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ON THE CALCIUMCARBONATE CONTENT OF YOUNG MARINE SEDIMENTS

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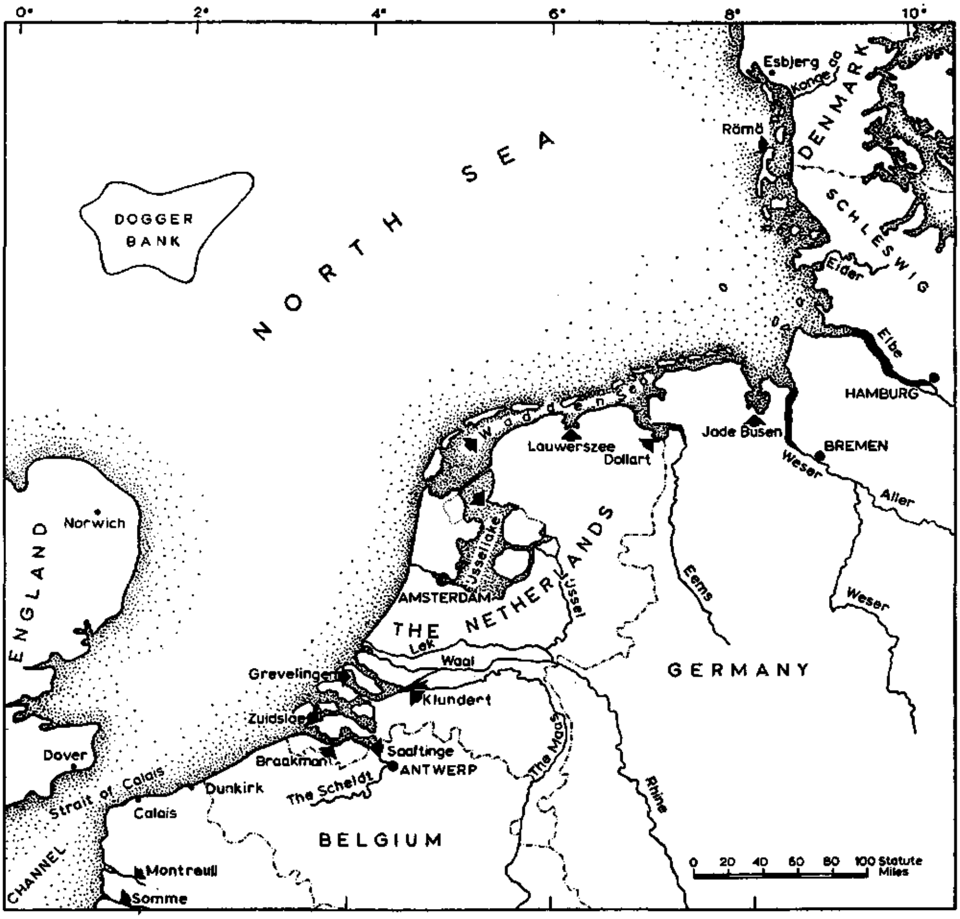
TABLE OF CONTENTS


0°
2°
4°
6°
8°
10°
NORTH SEA
DOGGER BANK
ENGLAND
Norwich
Dover
Strait of Calais
CHANNEL
Calais
Dunkirk
Montreuil
Somme
BELGIUM
The Scheldt
ANTWERP
Braakman
Saaftinge
Zuidsloe
Grevelingen
Klundert
THE NETHERLANDS
AMSTERDAM
IJssellake
Lek
Waal
The Maas
IJssel
Rhine
Waddenzee
Lauwerszee
Dollart
Eems
GERMANY
Jade Busen
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SCHLESWIG
DENMARK
Römö
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0 20 40 60 80 100 Statute Miles

1. INTRODUCTION

The $CaCO_3$-content of newly deposited marine sediments is rather variable. In view of this variability, many samples of sediments have been analysed on $CaCO_3$-content in the laboratories of the Zuiderzeepolders Development and Colonization Authority.

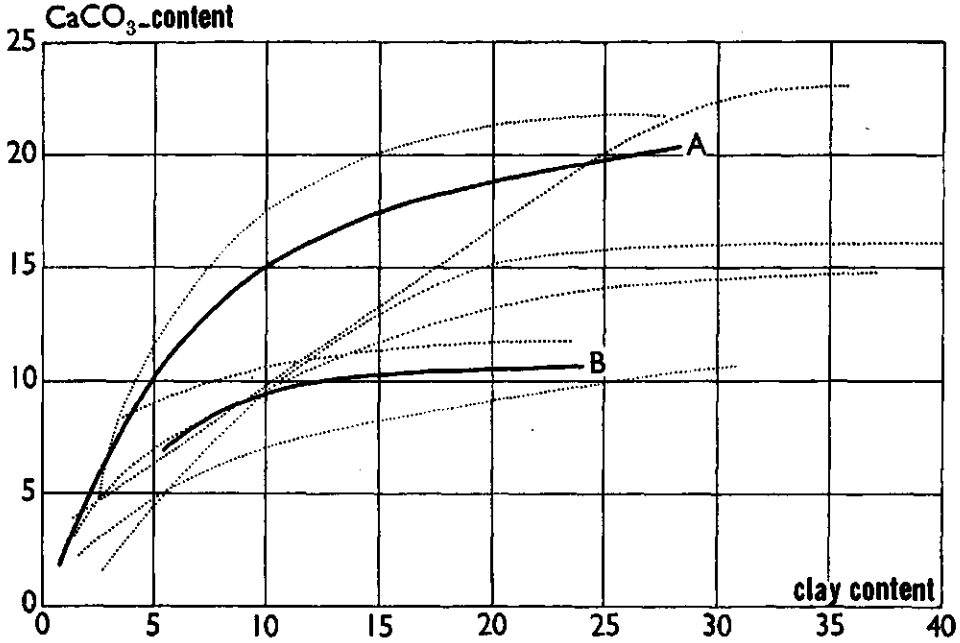
Since, in 1956, the determination of calciumcarbonate became part of the determination of the clay content (by pipet analysis), the number of available $CaCO_3$-figures increased considerably.

With respect to the Dutch coast thousands of $CaCO_3$-figures were available (not included those data which have been gathered by other institutes); moreover about 60 samples were taken along the Danish coast (southern Jutland), the German and Belgian coast and along the French coast (Départements Nord, Pas de Calais and Somme). Nearly 240 samples from the English Northsea coast proved to be of some use and 53 samples from the bottom of the Northsea gave information on the $CaCO_3$-content of sediments farther from the coast (see map).

It has to be stated that only newly deposited sediments may be taken in account. As soon as soil development starts, the relations mentioned above are disturbed, the rate of decrease of $CaCO_3$-content caused by soil development being very unequal (BEEFTINK, 1962) and depending on conditions of soil formation (FIG. 1).

In comparing $CaCO_3$-contents of young marine deposits, it, moreover, has to be kept in mind that, generally, the carbonate-content of not full-marine estuarine deposits is relatively low.

◀ **Topographical map of the greater part of the considered coast**



A bare sediments
B sediments covered with Spartina

Fig. 1. Relation between calciumcarbonate-content and clay content (both in g per 100 g dry matter) in young sediments in the Grevelingen area

2. METHODS OF ANALYSIS

2.1. Clay and silt

20 g of soil (sandy soils 40 g) are treated with H_2O_2 30 % and HCl 0,2 n. After decanting, the soil is peptised with $Na_4P_2O_7$ and clay- (and silt)content is determined by pipetting samples of the suspensions after a fixed time and on a predetermined depth.

After 1956 the quantity of H_2O_2 used has been standardized, the quantity of HCl is in accordance with the $CaCO_3$-content of the sample and $Na_4P_2O_7$ replaced the Na_2CO_3 used formerly. These changes caused slightly higher (HOOGHOUDT, 1945 ; HOFSTEE, 1955) and decidedly more accurate figures than the former method.

2.2. $CaCO_3$

1—3 g of soil are shaken with ± 20 ml HCl (8 à 10 %) and the produced CO_2 is measured volumetrically. Influence of temperature and atmospheric pressure is controlled by using a standard and a blank (for detailed description, see HOFSTEE, 1957).

2.3.

In some samples it has been tried to make a division between $CaCO_3$ and $MgCO_3$. It was supposed (BRUIN, 1938) that both $CaCO_3$ and $MgCO_3$ solve in HCl and that only $CaCO_3$ solves in $H_4C_2O_2$. A second method was used in which $MgCO_3$-content was approached by diminishing the Mg soluble in 8 % HCl by the exchangeable Mg. Agreement between the two methods was reasonable (BEVERWIJK, 1958).

A third method, described by SKINNER a.o. (1959), has been introduced later. This is also a gasiometrical one, in which the rate of reaction between carbonates and HCl is taken in account. The CO_2 evolved is measured with intervals of 10 seconds and the reaction with $CaCO_3$ is assumed to be completed within one minute. The remaining evolution of CO_2 is due to dolomite. Some agreement has been found between this method and the two mentioned before.

2.4.

The required soil fractions were obtained by peptising field moist soil with diluted NH_4OH and siphoning off (in due time) the related fraction. In this way first the 0—2 micron particles were collected and later 2—8 micron and 8—16 micron. The fractions > 16 micron were fractionated by sieving over 35, 50, 75 and 1400 micron sieves. Of some coarse soils a large number of sand fractions has been prepared (75—105, 105—150, 150—210, 210—300, 300—420, 420—600, 600—850, 850—1400 and 1400—2000 micron).

Suspensions obtained were dried and grinded carefully in a mortar. These fractions, in particular the finer, also contain all other compounds solved in diluted NH_4OH (NaCl, humates, silicates). The amount of solved compounds was determined by treating the fractions with H_2O_2 and HCl and filtering under suction. The residue on the filter was weighed (this was the respective fraction without $CaCO_3$, organic matter and a great part of the solved compounds). In some samples, moreover, organic matter content of the fractions has been determined separately. There was a good agreement between the $CaCO_3$-content of the soil determined directly and the content calculated, using the $CaCO_3$-contents of the fractions.

2.5.

In order to study the decalcification of the deposits during sedimentation, a thin layer of sediment was leached in a Buchner funnel. The salinity of the leaching liquid varied, the microbial nutrition status was varied by addition of flour of lucerne and the degree of aeration was influenced by the technique (in particular the speed) of leaching.

3. RESULTS

3.1.

Figures 1, 2, 4, 5 and 7 show that, generally, the $CaCO_3$-content of young marine sediments increases with increasing clay content until a certain level and that at higher clay contents, $CaCO_3$-content is fairly constant or even diminishing slightly with

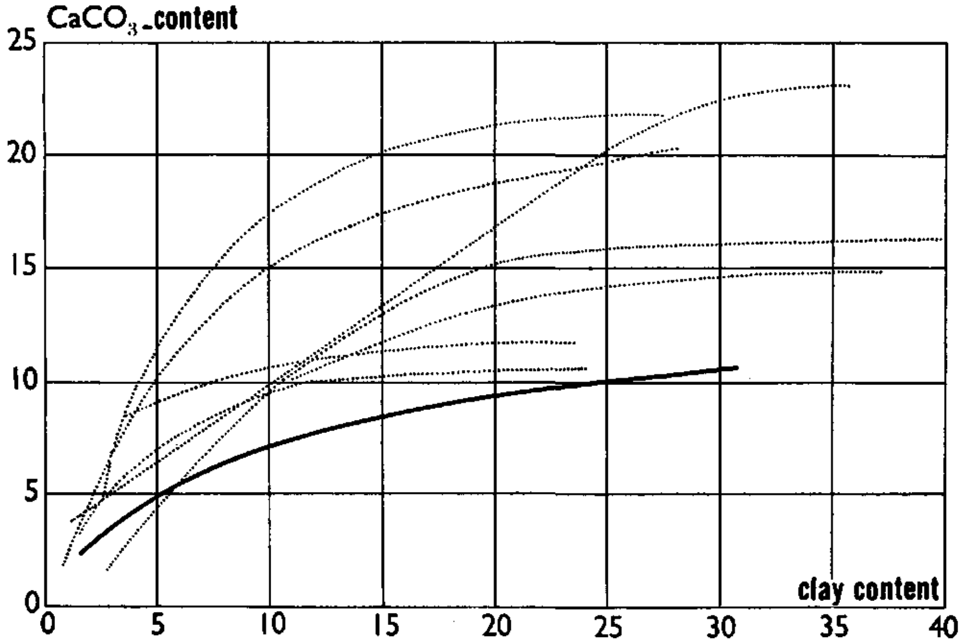


Fig. 2. Relation between calciumcarbonate-content and clay content (both in g per 100 g dry matter) in recent Zuiderzee-sediments

increasing clay content. This fact has been stated too by Trilling (1928), Maschhaupt (1933, 1948), Zuur (1936), Dechering (1942) and Wiggers (1955).

In order to get more information on the background of the relation shown in these figures, nearly 35 samples have been fractionated and the $CaCO_3$-content of each fraction has been determined.

In all full-marine sediments the fractions 2—8 and 8—16 micron show the highest $CaCO_3$-contents, the coarser fractions (16—35, 35—50 and 50—75 micron) have a lower $CaCO_3$-content and in all sediments the clay fraction proves to be relatively poor in carbonates (TABLE 1 and FIG. 3) (See: Bruin en ten Have, 1935).

In view of this point it should be more logical to plot the $CaCO_3$-content against the silt fraction (2—16 micron) than against the clay fraction.

TABLE 1. Relative calciumcarbonate-percentages in fractions of marine sediments. The highest calciumcarbonate-content is indicated as 100 %

Fraction in micron	Relative $CaCO_3$-percentages			
	France	Zuidsloe	Waddensea	Denmark
0— 2	38	25	14	12
2— 8	100	100	100	100
8—16	96	83	97	93
16—35	81	61	89	71
35—50	73	57	71	53
50—75	68	56	60	48
Clay content	19,0	39,5	46,3	43,9
Total $CaCO_3$ content	36,7	18,4	9,7	6,4

Note

This table is not quite correct. It should have been better to determine the $CaCO_3$-percentage of the various fractions based on mineral matter only. However, sufficient data (a.o. organic-matter content) were not available for all fractions. Pertinent controls showed that the figures for $CaCO_3$-percentages on a mineral matter base do not differ substantially from those in the table.

Moreover it goes from the data obtained that within one region the $CaCO_3$-content of at least the finer fractions is reasonably constant (and independent of the abundance of the particular fraction in the sample) (TABLE 2). This too has been found earlier by Zuur (1936).

TABLE 2. Calciumcarbonate-percentages in fractions of marine Zuiderzee-deposits

No of sample	Total $CaCO_3$	Fraction in micron	0—2	2—8	8—16	16—35	35—50	50—75
13179	10,1	% fraction	22,8	9,7	7,4	16,0	6,4	23,6
		% $CaCO_3$ per fraction	1,4	17,2	19,9	12,2	8,8	6,2
13181	9,9	% fraction	34,6	11,5	8,7	22,1	5,2	9,4
		% $CaCO_3$ per fraction	1,1	17,6	16,3	12,9	9,4	8,9

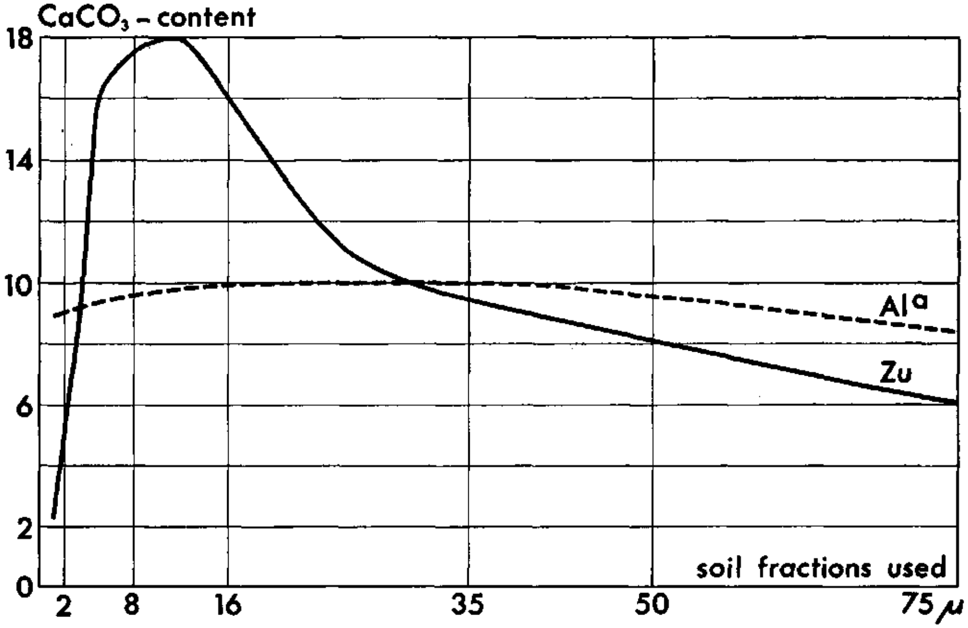


Fig. 3. Calciumcarbonate percentages in fractions of Zuiderzeedeposits (Zu) and of sediments from the former lake Almere (Al a)

As far as clay soils are concerned this conclusion does not hold completely for the fraction 75—1400 micron and does not hold at all for the fraction over 1400 micron. The amount of this fraction in clay soils being small, the calciumcarbonate content is rather variable, according to the presence, yes or no, of more or less shell fragments. In the marine deposits of the Zuiderzee this fraction consists for 60—95 % of $CaCO_3$. The slightly brackish lagoon sediments of the former lake Almere (which preceded the Zuiderzee) and the clayey coastal deposits proved to contain only 5—25 % $CaCO_3$ in the fraction $>$ 1400 micron.

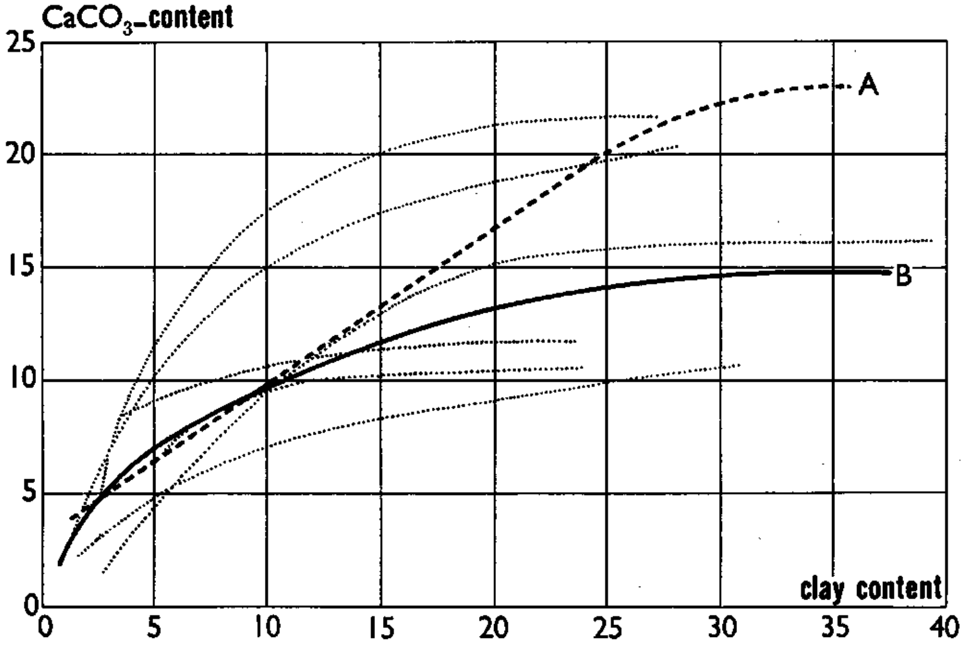
In sandy soils, however, it seems that also the carbonate content of the coarser fractions is reasonably constant. The small number of sandy soils examined and the low $CaCO_3$-content of the coarse fraction rendered this conclusion somewhat less safe. The existence of a relation between the $CaCO_3$-content of the coarser fractions and the granulometric composition of the sample — as, perhaps, might be concluded from the data of ZUUR (1936) on the old sea clay in the Wieringermeer — could not be shown for the recent sediments in the Zuiderzee area.

From the foregoing it has to be concluded that within one region the $CaCO_3$-content of sediments with the same clay content is governed by the frequency distribution of the other fractions. A fine example is given in FIG. 5 (Zuidersloe, compared with Braakman). Another example is to be found in the thesis of WIGGERS (1955).

Finally it has to be mentioned that in the Dutch Waddenarea the material suspended in the seawater and the coastal sediment showed nearly the same distribution of $CaCO_3$ over the various soil fractions.

3.2.

Along the continental coast of the Northsea the $CaCO_3$-content of newly deposited sediments with comparable clay content decreases from the south to the north. In TABLE 3 and FIG. 4 may be seen how substantial these differences are for the clay soils. The $CaCO_3$-content of all fractions decreases from beyond Montreuil to Esbjerg, but the relations between the contents of the various fractions prove to be rather identical, irrespective of the origin or the granulometric composition of the sample (TABLE 1).
The relative $CaCO_3$-content of the clay fraction, indeed, seems to decrease from France to Denmark (i.e. with decreasing $CaCO_3$-content of the sediments), but for the rest the distribution of the calciumcarbonate shows the same trend for all samples.



A Zuidersloe B Wadden area

Fig. 4. Relation between calciumcarbonate-content and clay content (both in g per 100 g dry matter) in sediments from the Zuidersloe and from the Dutch Waddensea

TABLE 3. Relation between calciumcarbonate-content and clay-content in young marine muds

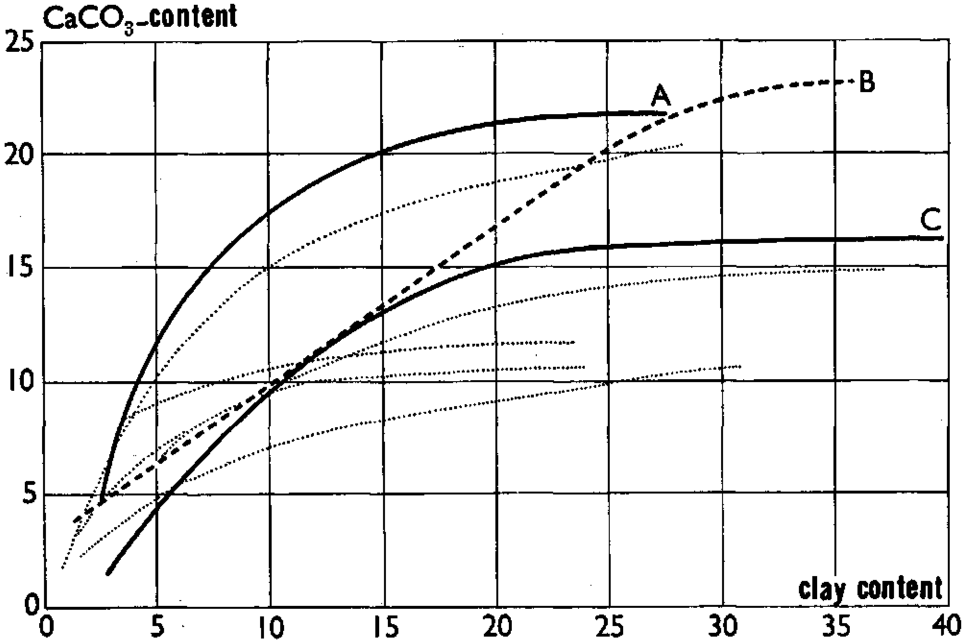
Region	Clay content	$CaCO_3$-content
France (Northseacoast)	19,0	36,7
Belgium	34,2	24,1
Western Schelde (Sloe)	30,0	22,2
Grevelingen	28,6	19,2
Waddensea	31,5	14,0
Jadebusen	28,1	11,7
Schleswig-Holstein	37,8	5,9
Denmark (S.W. Jutland)	37,7	5,4

Note

The figures for the Dutch regions are averages of many data. For the other regions, generally, only a few figures could be averaged.

3.3.

In estuaries the $CaCO_3$-content of the sediment also decreases with decreasing salinity of the sedimentary conditions (FIG. 5).



A Braakman Average salt content of the Westerschelde on the spot: 23—27 g NaCl per l.
B Zuidersloe Average salt content of the Westerschelde on the spot: 25—28 g NaCl per l.
C Saaftinge Average salt content of the Westerschelde on the spot: 13—19 g NaCl per l.

Fig. 5. Relation between calciumcarbonate-content and clay content (both in g per 100 g dry matter) in sediments along the Westerschelde

Notwithstanding this fact, here, in the brackish environment, too the relation between the $CaCO_3$-content of the fractions remains about the same as under full-marine conditions (TABLE 4).

TABLE 4. Relative calciumcarbonate-percentages in fractions of slightly brackish deposits (lower Rhine near Klundert). The highest calciumcarbonate-content is indicated as 100 %

No of sample	Clay content	Total $CaCO_3$	Fraction in micron					
			0—2	2—8	8—16	16—35	35—50	50—75
28611	17,4	14,4	24	89	100	75	64	71
68161	11,1	9,5	24	79	100	75	85	60

However, this does not hold for the lake Almere sediments in the Zuiderzee-area which show a deviating pattern of $CaCO_3$-fractionation. Remarkable is the even distribution; the $CaCO_3$-content of the fractions varies only slightly (TABLE 5 and FIG. 6).

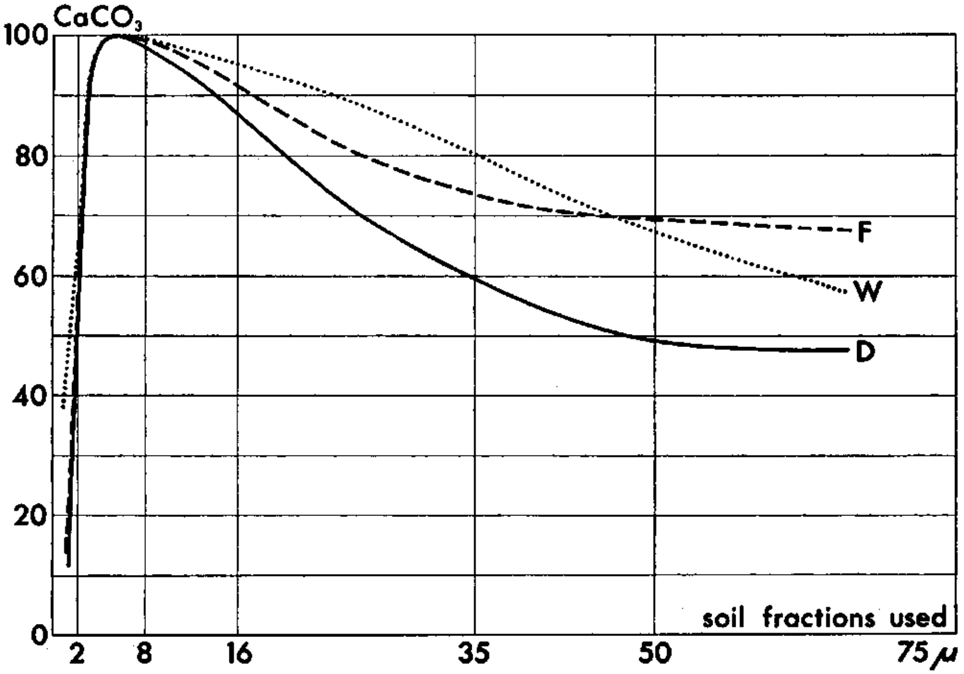


Fig. 6. Relative calciumcarbonate-percentages in fractions of marine sediments from France (F), Dutch Waddensea (W) and Denmark (D). The highest calciumcarbonate-content is indicated as 100%

TABLE 5. Calciumcarbonate-percentages in fractions of Zuiderzee- and lake Almere-deposits

Type of sediment	Fraction in micron						Total $CaCO_3$ in %
	0—2	2—8	8—16	16—35	35—50	50—75	
Zuiderzee-deposits	2	16	18	12	9	7	9,2
Brackish Almere deposits	1	18	16	12	8	5	6,2
Fresh * Almere deposits .	9	9	10	10	10	9	11,3

* Fresh means in this case a salt concentration during sedimentation of less than ± 1,5 g per liter.

It stands to reason, that for these freshwater sediments the relation between $CaCO_3$-content and clay content is different from the relation valid for marine deposits (FIG. 7). In this graph not the data of the old lagoon deposits of lake Almere have been plotted, but figures of very recent Yssellake sediments (deposited after enclosure of the Zuiderzee).

Not only data regarding the size of the $CaCO_3$-particles have been gathered, also the character of the particles and their chemical composition have been studied.

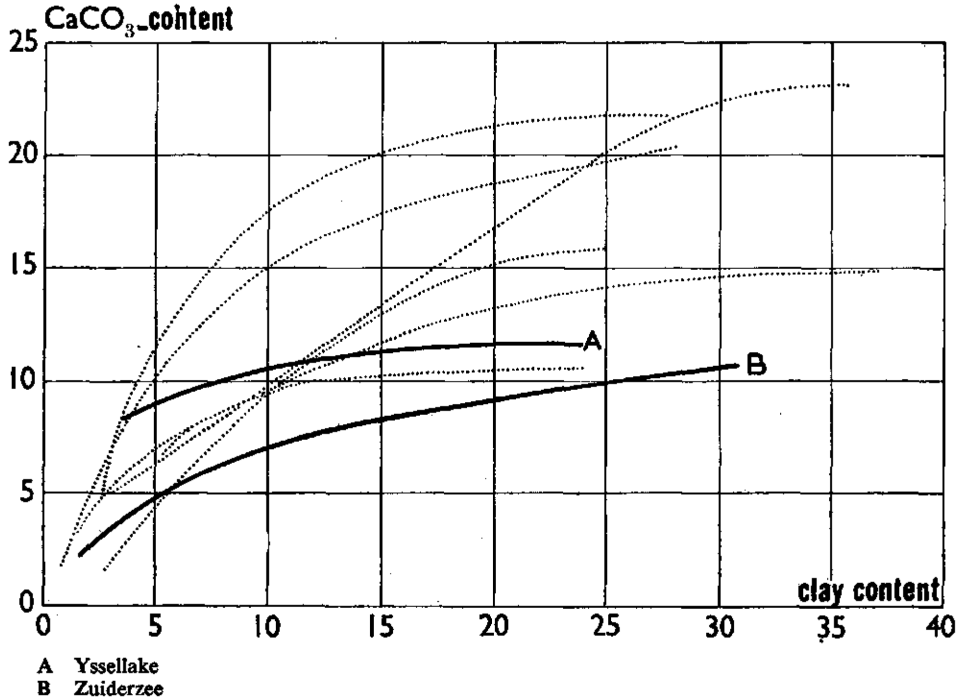


Fig. 7. Relation between calciumcarbonate-content and clay content (both in g per 100 g dry matter) in recent Yssellake deposits and in Zuiderzee sediments

3.4.1.

Thus, the fractions of six samples were examined (by Dr. FAVEJEE) under the microscope. It proved that in all samples the organogenic $CaCO_3$-particles form an important part of the total $CaCO_3$, often the bulk of these particles could not be determined, but fragmented shells, Foraminifera, Ostracoda and spines of Echinodermata are found and in particular in the fine fractions (below 16 micron) some rhomboedra and fine, needleshaped particles are present. The number of Foraminifera seems to decrease from south to north; in the French sample (examination by Dr. VAN VOORTHUYSEN), indeed, these Foraminifera partly are fossile (Cretaceous).

3.4.2.

Further $MgCO_3$-content has been determined. Results of the various methods diverge somewhat, but, perhaps, comparison is not correct because it is not always clear as to how far the determined "$MgCO_3$" in fact is dolomite and which is the $MgCO_3$-content of this dolomite. TABLE 6 provides some data, the figures have been obtained by averaging results of various methods and comparable samples. These figures do not differ markedly from those of BRUIN (1938), CROMMELIN (1943) and VAN DER MAREL (1950).

TABLE 6. CO_2 bound to Mg, as percentage of total carbonates

Sampling region	Number of samples	CO_2 bound to Mg in % of total CO_2
Harbour of Dunkirk	1	5
Zuidsloe	16	7
Zuiderzee		
Yssel delta	1	6
Lake Almere deposits	2	22
Zuiderzee deposits	2	18
Lauwerszee	1	10
Schleswig		
Southern part	6	30*
Northern part	2	18
Holbeach marsh	1	27

* Results of 1 method only.

Some fractions have been analysed too. However, the number of data is too small to allow established conclusions. It seems, indeed, that the highest $MgCO_3$-contents (in relation to $CaCO_3$) are found in the middle group of the analysed fractions (TABLE 7).

TABLE 7. CO_2 bound to Mg, as percentage of total carbonates in sample 68161 from Klundert (lower Rhine)

Fraction in micron	0—2	2—8	8—16	16—35	35—50	50—75	> 75
CO_2 bound to Mg in % of total CO_2	11	11	6	26	39	21	11

Analyses of some sandy soils indeed showed that in the fractions larger than 75 micron the $MgCO_3$-content was low and in the fractions above 105 micron no $MgCO_3$ could be detected.

3.4.3.

The lower $CaCO_3$-content of brackwaterdeposits may be explained by decalcification during the sedimentation, due to a high CO_2-production (BENNEMA, 1953) and/or oxidation of sulphides (VAN DER SPEK, 1952). The related experiments only showed slight indications that hampering the CO_2 from escaping into the air promoted the decalcification and that, in particular in the more or less aerated samples, the addition of organic matter also increased the loss of $CaCO_3$. But none of the differences found proved to be significant. Maybe the carrying out of the experiments was not adequate.

4. DISCUSSION

4.1.

The first point to be discussed is the origin of the $CaCO_3$ in the relative marine sediments. In view of the data gathered, the only reasonable explanation for the wide gap in $CaCO_3$-content between samples of the Channel coast and those of the Rømødam is presented by the supposition that the materials from which the sediments originate show differing $CaCO_3$-contents.

The various opinions (BROCKMANN, 1937; CROMMELIN, 1943; KÖPPEN, 1951) with respect to the origin of the sediments will not be discussed here. Whether the sediments along the coast of Schleswig and southern Jutland come from the Northsea (WETZEL, 1931) or from reworked Waddendeposits (DITTMER, see Verslag etc., 1952) is not important. The source for the coastal accretion will be mainly pleistocene material, as such, generally, relatively poor in calciumcarbonate. Probably this material has been enriched with chalk due to fluviatile admixtures (DE GROOT, 1962), by a rather abundant life of $CaCO_3$-curasses bearing beings (GOEDECKE, 1936, PRATTJE, 1931), or by the activities of diatoms (DE GROOT, 1962). Anyhow, the low $CaCO_3$-contents of the Danish sediments cannot be explained by influence of acid, fresh riverwater (DE SMET, 1954), the water near the Rømødam being completely marine (SANDERS en VERHOEVEN, 1956). Neither it is plausible (SVERDRUP, JOHNSON and FLEMING, 1946) that the temperature gradient along the respective coast can cause a gradient in $CaCO_3$-content as mentioned (compare ZONNEVELD, 1959). In many carefully taken samples the author could not detect any significant difference in $CaCO_3$-content between summer- and wintersediments. And comparable differences found by ZONNEVELD (1960) in river sediments seem to have other causes than differences in temperature (private communication, ZONNEVELD). Moreover marine sediments sampled along the Portugesian and Spanish coast often showed low $CaCO_3$-contents.

Along the southern stretch of the considered coastline the transport through the Channel (VAN VEEN, 1936) and erosion of the claybanks (TESCH and REINHOLD, 1946) in the southern part of the Northsea (BAAK, 1936) call into being sediments rich in $CaCO_3$. Arguments for these statements may be that Dr. VAN VOORTHUYSEN, examining one of the French samples, found fossile Foraminifera and moreover mentioned the fact that such Foraminifera were found northward till far in the Northsea (see also: van Voorthusen, 1950). Samples from the claybanks mentioned, indeed, showed high carbonate-contents (between 20 and 30 %).

Though it goes from the foregoing that the main part of the chalk in the coastal deposits will be brought there with the sediment (according to the size-distribution (Doeglas, 1950) this, probably, holds too for the coarser $CaCO_3$-particles), it is definitely not claimed here that the origin of all the chalk and of the other mineral parts is quite the same. May be part of the $CaCO_3$ is mixed into the sediment during transport. And the share of this part in the total carbonate-content may depend e.g. on living conditions for the $CaCO_3$-producing fauna en route and the $CaCO_3$-content of the seabottom over which the sediment is transported.

With respect to this point one can imagine that the route of transport can cause more or less local variations in the $CaCO_3$-content of coastal sediments (Sverdrup, Johnson and Fleming, 1946). Moreover sedimentation conditions may influence carbonate-content of the deposits (shell banks). Compare in relation to these points, the deviating distribution of $CaCO_3$-fractions in Camargue-sediments (Cerighelli et Gand, 1952).

Some other possible sources of chalk have to be mentioned. In agreement with the ideas of Maschhaupt (1948), in the Northsea (bio)-chemical precipitation cannot be of major importance (this, perhaps, in contrast with tropical regions), precipitated $CaCO_3$ being finely grained (Bruin en ten Have, 1935) and in the marine sediments under consideration fine particles of $CaCO_3$ being scarce; moreover even in the finer fractions crystals only form a small part of the total calciumcarbonate. Some formation of chalk by diatoms has been demonstrated by de Groot (1962).

In coastal sediments of the area studied, formation of calcareous curasses and skeletons by organisms on the place of sedimentation is, in general, neither a predominant factor, otherwise there was a fair chance that the $CaCO_3$-content should be related with the rate of sedimentation, which generally is not the case. Another striking fact is the observation that in the Wadden area the suspended matter and the coastal deposits show the same content and about the size distribution of $CaCO_3$ (table 8). No doubt, in the ocean, where suspended matter of clastic origin hardly is present, the growth of calcareous plankton may govern the $CaCO_3$-content of the deposits (Twenhofel, 1925). Moreover in rivermouths and on some tidal flats where plenty of food is available (Brockmann, 1929), a luxurious development of small organisms (among them Foraminifera) surely may raise the $CaCO_3$-content of the sediments (Goedecke, 1936; Prattje, 1931), but obviously not so much that the

Table 8. Calciumcarbonate-percentages of suspended matter and of coastal deposits in the Dutch Wadden-area

Kind of sample	Clay content	Total $CaCO_3$	Fraction in micron					
			0—2	2—8	8—16	16—35	35—50	50—75
Suspended matter	56,0	9,6	1,4	21,3	21,6	19,7	17,3	14,9
Coastal deposit	36,7	9,8	4,5	21,0	19,8	18,4	13,2	10,4

relation between $CaCO_3$-content of the sediments and their geographical position (or better said their origin) is completely disturbed.

4.2.

The fact that the major part of the chalk in the coastal deposits has been transported to the coast from elsewhere, makes for the supposition that the uniform size-distribution of the chalk in all sediments considered will be due to disintegration of the chalk-particles during transport. Maybe that the deposits from which the sediments originate show already a comparable fractionation of the $CaCO_3$, but even in that case it has to be explained why in these deposits the $CaCO_3$ is distributed in this way. From the data (size distribution of the chalk, microscopial observation of $CaCO_3$-particles, $CaCO_3/MgCO_3$ relation in the fractions studied) it may be supposed that the greater part of the $CaCO_3$ comes into the sediment in a rather large form (varying between complete shells with a length of several cm and Foraminifera with a size of e.g. half of a millimeter). MASCHHAUPT's (1950) supposition that precipitation of $CaCO_3$ must occur because in all sediments $MgCO_3$ is found too, does not hold. Shells, indeed, according to MASCHHAUPT (1948) as well as to own analyses only contain slight quantities of $MgCO_3$. In samples of *Cardium edule* from Denmark, the Wadden area and the Delta region hardly any $MgCO_3$ could be demonstrated. But the $MgCO_3$ may originate from other marine beings than shells (TWENHOFEL, 1925).

It might be supposed from TABLE 7 that in the coarser fractions the shell fragments are somewhat more important whereas the relatively low $MgCO_3$-figures of the finest fractions might point to a slower disintegration of $MgCO_3$- (or $MgCO_3 . CaCO_3$-) compounds. (Sands, indeed show a much lower $MgCO_3/CaCO_3$ quotient than clays from the same area). During transport disintegration of the $CaCO_3$-particles occurs and hence there is a steady supply of $CaCO_3$ from the coarser fractions to the finer ones.

The level of $CaCO_3$ in each fraction is depending upon this supply and upon the removal of chalk to a finer fraction. The rate of supply and removal probably depending on the quantity of $CaCO_3$ present and upon the rate of weathering, the latter (under comparable conditions) for each fraction probably also being governed mainly by this very level of carbonates in the relative fraction. This makes for the similarity in the relation between the $CaCO_3$-percentages of the various fractions, irrespective of the clay content and the origin of the samples. As the fractions become finer, disintegration goes relatively slower (GALLOWAY, 1922), as quoted by TWENHOFEL, 1925) and a higher $CaCO_3$-content is required to keep supply and removal in equilibrium. Hence a gradual increase in carbonate-content from coarser to finer fractions is observed.

The finer fractions (below ± 25 micron (FAVEJEE, 1951)) are flocculated (even in brackish deposits (BOURCART, 1939)) and the $CaCO_3$ which comes into these fractions probably is protected against further disintegration, this may explain why the finest $CaCO_3$-particles are scarce (TABLE 1). In the Almere-sediments, which have been deposited in a peptised state, this protection against weathering failed and here the

clay fraction shows the same $CaCO_3$-content as the other fractions and moreover the maximum in 2—16 micron fractions disappeared (TABLE 5).
Maybe that the French samples contain some more $CaCO_3$-particles below 2 micron (TABLE 1), because this material has been formed (at least partly) by erosion of the limestone rocks.

4.3.

The author has no unassailable explanation for the comparably low $CaCO_3$-content of brackwaterdeposits in river mouths. Perhaps the causes vary from case to case and maybe that even in one and the same estuary various processes prove to occur (ZOBELL, 1946). During sedimentation decalcification caused by abundant production of CO_2 (decay of organic matter) or by oxidation of sulfides is, perhaps, not negligible. Probably a luxuriant microbial life in the brackish region — mentioned by many authors (GOEDECKE, 1936; BROCKMANN, 1929) and perhaps testified by the high fosfate- and organic-matter contents of these brackwatersediments — withdraws an appreciable quantity of $CaCO_3$. The Ca may be found back in various organic or organogenic compounds and, perhaps, just outside the estuaries (PRATTJE, 1931).
In some cases the acidity of the riverwater may cause a lowering of the $CaCO_3$-content of the sediments; the whole $CaCO_3$-regime shows a close correlation with the salinity of the environment (KÜHL und MANN, 1953); some estuarine deposits are mixtures of marine and fluviatile sediments, the latter sometimes being less rich in $CaCO_3$.
Except, possibly, in the last case one should always expect a decrease of the $CaCO_3$-content of the finest fractions, unless the disintegration of the $CaCO_3$-particles should proceed fastly. This, anyhow, may be shown in TABLE 9, which is based on the assumptions that in the brackwatersediments of the lower Rhine the coarsest fraction shows no loss of $CaCO_3$ and that the original $CaCO_3$-contents of the fractions had the same frequency distribution as the Zuidersloe-sediment. It is obvious that the 0—2 micron and — even more — the 2—8 micron fraction lost a considerable part of their $CaCO_3$, this in contrast with the coarser fractions.

TABLE 9. Relative calciumcarbonate-percentages in fractions of comparable full-marine and brackish sediments

Type of sediment	Fraction in micron					
	0—2	2—8	8—16	16—35	35—50	50—75
Zuidsloe	25	100	83	61	57	56
Lower Rhine	20	71	85	64	64	56*

* This figure has been made equal to that of the Zuidsloe.

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SUMMARY

Samples have been analysed from freshly deposited marine sediments along the continental coast of the Northsea and from the material suspended in the seawater of the Dutch Wadden area (see map).

In the coarser sediments the $CaCO_3$-content increases with increasing clay content, in the more clayey sediments the carbonate-content often is next to constant. Within one region the $CaCO_3$-content of each soil fraction is nearly constant. Below 75 micron the carbonate-content of the fractions increases with decreasing particle size. The clay fraction, however, is relatively poor in calciumcarbonate. This size distribution of the $CaCO_3$ will be caused mainly by disintegration during the transport.

In deposits with comparable clay content the $CaCO_3$-content decreases from south to north. In the brackish region of river mouths it decreases in inward directon. However, the relations between the $CaCO_3$-contents of the various fractions are rather similar all along the coast in question. These geographical differences in $CaCO_3$-content may be governed mainly by the $CaCO_3$-contents of the material from which the sediments originate. Locally other factors play a part too.

The calciumcarbonate consists chiefly of more or less recognisable material of organic origin: crushed shells, Foraminifera, Ostracoda, spines of Echinodermata etc. In the finer fractions some crystals have been found too, rhomboeders or fine needles.

Generally, about 5—30 % of the total carbonates is bound to magnesium.

In order to avoid a too frequent use of the term $CaCO_3$, the words carbonates and chalk are also used.

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