Calcium carbonate in Schelde-estuary bottom sediments

by S. WARTEL & R.W. FAAS

Abstract

Mineralogical examination of Schelde estuary bottom sediments indicated low-Mg calcite in every size fraction, aragonite in the fraction > 0.250 mm and dolomite in the fraction < .125 mm. Occurrence of $CaCO_3$ is attributed to remains of recent organisms from the North Sea and of fossils from eroded Quaternary or Tertiary sediments in the estuary on the one hand and to material in solution on the other. Mechanical fragmentation along transport, attack by micro-organisms and precipitation favours increase of carbonate in the < 0.125 mm fraction and minimum occurrence in the 0.355 - 0.125 mm fraction. A landward decrease observed in the < 0.044 mm fraction is attributed to mixing of carbonate-rich marine sediments with carbonate-poor river sediments.

Résumé

L'analyse minéralogique des sédiments du fond de l'estuaire de l'Escaut montre la présence de la calcite faiblement magnésienne dans toutes les fractions granulométriques, de l'aragonite dans les fractions > 0.250 mm et de la dolomite dans les fractions < 0.125 mm. $CaCO_3$ est dérivé des restants d'organismes récents de la Mer du Nord et des fossiles, provenants des sédiments Quaternaires ou Tertiaires, érodés dans l'estuaire d'une part et de la matière en solution d'autre part. Fragmentation pendant le transport, attaque par des microorganismes et précipitation favorisent l'augmentation en carbonate dans les fractions < 0.125 mm et un minimum dans les fractions 0.355 - 0.125 mm. Dans la fraction < 0.044 mm un pourcentage en carbonates décroissant de la Mer du Nord vers l'estuaire est supposé du à un mélange de sédiments de la Mer du Nord riches en carbonates avec des sédiments de l'estuaire et du Rupel pauvres en carbonates.

Introduction

The occurrence and distribution of carbonates in recent bottom sediments of the Schelde estuary and the North Sea (fig. 1) have been previously discussed among else by Della FAILLE (1961), LAURENT (1969) and SALOMONS (1975). Della FAILLE showed that regional differences occur which must be related to sediment transport and geochemical environments. The purpose of the present study is to show the relationship of the carbonate content to the overall sediment distribution and to discuss a possible origin of the carbonate distribution.

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Methods

Sediments were collected during the period 1967 - 1980 in the Schelde, the Wester-Schelde and the Ooster-Schelde using a Shipek-bottom sampler. Grain-size distributions of the Schelde sediments have been reported previously (WARTEL, 1977). Total carbonate was determined gasometrically with a Scheibler-Dietrich calcimeter, using 1N HCl, and the amount of CO_2 liberated converted to percent $CaCO_3$. The mineralogical nature of carbonates was examined microscopically, by X-ray powder diffraction (XRD) with a Philips diffractometer using Ni-filtered Cu-radiation at a scanning speed of 1/4 degree 2θ/minute, and scanning electron microscopy (SEM) combined with semiquantitative energy dispersive X-ray analysis (EDAX). The magnesium content of Mg-bearing calcite was determined according to GOLDSMITH *et al.* (1955) using fluorite as an internal standard.

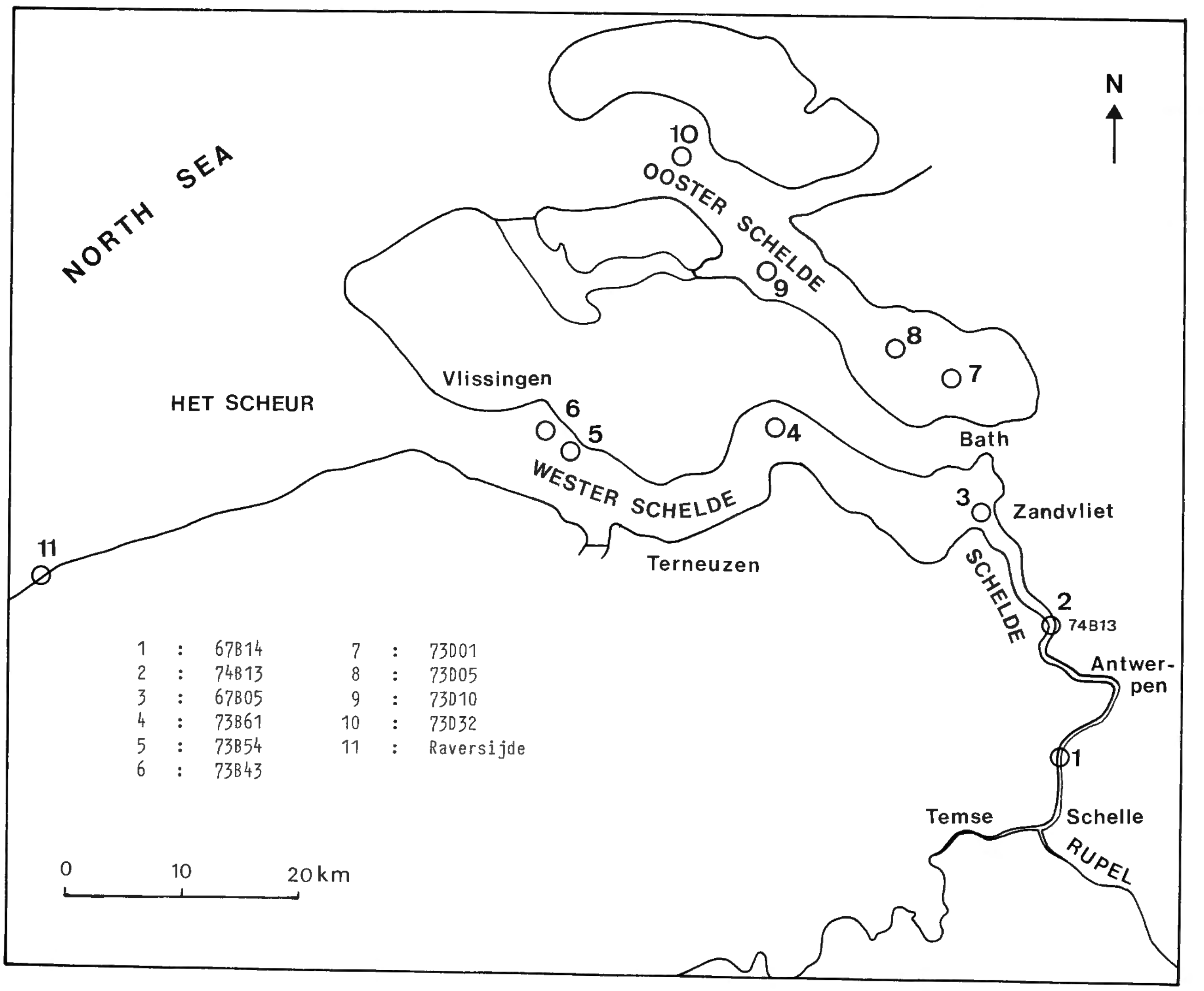
Composition of carbonates

The carbonate minerals observed are: low-Mg-calcite, aragonite and a mineral showing a broad X-ray diffraction peak at 2.88A for d_{104}, until further notice called "dolomite". Table 1 summarizes the distribution of carbonate minerals in different size fractions for a sample from the Schelde estuary and for one from the Ooster-Schelde estuary.

Low-Mg-calcite is present in every grain-size fraction and the magnesium content varies from a minimum of 0.5 to a maximum of 4 mole percent $MgCO_3$, the latter value having been observed in a sample from the Ooster-Schelde estuary. Generally the highest value for a sample is 2 - 3 mole percent $MgCO_3$. Low-Mg-calcite is a common constituent of the calcareous parts of marine organisms and generally contains 4 to 11 mole percent $MgCO_3$ for seawater temperatures between 10 and 15 degrees celsius (CHAVE, 1954a). This is more than the observed temperature values for the Schelde estuary. Loss of magnesium from Pleistocene and older calcitic skeletons by diagenesis has been shown by CHAVE (1954b) and LAND (1967). Since most molluscs and foraminifera occurring in the Schelde estuary have a Tertiary or Quaternary age (WARTEL *et al.*, 1983) diagenesis can explain the low magnesium content. Furthermore SEM analysis on samples 2, 4 and 5 revealed the occurrence of rhombohedra varying in size from 1 to several tens of micrometers (photo 1 and 2) and containing, according to EDAX analysis, Ca or Ca and Mg (maximum 8%) or Ca, Mg and Fe (maximum 18%) in varying proportions, and Fe (87%) and Ca (13%) (sample 4). The carbonate composition thus seems to be much more complex than was indicated by XRD. Furthermore, the occurrence of well-crystallized carbonate minerals in these finest fractions suggests carbonate precipitation.

Aragonite is only observed in sizes fractions greater than 0.250 mm. For fractions greater than 0.500 mm, it is detected by XRD of the whole fraction, and by microscopic examination and X-raying of isolated grains in the 0.5 - 0.25 mm fraction. Aragonite is a commun constituent of the skeletins of bryozoa and molluscs (LOWENSTAM, 1954; CHAVE, 1954, 1962; TAYLOR *et al.*, 1969). A decrease in aragonite content toward the fine size fractions has

Figure 1. – *Map showing sample locations (full registration number of each sample is given in the insert).*



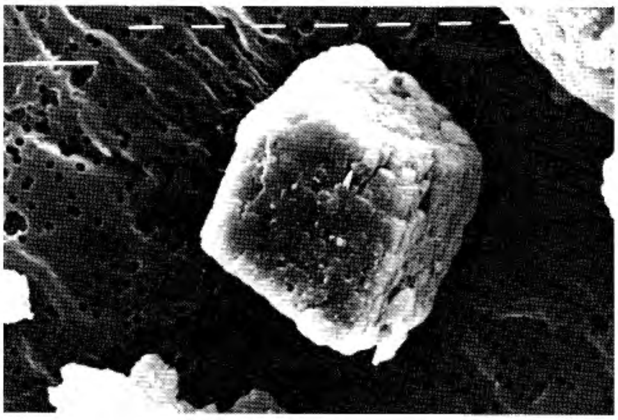


Photo 1 – *Rhombohedral crystal, probably calcite. EDAX showed calcium (100%). The mark represents .001 mm. (Sample 74B13).*

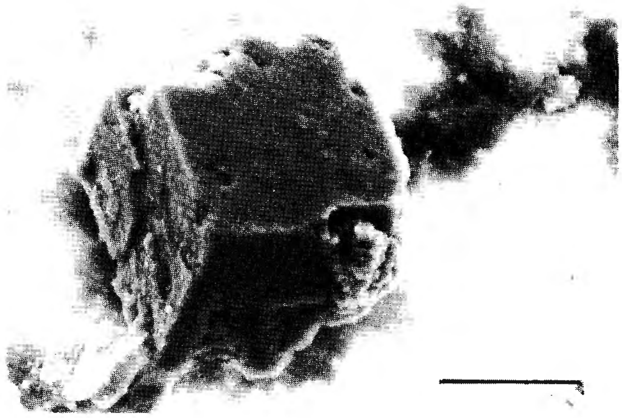


Photo 2 – *Rhombohedral crystal, probably calcite. EDAX showed calcium (78%), iron (18%) and magnesium (4%). The mark represents .01 mm. (Sample 73B61).*

been observed previously (among others: CHAVE, 1954 and 1962). Selective loss of this mineral by solution (aragonite being more unstable in seawater than calcite) offers the best explanation for this phenomenon (CHAVE, 1962). Furthermore a high surface to volume ratio favours solution of the finest particle sizes. Inversion of aragonite to either calcite or dolomite has been demonstrated experimentally by LAND (1967) but it can be questioned whether the appropriate physico-chemical conditions for it to occur prevail in the Schelde estuary.

Dolomite generally occurs in the 0.125 - 0.004 mm fraction although it was not always observed in the fractions below 0.032 mm. LAURENT (1969) figured small rhombohedra, considered as dolomite, from a 0.062 - 0.032 mm fraction (sample from the right bank of the Wester-Schelde near Hansweert in which dolomite was detected only by XRD - further confirmed by private communication, june 1977) and considered them as autochthonous formed by diagenesis of low-Mg-calcite or aragonite. This process has been mentioned (CHAVE, 1954; LAND,

Table 1.
Carbonate content and minerals observed by XRD in different size fractions of a Schelde and an Ooster-Schelde sample:

a) *Schelde (sample 2)*

size fraction	carbonate content (%)	calcite	$MgCO_3$ (*)	aragonite	dolomite
> .500		++	< 1	++	–
.500 - .250		++	< 1	–	–
.250 - .125		++	1 - 2	–	–
.125 - .063		++	1 - 2	–	+
< .063		++	1 - 2	–	+

b) *Ooster-Schelde (sample 10)*

size fraction	carbonate content (%)	calcite	$MgCO_3$ (*)	aragonite	dolomite
> .500	59.1	++	.5 - 1	++	–
.500 - .250	1.8	++	.5 - 1	–	–
.250 - .125	2.0	++	2 - 3	–	–
.125 - .063	5.9	++	3 - 4	–	+
< .063	19.6	++	1 - 2	–	+

++ : major diffraction peak (d_{104} for calcite and dolomite, d_{111} for aragonite)
\+ : minor diffraction peak
– : not observed
(*) : values expressed as mole percent.

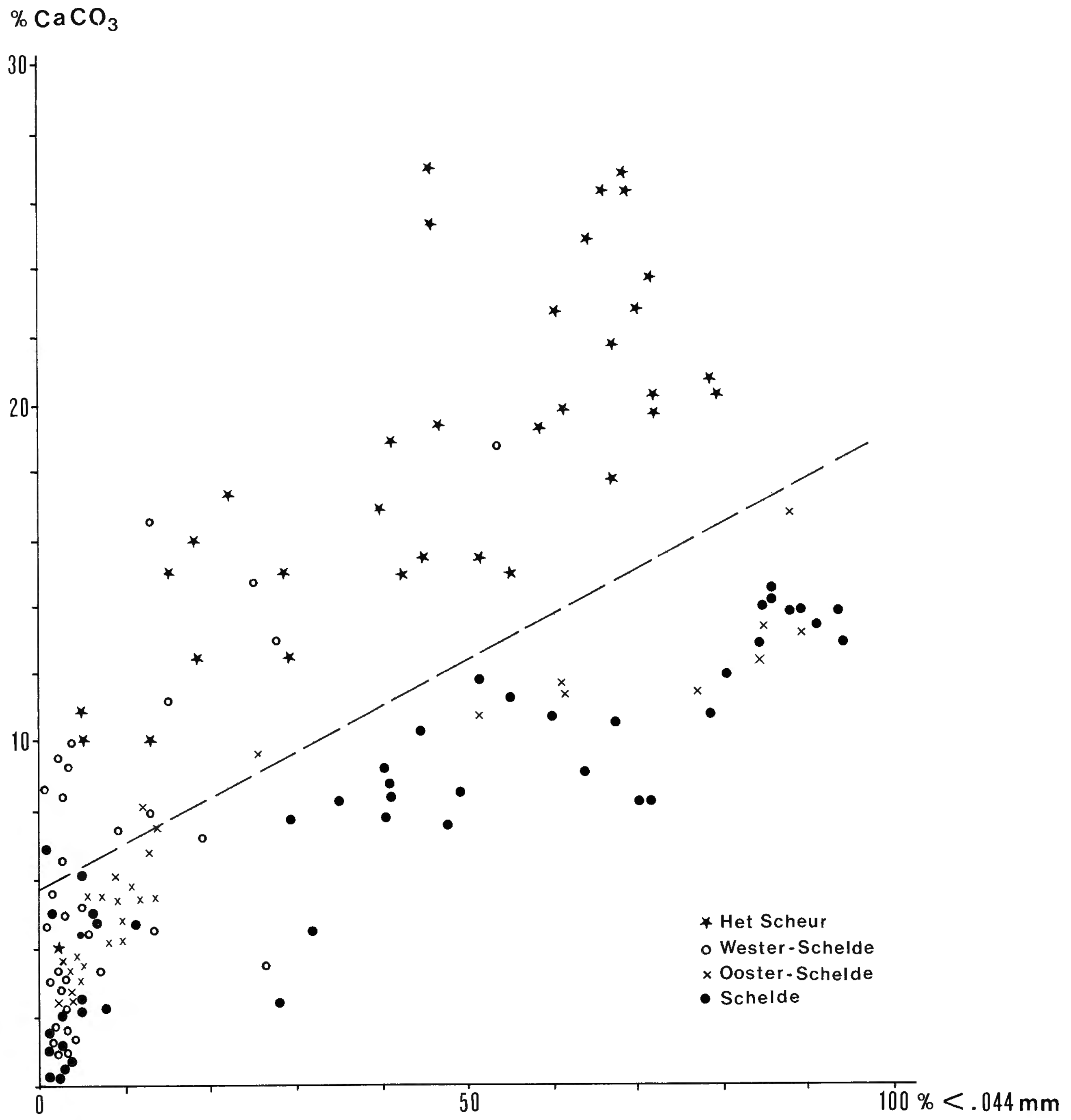


Figure 2. – *Carbonate content compared with the fraction smaller than .044 mm. The dashed line separates Het Scheur and Wester-Schelde samples (above it) from Schelde and Ooster-Schelde samples (below it). No distinction can be made for samples containing less than 20% particles smaller than .044 mm.*

1967; MULLER *et al.*, 1972 and LIPMANN, 1973) and can be assumed to occur in the Schelde estuary. The muddy environment of the tidal flats (not considered in this paper) where high concentrations of organic matter and bacterial activity create conditions of high alkalinity, will be a more appropriate environment for this to occur than the sand bottom of the river channel. However, EDAX analysis never showed Mg-concentrations higher than 8% in Ca-Mg-rhombohedra and thus the question remains open whether the diffraction peak at 2.8 A is from dolomite.

Distribution of carbonates

The total carbonate content of a large number of bottom samples from the Schelde estuary and the Scheur is summarized in table 2. The highest values are observed in the Wester-Schelde between Vlissingen and Terneuzen and in the Schelde between Zandvliet and Antwerpen. Elsewhere total carbonate content never exceeds 7% and is generally less than 5%. The high values observed between Antwerpen and Zandvliet are explained by the occurrence of shell deposits (Quaternary or Tertiary) in that area (WARTEL *et al.*, 1983). The data for the Wester-Schelde and the Ooster-Schelde are similar to data for North Sea sediments sampled in front of their respective mouths (GULLENTOPS *et al.*, 1976) and imply a similar relationship.

When more than 20% particles < 0.044 mm are present a positive correlation is seen between the amount of carbonate in the total sediment and the fraction < 0.044 mm (fig. 2). This correlation varies quantitatively depending on the area. The carbonate content for a given amount of particles < 0.044 mm is higher in the Wester-Schelde than in the Schelde and Ooster-Schelde. The dashed line in figure 2 separates both fields of data. Sediments from the Scheur (BASTIN, 1975) behave similar to those from the Wester-Schelde.
The distribution of carbonate over different size fractions (0.25 phi interval) for eight representative samples of the Schelde, the Wester-Schelde, the Ooster-Schelde and the Belgian North Sea beach (sample 11, fig. 1), is given in table 3. Although data vary from one sample to another, the carbonate content is minimum in the fine and medium sand fractions (0.125 - 0.250 mm). This distribution seems independent of the grain-size distribution as shown for 3 samples in figure 3.
When the carbonate content of the fraction < 0.044 mm for sediments of the Schelde estuary is considered and plotted as a function of the distance from the sea (fig. 4) a continuous landward decrease is seen.

Table 2.
Extreme values of carbonate content of bottom sediments expressed as weight percent of total sample.

Locality	*Carbonate content (%)*
Wester-Schelde (between Vlissingen and Terneuzen)	3 - 10 (exceptionally 17%)
Wester-Schelde (between Terneuzen and Zandvliet)	1 - 5
Schelde (between Zandvliet and Antwerpen)	8 - 13
Schelde (between Antwerpen and Schelle)	1 - 5
Schelde (upstream of Schelle)	1 - 3
Rupel	2 - 7
Ooster-Schelde	1 - 2 (exceptionally 4%)

Discussion

The amount of carbonates differs regionally as with grain size as well. Three grain-size fractions can be considered: a coarse fraction (> 0.500 mm), a fine fraction (<0.125 mm) and a intermediate fraction

Table 3.
Carbonate content (expressed as weight percent) of different size fractions of bottom sediments (lower limits of size classes are given).

Sample n°	1	3	4	5	7	8	9	11
.800 mm	7.5						24.7	72.2
.630	4.5						13.2	63.2
.500	2.4	85.0				9.4	3.4	62.3
.425	0.2	63.0		36.8	13.4	2.1	1.1	38.2
.355	0	25.8	16.1	9.5	4.0	0.9	0.3	25.3
.297	0	5.8	12.7	4.2	5.3	0.4	0.1	17.7
.250	0	3.2	4.5	2.6	6.0	0.5	0	13.6
.210	0	2.0	1.6	1.8	5.3	0.7	0.2	8.9
.177	0.2	2.2	1.2	1.8	2.3	0.8	0.8	7.4
.149	0.4	3.2	2.0	4.0	1.4	1.5	3.0	7.6
.125	1.2	4.6	3.9	6.3	1.9	3.0		10.3
.105	4.2	6.9	6.0	9.7	3.2			18.9
.088	5.8	7.5	7.2	12.5	4.6			
.074	6.8	15.5	7.8	14.4	6.0			
.63	7.7				6.5			

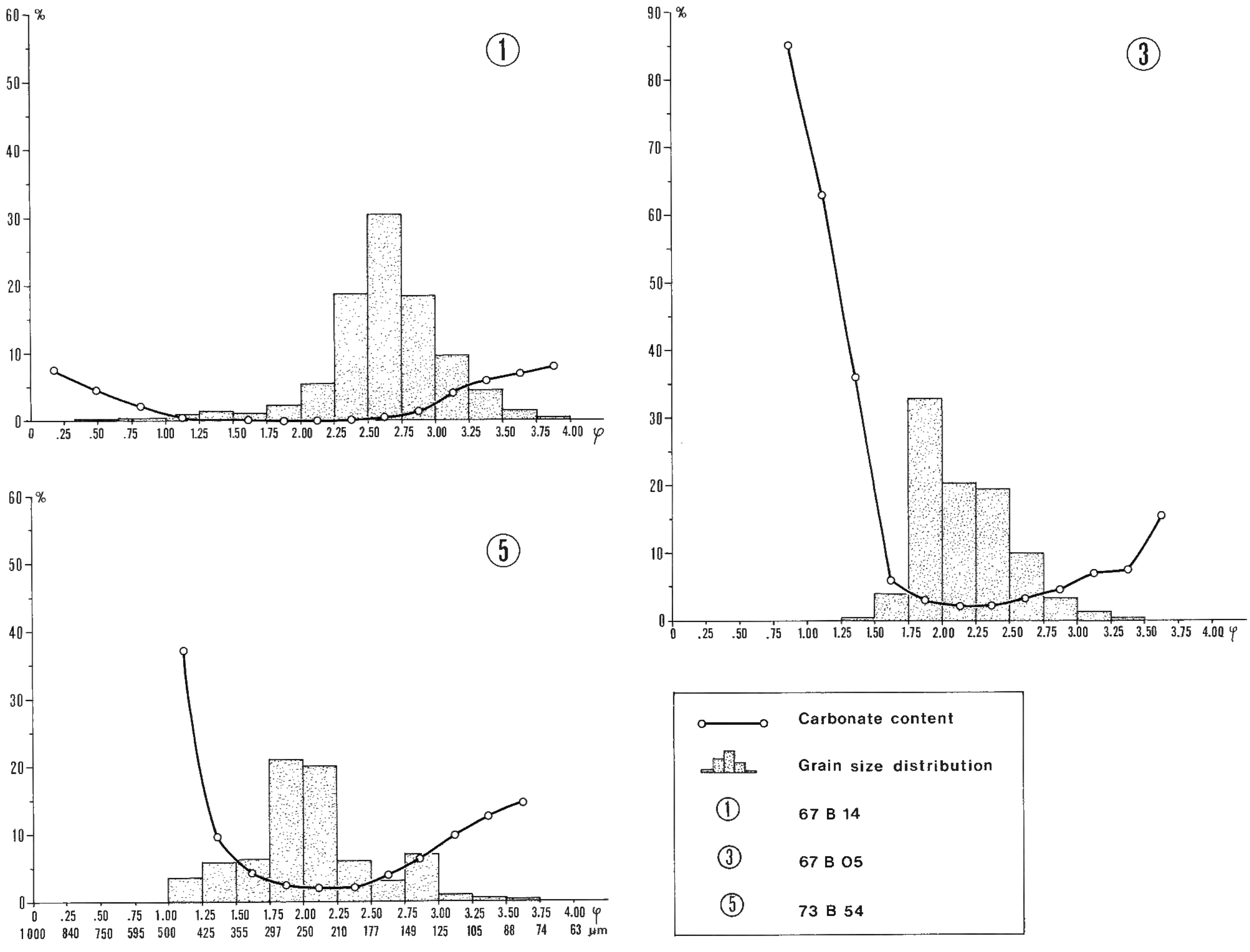
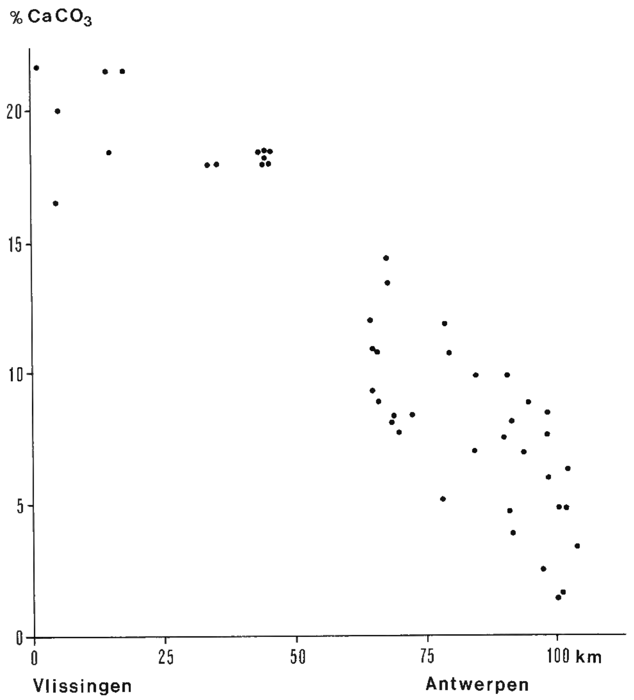


Figure 3. – *Carbonate content of different grain size fractions.*



(0.500 - 0.125 mm). The carbonate of the coarse fraction is mostly allochthonous and of bioclastic origin. Carbonate content is relatively high in the Schelde between Zandvliet and Antwerpen and is derived from locally eroded Tertiary and Quaternary deposits containing considerable amounts of molluscs (WARTEL *et al.*, 1983). For the Wester-Schelde, the Ooster-Schelde and the North Sea recent molluscs also contribute to a greater or lesser degree (GULLENTOPS *et al.*, 1976, for North Sea sediments). Progressive crushing during transport and dilution with an increasing amount of non-carbonate sediment can explain the decreasing carbonate content from the coarse toward the intermediate fractions. The gradient of decrease is rather steep (fig. 3) and seems to be independent of the grain-size distribution of the non-carbonate fraction. This contrasts with the increase in carbonate toward the fine fractions. Microscopic and SEM examination of the coarse fraction showed that the carbonate particles generally exhibit smooth surfaces with well-rounded edges or, in Wester-Schelde

Figure 4. – *Graph showing the landward decreasing carbonate content for the fraction smaller than .044 mm.*

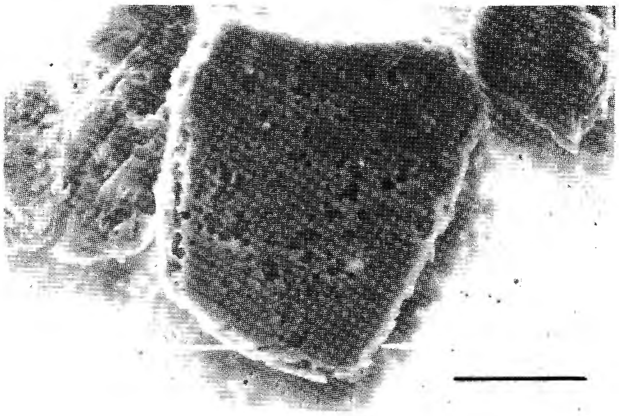


Photo 3 – *Perforated shell fragment. The mark represents .01 mm. (Sample 74B13).*

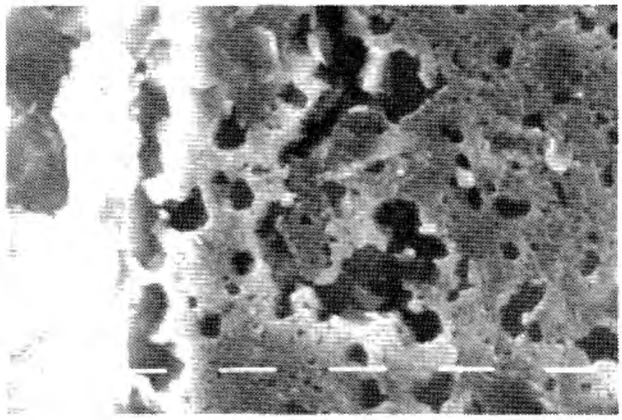


Photo 4 – *Detail of photo 3. The mark represents .001 mm.*

samples, fracture surfaces with sharp edges. Many carbonate particles in this fraction are also perforated by a large number of sinuous and ramified tubes, exhibiting diameters from several millimeter to a few tens of a micrometer (photo 3 and 4) and produced by boring organisms (bacteria, fungi, algae, sponges, bryozoa and others). This phenomenon has been described in detail by ALEXANDERSSON (1979) and DARTEVELLE *et al.* (1977). These perforations permit the mechanical fragmentation of the particles into much smaller particles (< 0.125 mm). Natural maceration, a concept introduced by ALEXANDERSSON to describe the disintegration of skeletal fabrics into their microscopic constituents has also been observed. It leads to either lath-shaped or irregular very fine silt- to clay-sized particles. Both microboring and maceration are probably of major importance to understand the observed increase in carbonate content in the fine fractions. They probably also explain, at least partly, the distribution of aragonite. This mineral is more soluble in sea water than calcaire (CHAVE, 1962) and is unstable in the interstitial water of Schelde estuary sediments (LAURENT, 1969). The fragmentation of coarse carbonate particles will increase the surface to volume ratio and hence the dissolution of aragonite, which consequently will be best represented in the coarser fraction, less in the intermediate fraction and rare, if present at all, in the fine fraction.

The main part of the carbonates in the fine fraction thus derives from mechanical or bioclastic abrasion of carbonate skeletons. Precipitation can also be considered as is suggested by the occurrence of small rhombohedra containing Ca, Ca and Mg or Ca, Mg and Fe in varying proportions. MASCHHAUPT (1948), BERNER (1971) and LIPPMAN (1973) stressed the possibility of precipitation of carbonate by the activity of nitrate reducing bacteria. In the Schelde and Wester-Schelde a landward increasing number of nitrate reducing bacteria (WOLLAST, 1973 and DE PAUW, 1974) and a corresponding gradual increase in NH_4-ions, from 2 mg/l at Vlissingen to 12 mg/l at Schelle occur (WOLLAST, 1973). Precipitation can thus be postulated and will be more effective toward Zandvliet.

The landward decreasing content of carbonates in the fine fractions probably results from the mixing of carbonate-rich North Sea sediments transported landward during flood periods, with carbonate-poor sediments derived from the Schelde basin. This view fits well with SALOMONS (1975) observations on the Haringvliet (an estuary north of the Ooster-Schelde) in which 70% of the carbonate in the bottom sediment is derived from the North Sea. However, it does not fit however with the high carbonate contents observed in the coarse fraction of bottom sediments between Zandvliet and Antwerpen from which a higher amount of carbonates in the fine fraction could also be expected. It appears that either the degrading activity (boring by organisms or natural maceration) or the present amount of coarse carbonates is too small to affect the shape of the landward decreasing carbonate content curve. It is also possible that most, if not all of the observed skeleton perforations are much older and occurred prior to the establishment of the actual Schelde estuary environment. An argument for this is given on the one hand by the smoothed edges of many perforations, and on the other hand, by the anaerobic conditions which are unfavourable for most boring organisms between Antwerpen and Zandvliet.

If the presumed landward transport of the fine carbonate fraction also holds for the fine non-carbonate sediment one must assume that the fine river sediment is not, or only to a lesser degree being transported to the North Sea. It can be argued that this fraction is trapped within the turbidity maximum (Anywerpen - Zandvliet). This implies that the Schelde estuary does not export all of its suspended mud toward the North Sea and that the mud occurring in front of the Belgian coast may have a different origin.

Conclusions

Carbonates (including low-Mg-calcite, aragonite and dolomite) occur in very specific size fractions throughout the Schelde estuary. Aragonite is observed only in the fraction > 0.250 mm and is of biogenic origin. These coarse particles are broken and abraided during transport up the estuary and through the activity of boring organisms.

High values of carbonate in the > 0.250 mm fraction, located between Zandvliet and Antwerpen are derived locally from erosion of fossiliferous Pliocene and Miocene deposits and remain in the area due to convergence of the tidal transport system.

Aragonite, because of its greater solubility, is not found in size fractions < 0.250 mm, but low-Mg-calcite occurs in every grain-size. The carbonite content in the finest fractions (< 0.044 mm) decreases landward due to the mixing of carbonate-rich North Sea sediments with carbonate-poor river sediments. Microscopic rhombohedra of carbonate minerals suggest that precipitation of carbonate occurs in the estuary.

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