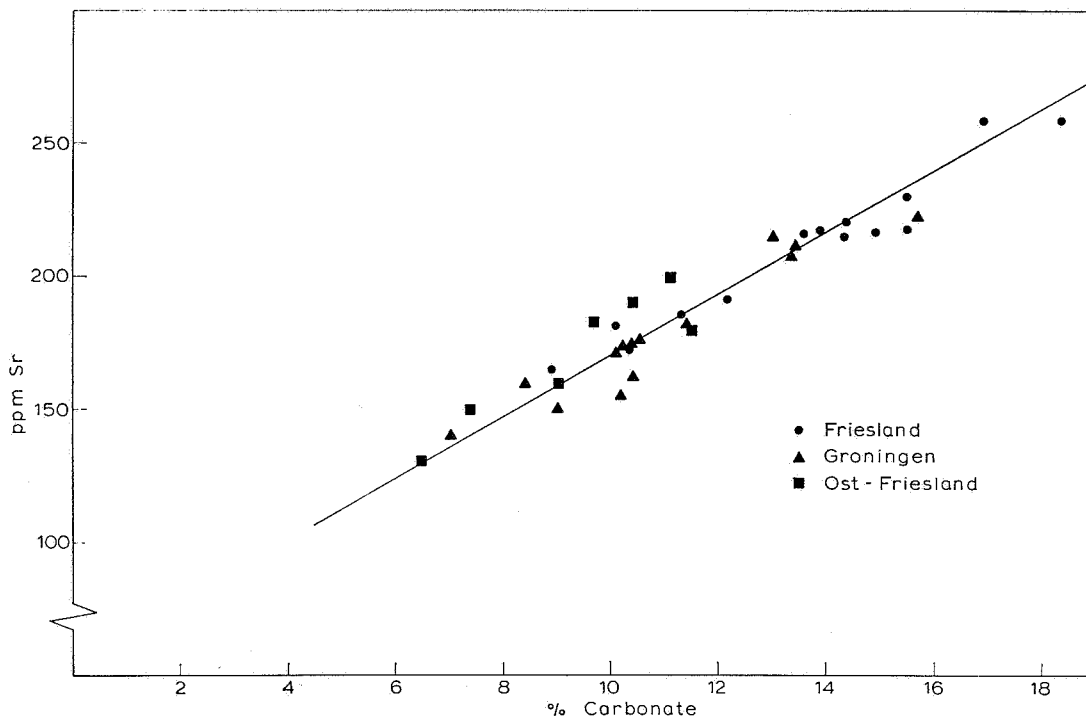
442   W. SALOMONS

FIG. 3.—Relationship between the total carbonate content and the strontium content for samples from the Wadden area.

were carried out by X-ray fluorescence spectrometry. Details are given by Salomons (1973). In Figure 3 the relationship between the total carbonate content and the total strontium content in sediment samples from the Wadden area is shown. Since part of the strontium is present in the silicates, the curve does not extrapolate through zero. The curve was determined by a least square procedure in order to determine the strontium content of the carbonates.

Stable Isotope Analysis

Full details on analytical procedures used can be found in Mook (1968) and Mook and Grootes (1973). Results are given relative to the PDB standard:

$$\delta(\%_0) = \frac{R_s - R_{st}}{R_{st}} \times 1000 \quad \begin{matrix} R = {}^{18}O/{}^{16}O; {}^{13}C/{}^{12}C \\ s = \text{sample} \\ st = \text{standard} \end{matrix}$$

The reproducibility of the analysis on pure carbonates is better than 0.1‰. Results are based on δ^{13}_{PDB} and δ^{18}_{PDB} values for NBS-20 of −1.06 and −4.14 respectively.

The spread in the isotopic composition of the carbonates in sediment samples from the same locality is about ±0.3‰. For most areas we

made representative samples by mixing a large number of individual samples. This sample was analysed in triplicate.

Carbon-14 Content

The carbon-14 analyses were also carried out by the Physics Laboratory of the University Groningen. The carbon-14 content is given in percentages of the NBS oxalic acid standard activity. On this scale recent carbonates formed in the marine environment under natural conditions have a carbon-14 content of about 100%. The carbon-14 content can be used to calculate the age of the sample analysed. However, the carbonates in soils and sediments are generally a mixture of carbonates of various ages, including carbonates with no measurable carbon-14 content at all. Therefore, a calculated C-14 age for these samples is not meaningful. However, the carbon-14 content is a very sensitive parameter to detect the presence of recent carbonates (younger than 50,000 years).

Sampling

The sediment samples were taken from the uppermost few millimeters of the deposited material. At each locality at least 20 samples
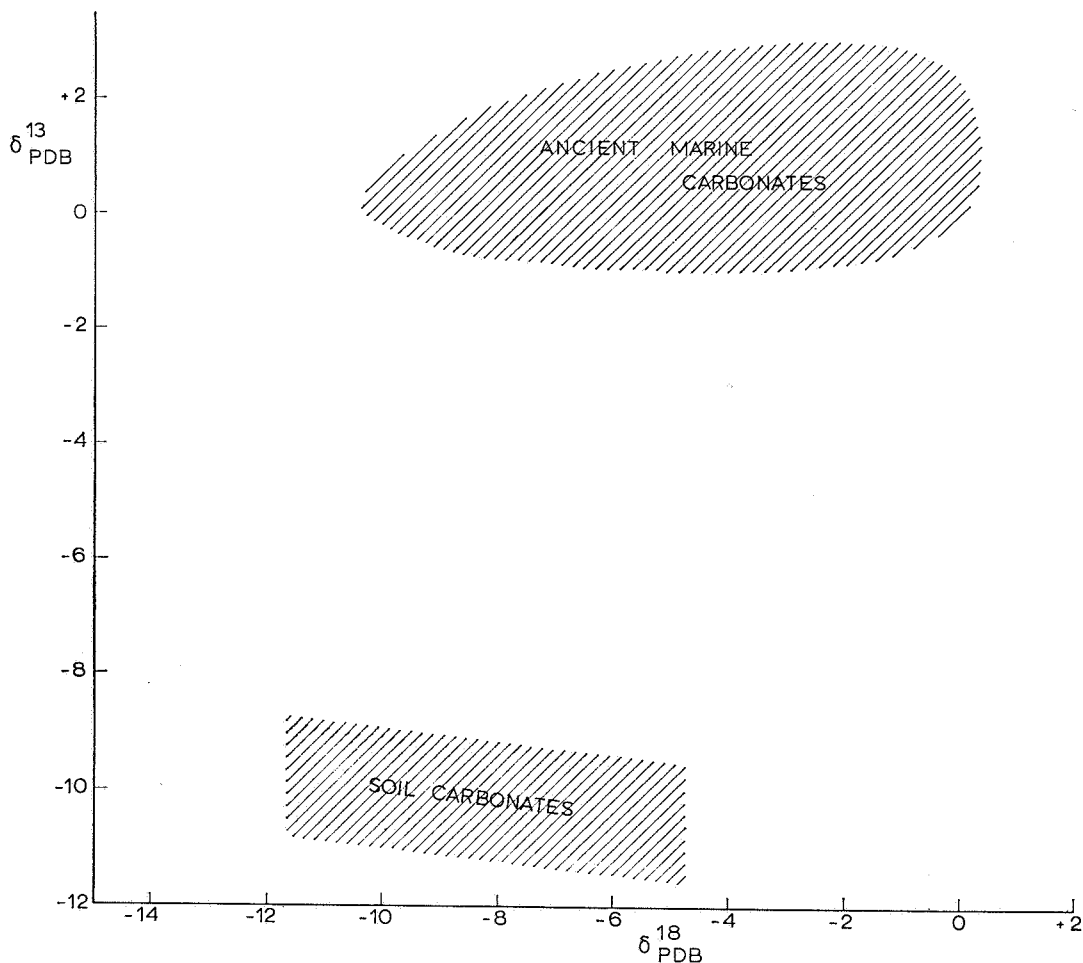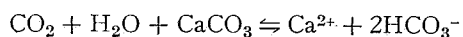
Fig. 4.—The stable isotopic composition of ancient carbonates (Keith and Weber, 1964) and of soil carbonates. The data for the soil carbonates were calculated using the fractionation factors given by Craig (1965) and Emrich et al. (1970) for the temperature range of 10-30°C. Oxygen isotopic composition of the groundwater $-7.5 \pm 1‰$, carbon isotopic composition of the dissolved bicarbonate $-12 \pm 1‰$.

were taken to insure that the whole range in grain sizes from about 20 to 80% particles less than 20 microns is obtained. In some cases the localities were sampled more than once. No significant difference in the composition of the carbonates between the various times of sampling were found.

CARBONATES IN SOILS

Soils occur in the first part of the erosion-sedimentation cycle studied. Carbonates in the soil are subject to dissolution which is caused by the high partial pressure of carbon dioxide in the soil atmosphere:

$$CO_2 + H_2O + CaCO_3 \rightleftharpoons Ca^{2+} + 2HCO_3^-$$

The isotopic composition of carbon dioxide in soils from temperate climates varies between -26.5 and $-23.5‰$ (δ^{13}_{PDB}) (Galimov, 1966). If ancient marine carbonate rocks with a carbon isotopic composition of about 0‰ (Keith and Weber, 1964) are dissolved, the resulting bicarbonate in the groundwater will have a carbon isotopic composition of about $-12‰$. A reprecipitation of the dissolved carbonates takes place deeper in the soil in the form of concretions. Reprecipitation of carbonates in the upper part of the soil is common for soils from semi-arid regions, which often results in the formation of calcrete. On the other hand, knowledge on the processes of reprecipitation in the upper part of soils from temperate climate regions is
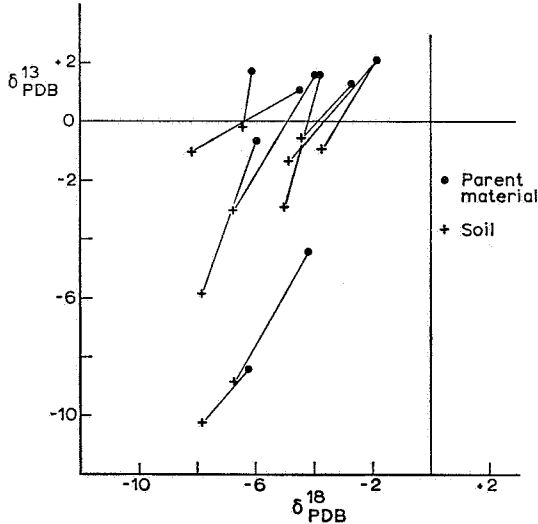
Fig. 5.—Isotopic composition of carbonates in the soil, compared with the isotopic composition of the underlying carbonate rock.

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

scarce. This part of the soil is important, since it is one of the sources for carbonates in fluviatile sediments.

If no reprecipitation takes place, the isotopic composition of the carbonates will be equal to that of the parent material (mostly ancient carbonate rocks). On the other hand if the carbonates are a mixture of parent material and authigenic carbonates, their isotopic composition may comprise the whole range from ancient carbonates to carbonates in equilibrium with groundwater. Especially the carbon isotopic composition is useful to detect the presence of newly formed carbonates (Fig. 4).

Soils Developed on Carbonate Rocks

The soils analysed were mainly formed on ancient marine carbonate formations from the Basin of Paris and from the Southern part of the Netherlands. In a few cases soils formed on ancient freshwater carbonate rocks were investigated. The topsoil (0–5 cm) and the parent material were analysed. The carbonates consisted of low-Mg calcite. The isotopic composition of the soil carbonates is in all cases different from that of the parent material (Fig. 5). This shift is caused by the presence of newly formed freshwater carbonates.

The amount of authigenic carbonates can be calculated from the stable carbon isotopic composition. The oxygen isotopic composition is not suitable, because of the seasonal variations
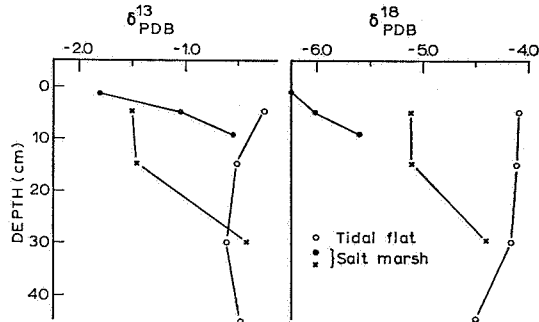
in the isotopic composition of rain water and the large temperature dependence of the fractionation constant between calcite and water. If we assume that the newly formed carbonates are in equilibrium with groundwater, their carbon isotopic composition is about $-10‰$. Using this value (δ^{13}(new)) and the carbon isotopic composition of the parent material (δ^{13}(p.m.)), we can calculate the amount of newly formed carbonates using the formula:

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

In the soils investigated the amount of newly formed carbonates varies between 10 and 50%.

Carbonates in Salt Marshes

The processes affecting carbonates in salt marshes are expected to be similar to the processes occuring in soils. To study the processes in the salt marsh, in as far as they affect the carbonates, we selected the Dollard area. After the last embankment in 1924, the continued sedimentation has resulted in the present salt marsh.

The carbonate content (given at 50% <20 microns) in the surface layers of the salt marsh is about 7%; the value for the tidal flat area is 11% (Table 2). This dissolution of carbonates is also reflected in the calcium content of the pore fluids in the salt marsh sediment.

The mean calcium content of 700 ppm is twice as high as the value found in the tidal flat sediments. Analysis of the carbon isotopic composition of the bicarbonate in the pore fluid showed that the dissolution is caused by the action of biogenic carbon dioxide (Salomons, 1973).

In Figure 6 the isotopic composition of the carbonates in two profiles from the salt marsh

and in one profile from the tidal flat area is given.

In the upper part of the profiles from the salt marsh the isotopic composition is shifted towards negative values. Additionally, we determined the isotopic composition of the carbonates in a large number of samples from the surface layer. The mean value for the carbon isotopic composition is $-1.7‰$ and for the oxygen isotopic composition is $-5.6‰$. Similar values for the tidal flat sediments are $-0.5‰$ and $-4.3‰$ respectively (Table 2). Apparently, as in the soils studied, part of the dissolved carbonates are reprecipitated.

CARBONATES IN ARGILLACEOUS SEDIMENTS OF RIVERS

The main sources for the carbonates in fluviatile sediments from temperate climates are eroded ancient marine carbonate rocks and soils. As we have seen in the foregoing sections, the isotopic composition of carbonates in soils is different from that of ancient carbonate rocks (Figs. 4 and 5).

The data on the carbon isotopic composition indicate that the composition of the river deposits investigated (Table 1) is influenced by

TABLE 1.—*The carbonate content (at 50% < 20 microns) and the isotopic composition of carbonates in fluviatile sediments*

River	Carbonate Content (%)	δ^{13}_{PDB} (‰)	δ^{18}_{PDB} (‰)	C-14 (%)
Seine[1]	31.5	−2.1	−4.4	–
Somme[1]	42.0	+0.0	−2.7	–
Rhine	16.0	−3.6	−9.6	14.8
Meuse	5.8	−3.3	−12.6	17.3
Ems	2.5	−5.1	−9.8	33.5
Rhône	–	−1.2	−5.7	–
Humber : Ouse	–	−0.6	−6.8	–
Humber : Trent	–	−0.2	−6.0	–

[1] Carbonate content at 30% < 20 microns.

the supply of pedogenic carbonates to a varying degree. The influence is relatively small in the rivers Ouse, Trent and Somme, but large in the Rhine, Meuse and Seine. Further proof for the presence of carbonates not derived from ancient carbonate rocks is found in the carbon-14 content which is about 15% for the rivers Meuse and Rhine. The carbonates in the river Ems are probably from recent biogenic origin, as is shown by the high strontium content and carbon-14 content (Table 2).

TABLE 2.—*Total carbonate content and dolomite content and the composition of the carbonates in argillaceous sediments. The spread in the values of the stable oxygen and carbon isotopic composition is about ±0.3‰. N refers to the number of samples analysed, σ to the standard deviation. The total carbonate content is given at 50% < 20 μm. The sampled localities from the southern and Wadden area are given in Figure 1. The Rhine-Meuse and the Ems estuary are shown in Figures 9 and 7 respectively.*

Locality	Total Carbonate		Dolomite Content			Strontium Content			Isotopic Composition				
	%	N	%	N	σ	ppm	N	σ	δ^{13}_{PDB} (‰)	δ^{18}_{PDB} (‰)	N	C-14 (%)	σ (C-14)
Southern areas													
Vlaamse Banken	25.7	22	0.7	6	0.1	1300	12	110	+0.3	−2.6	8	31.9	0.3
Zwarte Polder	20.4	15	0.4	4	0.2	1300	5	110	+0.0	−2.5	4	–	–
Grevelingen	20.2	19	1.0	5	0.2	1300	9	110	−0.5	−3.2	5	43.7	0.5
Rhine-Meuse estuary													
Oost-Biesbosch	5.8	14	0.9	5	0.4	850	10	140	−3.3	−12.6	3	17.3	0.4
Dordtse Biesbosch	16.0	20	2.1	7	0.2	850	14	140	−3.6	−9.6	8	14.8	0.3
Hollands Diep 1									−2.0	−8.7	3	–	–
Hollands Diep 2	12.0	43	0.9	5	0.2	950	6	150	−1.3	−7.0	3	–	–
Hollands Diep 3									−1.2	−6.4	2	–	–
Haringvliet	19.3	33	1.5	7	0.4	1150	15	130	−0.6	−4.5	4	29.3	0.3
Brielsche Gat	19.5	21	1.2	7	0.2	–	–	–	−0.6	−3.8	5	–	–
Wadden Sea Area													
Friesland	16.9	57	1.3	24	0.4	1100	14	60	−0.5	−3.6	4	22.2	0.4
Groningen	11.7	18	1.3	6	0.4	1100	16	60	−0.1	−4.0	9	28.6	0.4
Dollard	10.4	18	1.4	9	0.3	1100	20	60	−0.5	−4.3	12	15.7	0.4
Ost Friesland	11.0	18	–	–	–	1100	7	60	−0.4	−3.4	5	30.6	0.5
Ems estuary													
Diele	2.5	14	0.4	5	0.1	5600	12	600	−5.0	−9.8	2	33.5	0.6
Leerort	7.0	18	1.2	5	0.2	1350	19	160	−0.6	−5.6	3	–	–
Ditzum	10.0	14	1.4	4	0.3	1100	8	120	−0.5	−5.0	3	–	–

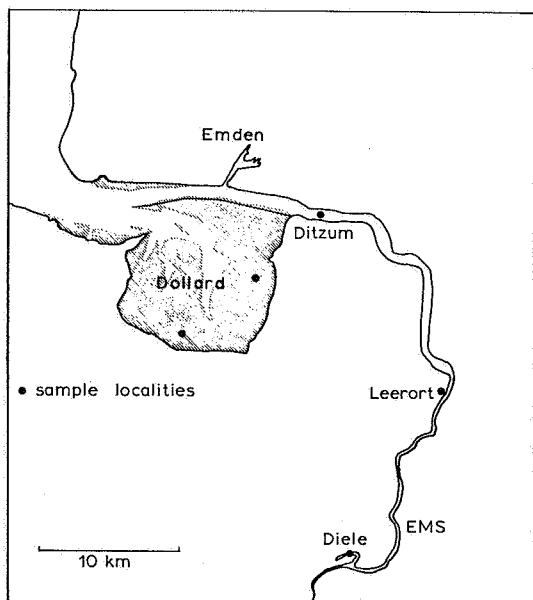446   W. SALOMONS

FIG. 7.—The estuary of the river Ems.

CARBONATES IN ESTUARINE
ARGILLACEOUS SEDIMENTS

The next part of the erosion-sedimentation cycle studied is located in the estuaries. There we have the transition from the fluviatile to the marine environment, the sediments being mixtures in various proportions of material supplied from both directions. In the next sections we will discuss the comparatively small Ems-estuary and the Rhine-Meuse estuary.

The Ems-Estuary

The Ems estuary (Fig. 7) is a relatively small river, compared to the river Rhine. The average discharge of water is 100 m^3/sec (Dorrestein, 1960). The mud discharge is estimated at 0.14×10^6 ton/year (McCave, 1973).

The freshwater sediments were sampled at Diele, the estuarine deposits at Leerort and Ditzum. The chlorinity of the water at Leerort varies between 0 and 1‰, at Ditzum between 1 and 7‰. The carbonates in the sediments were
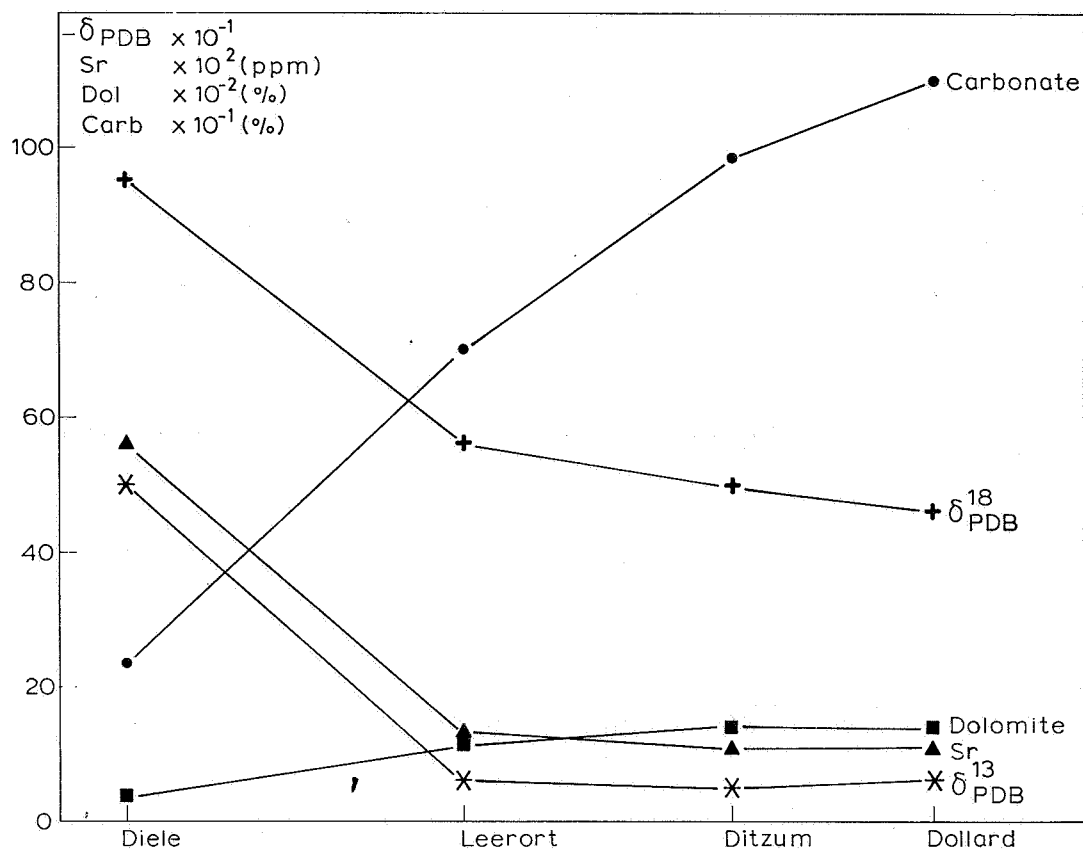

FIG. 8.—Total carbonate content, dolomite content and the composition of the carbonates in Ems sediments.

examined by X-ray diffraction and found to consist of low-Mg calcite and dolomite. The magnesium content of the calcite is below 1%.

The total carbonate content and dolomite content of the sediments increase in seaward direction (Table 2). Apparently, the carbonates deposited in the estuary are only partly of fluviatile origin. The strongest change in the composition of the carbonates is found at Leerort (Fig. 8). At Ditzum it is already comparable to that in marine deposits of the Dollard area. We may conclude from these data that the progressive change in the composition of the carbonates in seaward direction is caused by mixing of marine and fluviatile carbonates. The strontium content can be used as a sensitive parameter to determine the amount of marine carbonates in the Ems-estuary. At Leerort where the chlorinity of the water is about 1‰, already 90% of the carbonates deposited are of marine origin. Such a discrepancy between chlorinity of the water and carbonate composition of the sediments was also found in the Rhine-Meuse estuary.

The Rhine-Meuse Estuary

The estuarine and river samples were sampled before the closure of the Haringvliet and the Grevelingen. At present the discharge of river water from the Rhine and Meuse is mainly through the Nieuwe Waterweg to the North Sea.

The main mud discharge takes place through the Haringvliet whereas not more than 10% of the mud is discharged through the Krammer (Terwindt, 1967). The marine mud originates from the area south of the estuary and is transported in a northern direction along the Belgian and Dutch coast.

Freshwater sediment samples from the river Rhine were sampled in the Dordtsche Biesbosch, freshwater samples from the Meuse in the Oost-Biesbosch (Fig. 9). Estuarine sediments were sampled in the Hollands Diep, Haringvliet and Brielsche Gat. The Hollands Diep is comparable to the Ems between Leerort and Ditzum with regard to the chlorinity of the water. Only on the southern side of the Hollands Diep are conditions favourable for the intertidal deposition of mud.

The carbonates in the sediments investigated consisted of low-Mg calcite (Mg content <1%) and dolomite. In the estuary the total carbonate and dolomite contents in the sediments as well as the composition of the carbonates change in seaward direction (Table 2). For the Rhine-
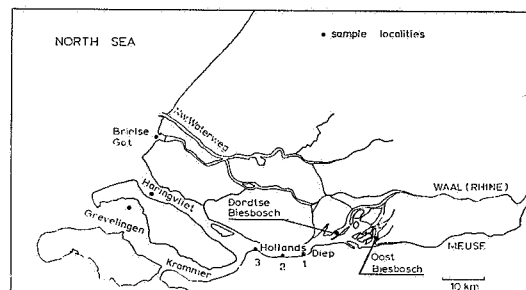

Fig. 9.—The Rhine-Meuse estuary.

Meuse estuary the most sensitive parameter to determine the ratio of fluviatile to marine carbonates is their isotopic composition. Since the oxygen isotopic composition for the Rhine differs from that for the Meuse, we will use mainly the carbon isotopic composition. In this calculation the carbon isotopic composition of fluviatile carbonates is taken as −3.6‰ and of marine carbonates as +0.3‰.

From the total carbonate content in the Hollands Diep one could assume that a mixing of Rhine with Meuse material takes place, resulting in a carbonate content of 12%. However, the carbon isotopic composition indicates that we have a mixing of marine and fluviatile carbonates; more than 40% of the carbonates being derived from the marine environment. The total carbonate content and the oxygen isotopic composition can be used to differentiate between carbonates from the rivers Rhine and Meuse. If we assume that in the Hollands Diep a mixing of Rhine sediments with marine sediments takes place in a ratio of 1:1, the oxygen isotopic composition of the carbonates in the Hollands Diep should be about −4.6‰ and the total carbonate content of the sediments about 18%. The values found show that this is not the case. A similar calculation for a mixing of Meuse and marine sediments gives a total carbonate content of the sediment of 13% and an oxygen isotopic composition of about −6‰, which corresponds rather well with the values found; respectively 12% for the total carbonate content and −7‰ for the oxygen isotopic composition. In the Hollands Diep very little mixing of Rhine and Meuse sediments is observed.

The carbonates deposited in the Haringvliet are derived for about 70% from the marine environment. The stable oxygen isotopic composition, the strontium content and the carbon-14 content of the carbonates all fit in with such a strong marine influence.

W. SALOMONS

TABLE 3.—*The amount of suspended matter transported annually in the area studied*

Source	Supply ($\times$ 10⁶ ton)
Rhine-Waal[1]	3.20
Meuse[1]	0.70
English Channel[2]	5.10
Scheldt[2]	0.40
Ems[2]	0.14

[1] After Terwindt (1967).
[2] After McCave (1973).

In the present estuary, the Rotterdam harbour and Nieuwe Waterweg the same strong influence on the composition of the carbonates is found (Salomons, 1973). This landward transport of sediments in an estuary has been described by Meade (1969) and by Postma (1967).

CARBONATES IN MARINE ARGILLACEOUS SEDIMENTS

Possible sources for the carbonates in marine sediments are: fluviatile carbonates, carbonates derived from eroded carbonate formations along the coast and recent biogenic carbonates.

Data on the present-day sources for the suspended matter in the area studied are given in Table 3.

Although the amount of suspended matter transported through the English Channel is large, its concentration in the water is low, it is transported in a northerly direction along the Belgian and Dutch coast. Sediments from this source are found at the localities 3, 4 and 5 (Fig. 1). North of the Rhine-Meuse estuary large amounts of suspended matter from the rivers Rhine and Meuse are added to this material. Part of the suspended matter is transported to the Wadden area, where an extensive accumulation of mud takes place (van Straaten, 1954; van Straaten and Kuenen, 1957). The finely grained carbonates in this area are therefore mainly derived from the area south of the Rhine-Meuse estuary and from the

rivers Rhine and Meuse. Furthermore, during transport and after deposition the addition of recent carbonates has to be taken into account. This causes the presence of aragonite and high-Mg calcite both with a high carbon-14 content. Yet, no aragonite could be detected. Apparently, crushed remains of aragonitic shells like Cardium and Mytilus, which occur abundantly in the area investigated, are not an important source for the carbonates in these finely grained sediments. Furthermore, the composition of the carbonates in the Wadden area is consistent with a mixture of Rhine-Meuse carbonates and carbonates derived from the southern areas (Table 4). It follows that the addition of recent carbonates during transport along the Dutch coast and in the Wadden Sea is small compared to the amount of detrital carbonates present.

Using the data in Table 4 a rough estimate can be made on the amount of fluviatile carbonates present. About one fifth of the carbonates are derived from the rivers Rhine and Meuse, the remainder originate from the southern areas. The fluviatile carbonates from the river Ems, with their high Sr-content, have no measurable influence on the composition of the carbonates found in the Wadden area.

CONCLUSIONS

(1) Part of the dissolved carbonates in soils from temperate climates are reprecipitated in the upper part of the soil.

(2) The carbonates in argillaceous sediments from the rivers Rhine, Meuse, Seine and Rhône are partly derived from soils. The carbonates in the river Somme are derived from eroded carbonate rocks.

(3) The carbonates in the estuaries of the rivers Rhine, Meuse and Ems are mainly derived from the marine environment.

(4) The carbonates in the marine argillaceous sediments from the Wadden area are for about one fifth derived from the rivers Rhine and Meuse.

TABLE 4.—*Mean values for the total carbonate content and the composition of the carbonates in the main areas*

Area	Total Carbonate Content (%)	Strontium Content (ppm)	δ^{13}_{PDB} (‰)	δ^{18}_{PDB} (‰)	C-14 (%)
Southern Areas	22	1300	-0.1	- 2.8	38
Rhine-Meuse	13	850	-3.5	-11.1	16
Wadden Sea Area	12	1100	-0.4	- 3.8	24
Ems	3	5600	-5.0	- 9.8	33

REFERENCES

CRAIG, H., 1965, The measurements of oxygen paleotemperatures: Spoleto Conf. on Stable Isotopes in Oceanographic studies and Paleotemperatures, Pisa 1965.

DORRESTEIN, R., 1960, Einige klimatologische und hydrologische Daten für das Ems-estuarium: in van Voorthuysen, J. H., and Ph. H. Kuenen (eds.), Das Ems-Estuarium (Nordsee), Verh. Kon. Ned. Geol. Mijnb. Gen., v. 19, p. 39-42.

EMRICH, K., D. H. EHHALT, AND J. C. VOGEL, 1970, Carbon isotope fractionation during the precipitation of calcium carbonate: Earth. Planet. Sci. Letters, v. 8, p. 363-371.

GALIMOV, E. M., 1966, Carbon isotopes in soil CO_2: Geochem. Intern., v. 3, p. 889-897.

GOLDSCHMIDT, J. R., AND H. C. HEARD, 1961, Subsolidus phase relations in the system $CaCO_3$-$MgCO_3$: Jour. Geology, v. 66, p. 278-293.

GROOT, A. J. DE, 1964, Origin and transport of mud in coastal waters from the Western Scheldt to the Danish frontier: in Developments in Sedimentology, Vol. I, Elsevier, p. 93-103.

KEITH, M. L., AND J. N. WEBER, 1964, Carbon and oxygen isotopic composition of selected limestones and fossils: Geochim. Cosmochim. Acta, v. 28, p. 1787-1816.

McCAVE, I. N., 1973, Mud in the North Sea: in Goldberg, E. D. (ed.), North Sea Science, p. 75-99.

MEADE, R. H., 1969, Landward transport of bottom sediments in estuaries of the atlantic coastal plain: Jour. Sed. Petrology, v. 39, p. 222-234.

MOOK, W. G., 1968, Geochemistry of the stable carbon and oxygen isotopes of natural waters in the Netherlands: Unpubl. Ph.D. Thesis, University of Groningen, 157 p.

———, 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. Jour. Mass. Spectr. and Ionic Phys., v. 12, p. 273-298.

POSTMA, H., 1969, Sediment transport and sedimentation in the estuarine environment: in Laufl, G. H. (ed.), Estuaries, Am. Assoc. Adv. Sci. Pub. 83, p. 158-178.

SALOMONS, W., 1973, Chemical and isotopic composition of carbonates during an erosion-sedimentation cycle: Unpubl. Ph.D. dissertation, University of Groningen. University micro films, Ann Arbor. Order no. 74-20094, 118 p.

STRAATEN, L. M. J. U. VAN, 1954, Composition and structure of recent marine sediments in the Netherlands: Leidse Geol. Med., v. 19, p. 1-110.

———, AND PH. H. KUENEN, 1957, Accumulation of fine grained sediments in the Dutch Wadden Sea: Geol. and Mijnb., v. 19, p. 329-354.

TERWINDT, J. H. J., 1967, Mud transport in the Dutch Delta area and along the adjacent coast line: Netherlands Journal of Sea Research, v. 3, p. 505-531.