

'BIG MAC' CALCARENITE CONCRETIONS (LOWER OLIGOCENE, NW-BELGIUM): CONCEPTUAL GROWTH MODEL DERIVED FROM STRATIGRAPHY, PETROGRAPHY AND GEOCHEMISTRY

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(24 figures, 2 tables)

ABSTRACT. 'Big Mac' calcarenite concretions were dredged at Wintham (Province of Antwerp, NW-Belgium). Small concretions are mostly spherical, larger ones circular but slightly flattened. They can coalesce, forming club-shaped bodies. Several large concretions show a subtle central indentation corresponding with a strongly bioturbated zone, providing them a 'hamburgerlike' shape (holotype). Grain-size composition and microfossil biostratigraphy of the enveloping sediment sampled in a nearby borehole, suggest that the concretions appear in the top of the Niel Formation, of which the upper(most) portion could have been (partly) eroded. This is evidenced by the occurrence of a level of reworked concretions, which is interpreted as a lag deposit. Most ichnofossils in the concretions belong to the *Cruziana* ichnofacies typical for a shallow-marine environment.

Variations in petrographical and geochemical concretion characteristics suggest a concentric growth that initiated at the core (nucleus). Their constituting sediment originally consisted of a fine-grained, slightly clayey sand, containing mainly quartz, feldspar, glauconite, mica and heavy minerals. The sediment was bioturbated, and pyrite framboids formed during early diagenesis in a reducing environment, in particular in bioturbations and microfossil tests. Cementation matrix consists mainly of micritic calcite, replacing particles originally present in the sediment.

$\delta^{18}\text{O}$ -values in the calcite matrix of the concretions decrease from the core to the rim (with extreme values up to -3.3 ‰ PDB). Compared to the mean $\delta^{18}\text{O}$ -value for Oligocene ocean water, these results suggest that the calcite precipitated from seawater with a slightly depleted composition. The more negative values at the outer zones might result from water-sediment interaction and/or recrystallisation by meteoric water. Calcite $\delta^{13}\text{C}$ -values increase from the cores to the margins of the concretions, and suggest that calcite precipitated from pore waters with active bacterial sulphate reduction. The slightly less depleted values at the concretion margin are interpreted in terms of contribution of bicarbonate derived from methanogenesis. However, recent surface alteration might also play a role.

Keywords: Calcarenite concretions, conceptual growth model, Oligocene, NW-Belgium.

1. Introduction

The 'Big Mac' calcarenite concretions were dredged in May 1992 in Wintham (Province of Antwerp, NW-Belgium) at topographic levels between -8 m and -11 m during enlargement of the canal connecting Brussels with the river Rupel (Fig. 1). All concretions were stored on a yard where they formed 3 piles of about 30 m (w) x 80 m (l) x 3 to 4 m (h) each. Although concretions of comparable size and form were previously reported from Waasmunster in 1969 (Jacobs & De Coninck, 1978) and in Ruisbroek in 1980, no reconnaissance study detected their presence, which negatively influenced dredging time and costs. The Ruisbroek calcarenite concretions probably occurred at the lower boundary of the Niel Formation (Gaemers, 1984; Steurbaut, 1986, 1992), but the stratigraphical position of the Wintham concretions remained uncertain until now.

The aims of the study were threefold: (1) determine the stratigraphical position and the depositional environment of both concretions and enveloping sediment; (2) investigate their formation and (3) reconstruct the event history during Lower Oligocene times in NW-Belgium.

2. Geological setting

The Belgian Tertiary strata consists of gently sloping (less than 0.5 ‰) mainly shallow-marine, siliciclastic sediment series of decametric to metric thickness. Also some continental and deltaic intercalations occur. Deposition took place in the southern bight of the North Sea, a ramp-type margin basin with a low-relief topography. Constant but slow uplift of the southern hinterland supplied sediment to this so-called intracratonic 'Belgian Basin' through



Figure 1. Location map with indication of sampling localities.

a mainly deltaic drainage system (Jacobs *et al.*, 1991; Steurbaut & Jacobs, 1993; Jacobs, 1995). Even minor but repetitive sea-level changes induced transgressions and regressions over large areas high up on the gently sloped continental shelf. They resulted in rapidly changing sedimentary conditions with deposition of alternating sands and clays, characterised by distinct vertical and lateral facies changes.

The Belgian Rupelian (Fig. 2) is composed of a lower sandy (Niel Formation) and an upper clayey part (Boom Formation). The Niel Formation (Steurbaut, 1992) comprises a lower Wintham Silt Member covered by an upper Ruisbroek Sand Member. This Ruisbroek Member

consists of fine sands overlain by clayey sands with shells in their uppermost part. It was probably deposited on the continental shelf in an open marine environment, influenced by tidal currents (Gaemers, 1984; Steurbaut, 1986, 1992). The overlying Boom Formation displays a rhythmic alternation of thin clayey silt and silty clay layers, that represents a renewed transgression on the continental shelf (Vandenberghe & Van Echelpoel, 1988). At numerous levels in this Formation septaria concretions (calcilutites) occur.

The micropaleontological content of Waasmunster, Ruisbroek and Wintham calcarenite concretions suggests an Oligocene age (probably Early Rupelian) (Jacobs & De

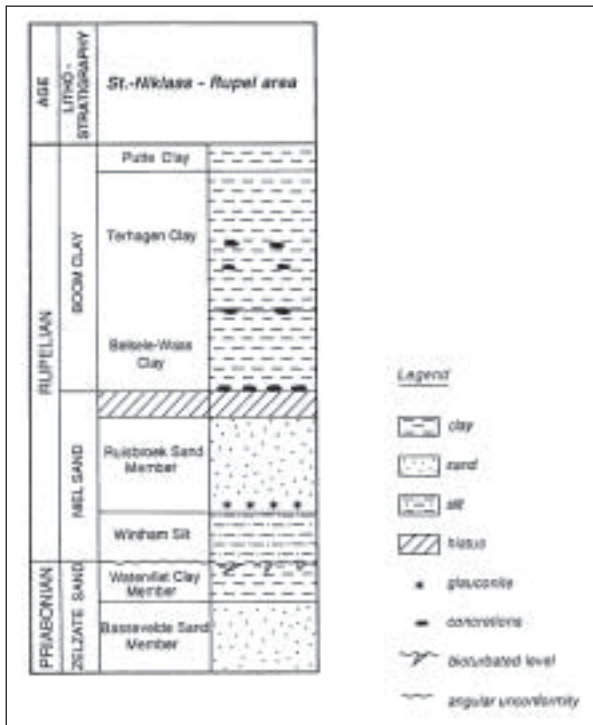


Figure 2. Priabonian (Eocene) and Rupelian (Oligocene) chrono- and lithostratigraphy in Belgium.

Coninck, 1978; Steurbaut & Jacobs, 1993). The organic-walled microfossils of a 'Big Mac' concretion (WHc) and two enveloping sediment samples yielded a significant dinoflagellate cyst fauna (table 1):

3. Methodology

Both Wintham (WH) and Waasmunster (WM) concretions were studied, but the investigation mainly focused on the Wintham specimens. Two relatively small 'Big Macs' (called WHa en WHc) were sampled at the storage yard of 'Dredging International Ltd' at Wintham. This company also provided sediment samples of a dry reconnaissance well. Here from 10 to 23 m well depth, samples were taken every 0.50 m, except between 13.50 m and 14 m, a level at which a concretion was found (core sample WK). Already in June 1969, a calcarenite concretion was sampled in Waasmunster (called WM) during excavations for the new E17 motorway Gent-Antwerp. From the Ruisbroek site, no samples were available but photographs show concretions embedded in their enveloping Ruisbroek sands (Fig. 3).

Grain-size composition (sieving and sedigraphy after carbonate dissolution) and contents of total organic car-

Dinoflagellate cyst taxa	-14/-14.50 m	WHc	-13/-13.50 m
<i>Vozzhennikovia cearaichia</i>	x	x	x
<i>Vozzhennikovia spinula</i>		x	
<i>Vozzhennikovia spinula ?</i>			x
<i>Wetzeliella symmetrica</i>	x	x	x
<i>Membranophoridium aspinatum forma C</i>	x	x	x
<i>Membranophoridium aspinatum forma C à D</i>			x
<i>Areoligera semicirculata</i>	x		
<i>Glaphyrocysta semitecta ?</i>	x		
<i>Distatodinium paradoxum</i>	x	x	x
<i>Thalassiphora aff. fenestrata</i>	x		x
<i>Planoperidinium gracile</i>	x	x	
<i>Gerdicysta conopeum</i>		x	x
<i>Ascotomocystis potane</i>		x	x
<i>Pentadinium lophophorum</i>			x
<i>Achilleodinium aff. biformoides</i>			x

Table 1. Significant dinoflagellate cyst fauna in a 'Big Mac' concretion (WHc) and its enveloping sediment (Dredging International Ltd. well with well depth intervals indicated in m) (after J. De Coninck, pers. comm.)



Figure 3. In situ flattened (bottom) and more spherical (top) 'Big Mac' concretions visible in 1980 during the excavations for the tunnel under the Rupel canal at Ruisbroek (near Boom, Province of Antwerp, NW-Belgium) (person in upper left corner for scale) (from Van Alboom, 1996; courtesy of Pieter Laga, Geological Survey of Belgium).

bon (Walkley & Black method), carbonate (volumetry) and glauconite (magnetic separation) of the enveloping sediment were analysed. Organic-walled microfossils were determined by J. De Coninck (Laboratory of Palaeontology, Ghent University). Petrographic thin sections of Wintham (WHa, WHc and WK) and Waasmunster (WM) concretions were examined using standard transmitted light microscopical techniques with staining for feldspars and carbonates (Fig. 4). Polished thin sections were studied by cold cathodoluminescence (Technosyn Model 8200 Mk II), while rock fragments and representative thin sections were studied in more detail by Scanning Electron Microscopy (Jeol JSM-6400).

Concretion geochemistry was mainly based on semi-quantitative energy dispersive x-ray micro-analysis (Tracor Voyager with absolute errors of 1 to 3 %). Reported values (see figs 21 & 22) relate to the averaging of the measured values at different areas across the concretion. Atomic absorption spectroscopy was occasionally used. 'Isotopic Analytical Services Ltd' at Aberdeen (Scotland, UK) determined the carbon and oxygen stable-isotope composition. Powder samples of 10 mg or less were taken with a fine dental drill and analysed by mass spectrometry. All data were corrected according to procedures modified by Craig (1957). Results are reported in pro mille relative to the PDB standard (PeeDee Belemnite). 3D-porosity measurements made use of highly-destructive mercury impregnation techniques (Micromeritics 5001), but 2D-porosity values were obtained by non-destructive x-ray computed tomography (CT) (Siemens Somatom+) (Jacobs *et al.*, 1995).

4. Results

4.1. Macroscopical observations

The Wintham 'Big Macs' are composed of pale-grey carbonate cemented fine-grained sand and are sometimes highlighted by a marginal crust of microcrystalline pyrite. Small concretions with a diameter of about 0.5 m are more spherical; larger ones with a diameter up to 1.5 m are circular but slightly flattened. These calcarenite concretions lack macroscopically visible concentric zonation or nuclei. Large specimens sometimes display a subtle central indentation (Fig. 5) corresponding with a strongly bioturbated horizon (Fig. 6), providing them a 'hamburgerlike' shape (hence the name 'Big Mac'). Concretions can coalesce (Fig. 7). Many are characterised by a pattern of cracks (like septaria), the walls of which are covered with calcite sometimes with an admixture of pyrite (Fig. 8). Concretions sampled in Waasmunster in 1969 (Jacobs & De Coninck, 1978) show comparable size and form.

The 'Big Macs' display a homogeneous texture with randomly oriented skeletal debris and absence of clear lamination. Concretion burrows are characterised by brown clayey infillings, that contrast strongly with the surrounding beige-grey sandy sediment. Most prominent ichnofossils resemble *Chondrites*, *Planolites*, *Asterosoma*, *Teichichnus*, *Paleophycus* and *Rhizocorrallium*, and form an association typical for the Cruziana ichnofacies (Seilacher, 1964). As ichnofossil cross-sections are circular, the concretionary bodies lithified before major compaction occurred.

4.2. Enveloping sediment characteristics

The grain-size distribution of the sediment above the concretion level differs from the one below (Fig. 9). All samples are 'sand' dominated, but the unit overlying the concretion level contains less of the >63 μm fraction. While in the lower unit an oscillating grain-size distribution is apparent, the upper one is characterised by a fining upward sequence. Statistical parameters (Folk & Ward, 1957) characterise the lower unit as a badly sorted, extreme leptokurtic, fine sand with a positive asymmetry and the upper one as a very badly sorted, extreme leptokurtic, very fine sand with a positive asymmetry. Also both units have different amounts of carbonate, total organic carbon and glauconite (Fig. 10).

4.3. Concretion petrography

4.3.1. The Wintham 'Big Mac' concretions

The primary detrital composition in the concretions is rather constant. Detrital components which are floating within a calcite matrix, constitute about half of the total volume (Fig. 11). Most sand is fine-grained, angular to

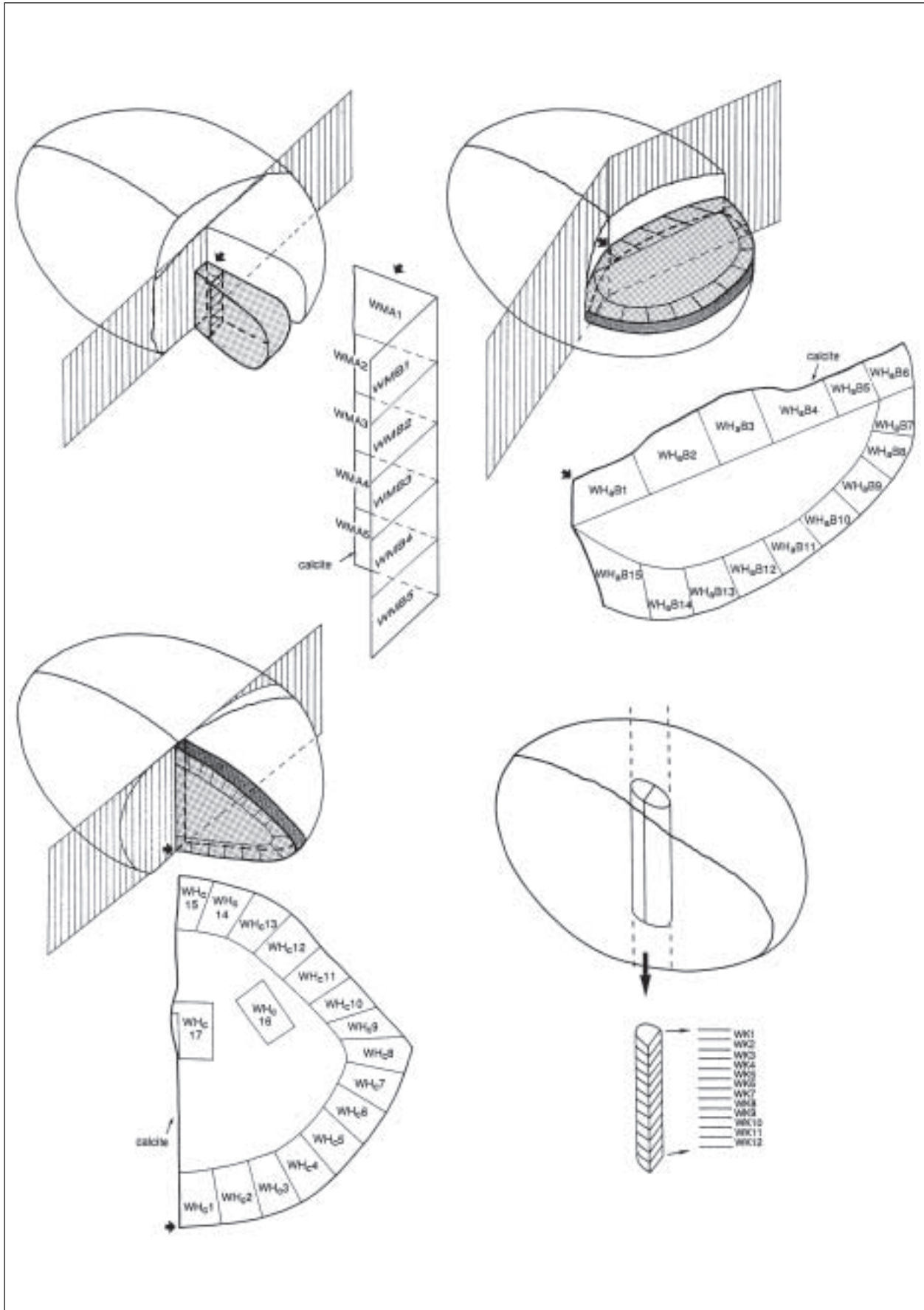


Figure 4. Schematic diagram of sampled concretions WM, WHa, WHc and WK with positions of thin section.



Figure 6. Detail of central indentation, corresponding with a strongly bioturbated horizon (Wintham).



Figure 8. Concretion displaying internal walls covered with calcite and typical crack pattern ('septaria') due to post-depositional compaction (Wintham)



Figure 5. 'Big Mac' calcarenite concretion ('holotype') with central indentation (Wintham).



Figure 7. Coalescence of concretions, forming club-shaped bodies (Wintham).

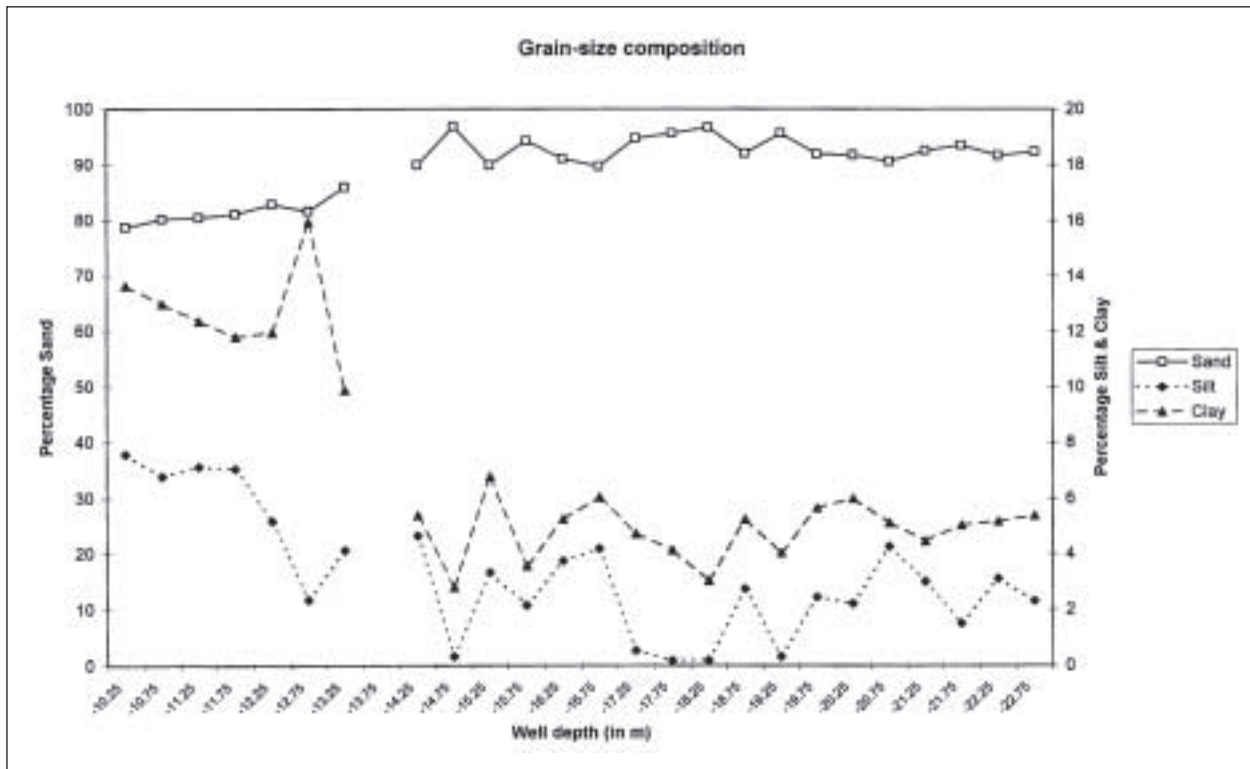


Figure 9. Grain-size composition of the enveloping sediment (concretion position between 13.50 m and 14.00 m well depth, left blank).

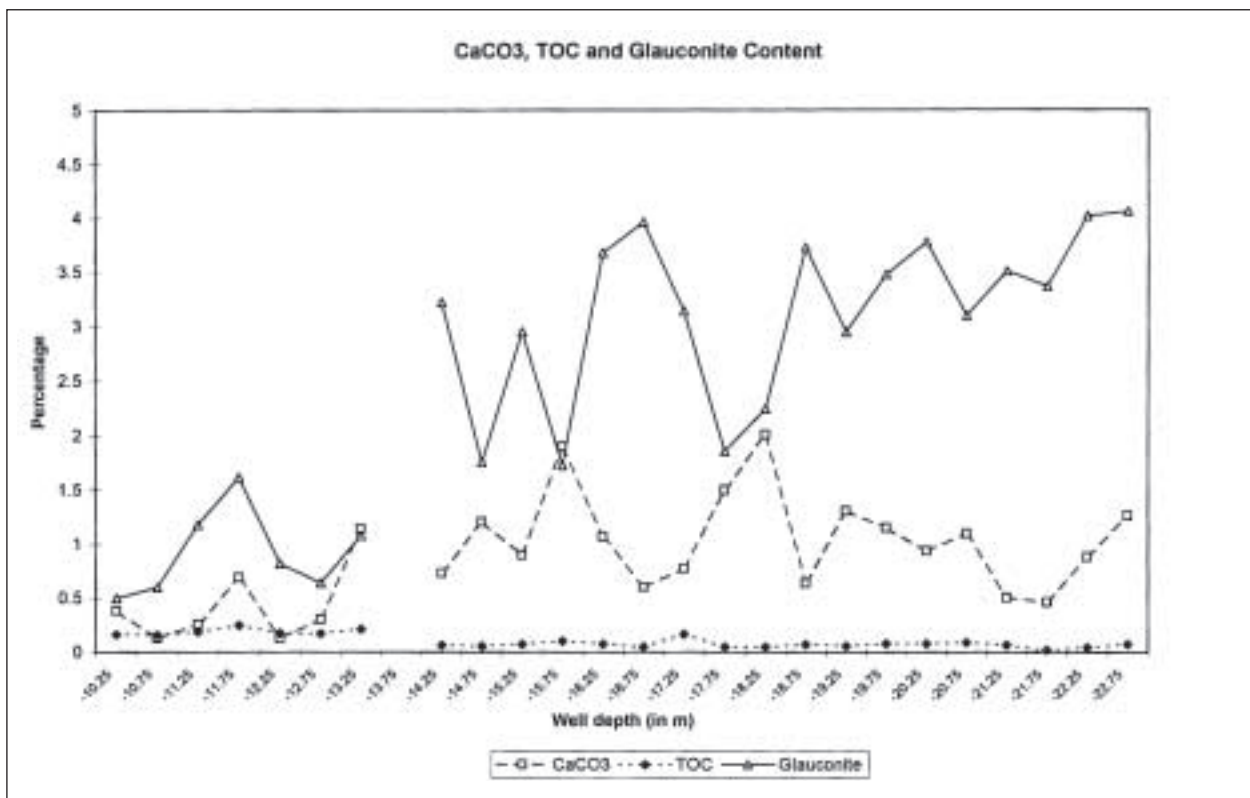


Figure 10. Carbonate, total organic carbon and glauconite contents in the enveloping sediment (concretion position between 13.50 m and 14.00 m well depth, left blank).

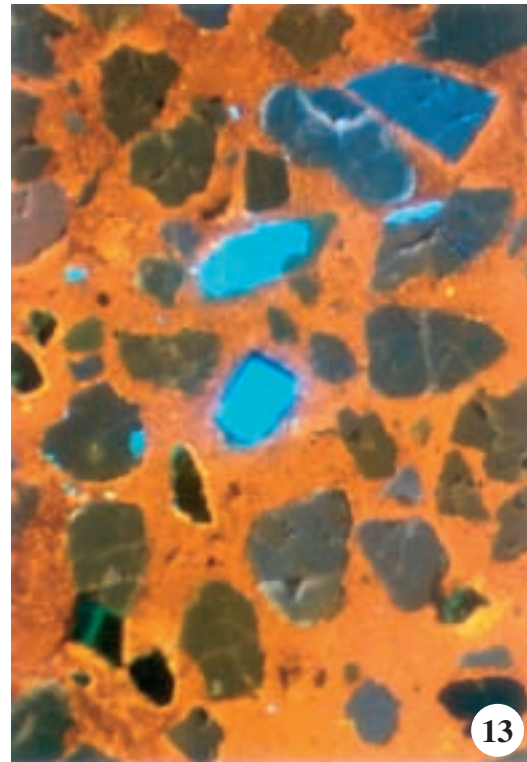
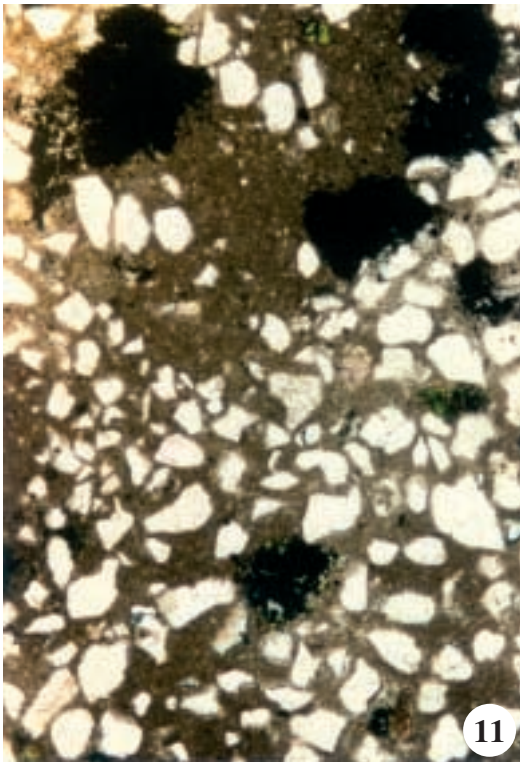
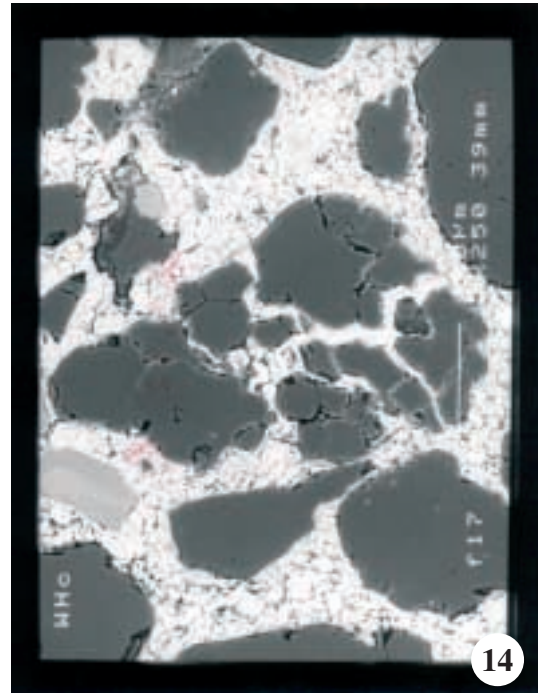
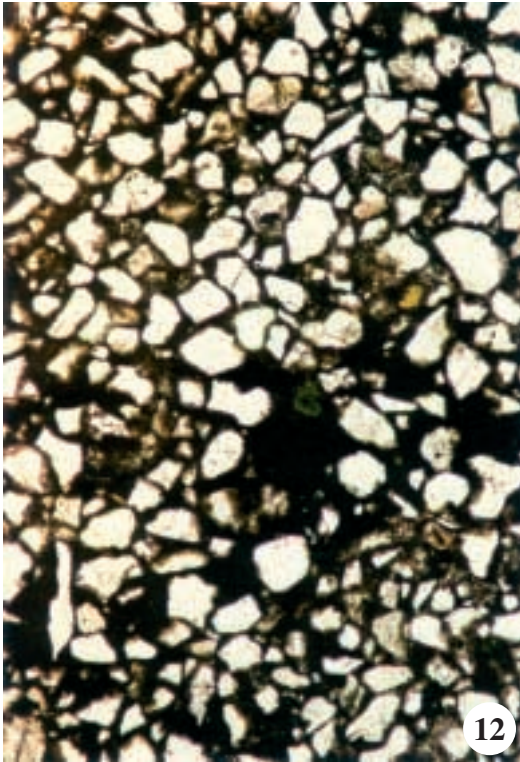


Figure 11. Photomicrograph of central portion of 'Big Mac' concretion consisting of detrital sediment (mainly quartz and some feldspars) with a clayey matrix cemented with micrite. Bioturbations are filled with fine-grained material. Glauconite concentrations are partly overgrown and replaced by pyrite aggregates (NPL (x 40) of thin section WHaB1).

Figure 12. Photomicrograph of outer 5 cm of 'Big Mac' concretion with more densely compacted detrital material and a matrix with an increasing clay content but a decreasing content of calcite cement (NPL (x 40) of thin section WHc10).

Figure 13. Cathodoluminescence photomicrograph of central part of concretion with micrite cement, brown to non-luminescent quartz and blue luminescent K-feldspar grains surrounded by a less intensively luminescent rim. Some detrital grains are partially replaced by luminescent calcite (bottom left) (x 100) of thin section WHc16).

Figure 14. BSE-image of quartz grain partially dissolved, corroded and replaced by calcite (x 250) of thin section WHc10).

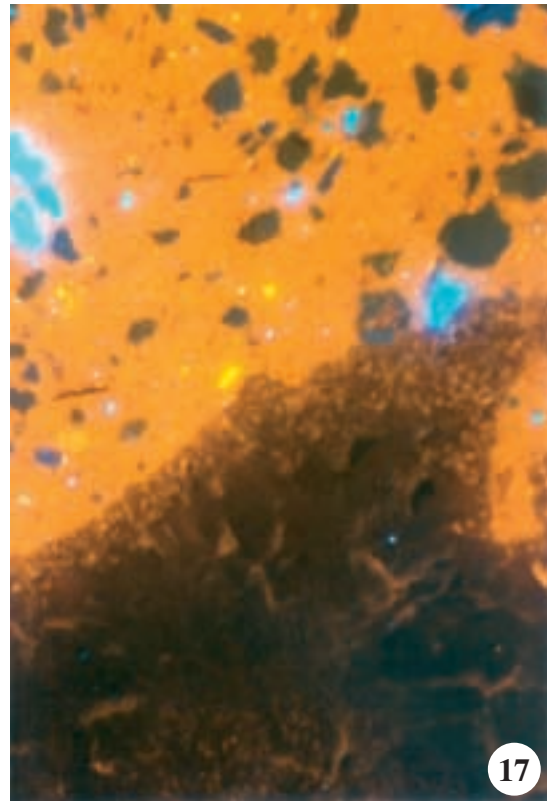
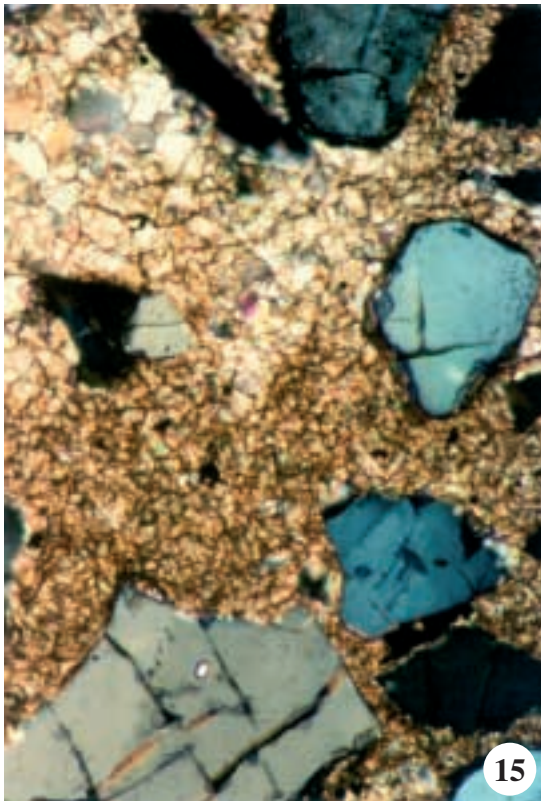
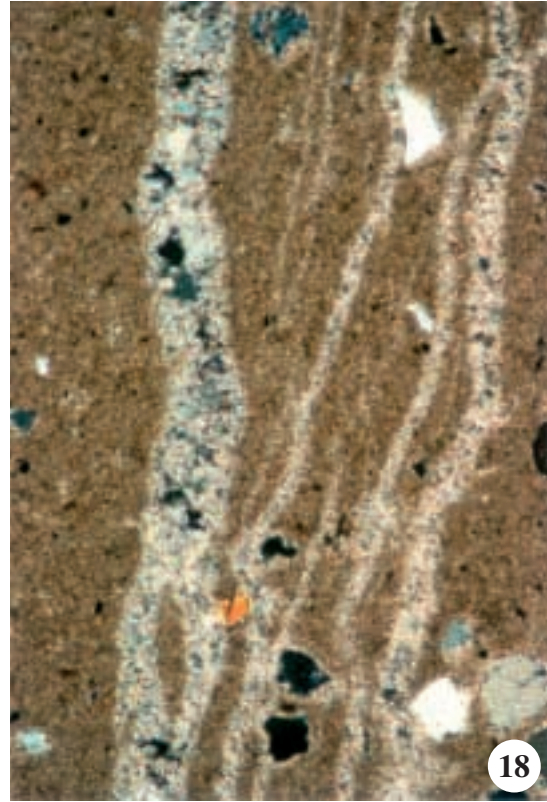
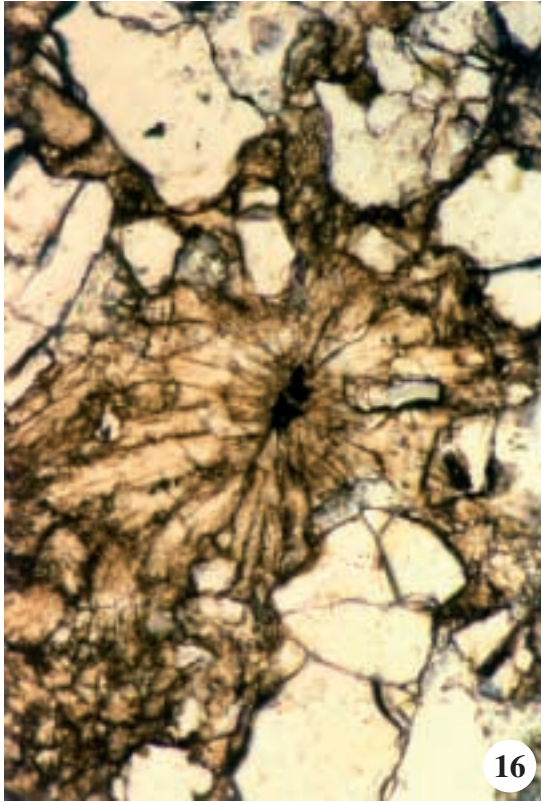


Figure 15. Photomicrograph of detrital sediment cemented with micrite and microsparite (PPL (x 200) of thin section WHc16).

Figure 16. Cluster of calcite crystals radiating from a small pyrite aggregate (PPL (x 200) of thin section WK12).

Figure 17. Cathodoluminescence photomicrograph of bright orange luminescent micrite cut by an irregular crack filled with dull luminescent sparite ((x 100) of thin section WHc16).

Figure 18. Photomicrograph of intensively cemented interval in a bioturbated zone, cut by small irregular and branching cracks cemented by calcite crystals (PPL (x 100) of thin section WMA3).

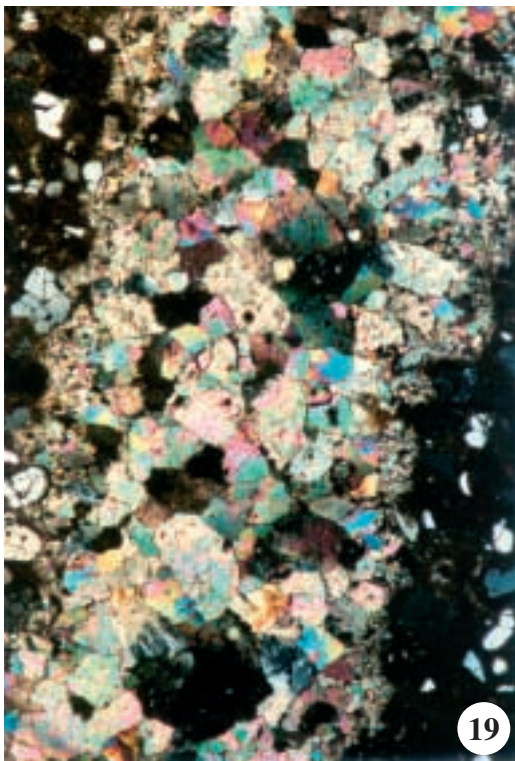
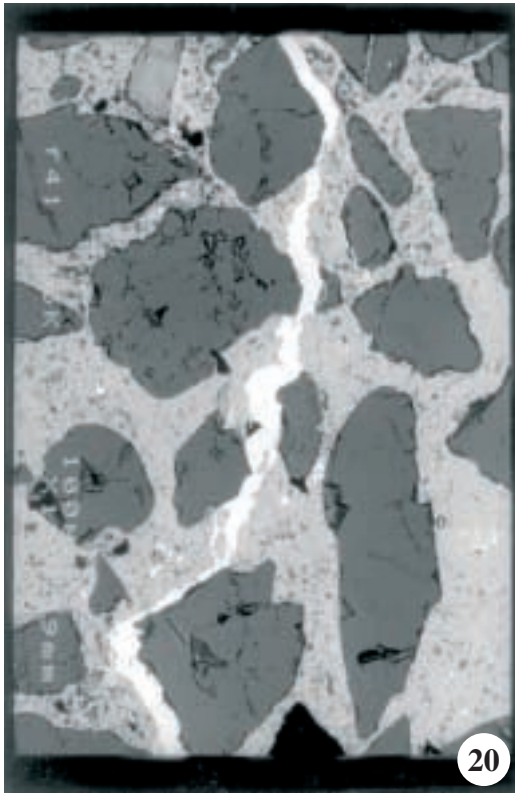


Figure 19. Photomicrograph of 2 mm wide crack filled with equigranular calcite crystals becoming larger towards the centre of the crack (PPL (x 40) of thin section WHc16).

Figure 20. BSE-image of quartz grains floating in a calcite matrix cut by an ironoxide vein that envelopes detrital quartz grains but occasionally cuts through the central grain. Notice the presence of (small bright) pyrite phramboids in the calcite. ((x 150) of thin section WK5).

slightly rounded, and shows low to medium sphericity. The primary sediment matrix is composed of clay particles, that become more abundant towards the concretion edge (especially the outer 5 cm, Fig. 12).

Quartz represents about 85-90 % of the detrital minerals and mostly displays uniform, but also undelous extinction. Chert and cryptocrystalline radial-fibrous chalcedony occur locally. About 5 % of the grains consist of feldspars, displaying traces of alteration; most are K-feldspars as demonstrated by their blue luminescence. Based on their yellow-green luminescence colour, about 5 to 10 % plagioclase grains could be differentiated. Some K-feldspars show a small less luminescent rim around the grain or along cleavage planes. Glauconite represents roughly 3 % of the detrital fraction; most glauconite seems reworked as many grains show traces of alteration. The framework also contains about 2 % muscovite, rare biotite and chlorite. Accessory heavy minerals are zircon, rutile and tourmaline, but also minor amounts of garnet, spinel, staurolite and epidote occur. Few opaque minerals, iron oxides or hydroxides, rock fragments and carbonate detritals are present. Beside these terrigenous components, the depositional fraction contains shells, shell fragments, microfossils and some bone fragments. Cathodoluminescence reveals that the quartz and in particular the feldspars suffered from dissolution and calcite replacement. Corrosion started at the edges and, for the feldspars, also along the cleavage planes. Some quartz grains were replaced partly or entirely by calcite, but their original shape can still be recognised in the replacing calcite, that usually luminesces brightly (Fig. 13). Some detrital grains thus became clearly fragmented (Fig. 14).

The sediment has not been strongly compacted before cementation, except at the outer concretion rims where framework grains constitute about 60 % of the bulk composition and where burrows are slightly deformed. In general, burrows are filled with clay and minor silt. Some show a concentric infilling pattern and much contain debris of organic material.

Small patches of pyrite (2 to 3 %), including framboids, cubes and cube-shaped aggregates, are omnipresent. But pyrite also formed in particular in burrows, within shells and microfossil tests.

Cementation of the sediment occurred with micrite and microsparite (Fig. 15) and with minor equigranular sparite patches. Sometimes cement replaces shell material and occasionally radiating calcite clusters occur (Fig. 16). The calcite is ferroan, with towards the concretion edges increasing iron content according its intenser staining colour. Most micrite and microsparite calcites possess a bright orange luminescence, but the sparite itself is characterised by a dull luminescence (Fig. 17). In general, the luminescence intensity diminishes from concretion core to rim.

Small irregular and branching cracks (Fig. 18) cut through the carbonate cement and are filled with small equigranular carbonate crystals (Fig. 19). In large cracks,

equigranular fine-grained sparite or microsparite crystals with a size of ten(s) of μm occur at the crack-edge while larger (100 - 200 μm) equigranular calcite crystals fill the crack-center. The main part of the calcite crystals in the cracks are however columnar, broader on the outer rims, and characterised by undulous extinction. Those crystals have a length of 500 μm to 3 mm and more. In general, the carbonate in the cracks displays no or only weak luminescence (Fig. 17). Staining colour of the calcite in the cracks is bright blue, implying that they are ferroan. Non-detrital iron oxides and hydroxides form a minor component of the concretion material (less than 1%). They colour rusty-brown and occur in aggregates and flakes, finely dispersed, in veins (Fig. 20), and as coatings on glauconite or other detrital grains.

4.3.2. The Waasmunster concretions

The Waasmunster concretions showed similar characteristics as the Wintham 'Big Mac' concretions, except for the overall grain size of the detrital sediment {very fine sand with a grain size between 62.50 μm and 125 μm , presence of some medium-sized sand grains (250-500 μm) and very few exceptionally coarse grains (500-1000 μm)} and the smaller amount of sparite.

4.4. Porosity

Sequential x-ray computed tomography (CT) scans of a small sample (9 x 24 x 10 mm) from the inner part of a

concretion show a constant tomographic density value of about 2200 Hounsfield Units (HU), while for a sample (6 x 14 x 10 mm) from the outer rim a decrease from 2150 HU to 2075 HU is noticed. For comparison, the same samples yielded a volume-% mercury porosity of 4.75 % and 7.2 % respectively.

4.5. Geochemistry

4.5.1. Major and trace element composition

Trends in the geochemical composition of the concretionary matrix (detritals + carbonate matrix) are about the same in concretions WHa (Fig. 21) and WHc. An increase and positive correlation between SiO_2 , Al_2O_3 and K_2O towards the outer parts of the concretions is apparent. Also Na_2O and Cl correlate positively, in some cases also showing higher concentrations at the margins. In all concretions, CaO reaches its highest concentrations in the core. In concretion WK (Fig. 22), highest concentration of iron (Fe : 6-2 %) and MgO (Mg : 1.15-0.5 %) also occurred in the central part. However, in the concretions WHa and Whc the concentration of these elements increases from the core to the margins (Fe : 2-6 %; Mg : 0.4-1 %). The cement present in the cracks is composed of calcium carbonate is slightly ferroan and enriched in magnesium (0.2-1 %). The cement in the cracks at the concretion rims possesses a higher concentration of iron and magnesium; concentrations also rise towards the central parts of the veins.

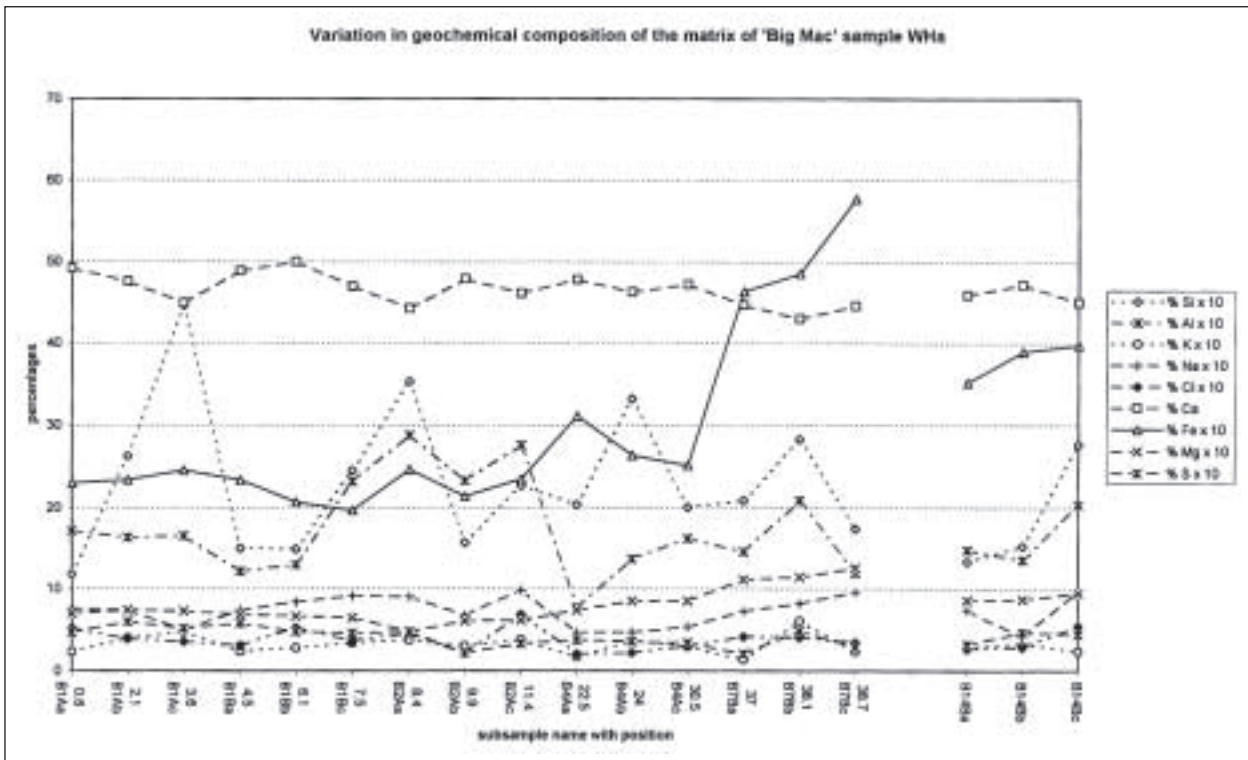


Figure 21. Variation in geochemical composition of the matrix within concretion WHa.

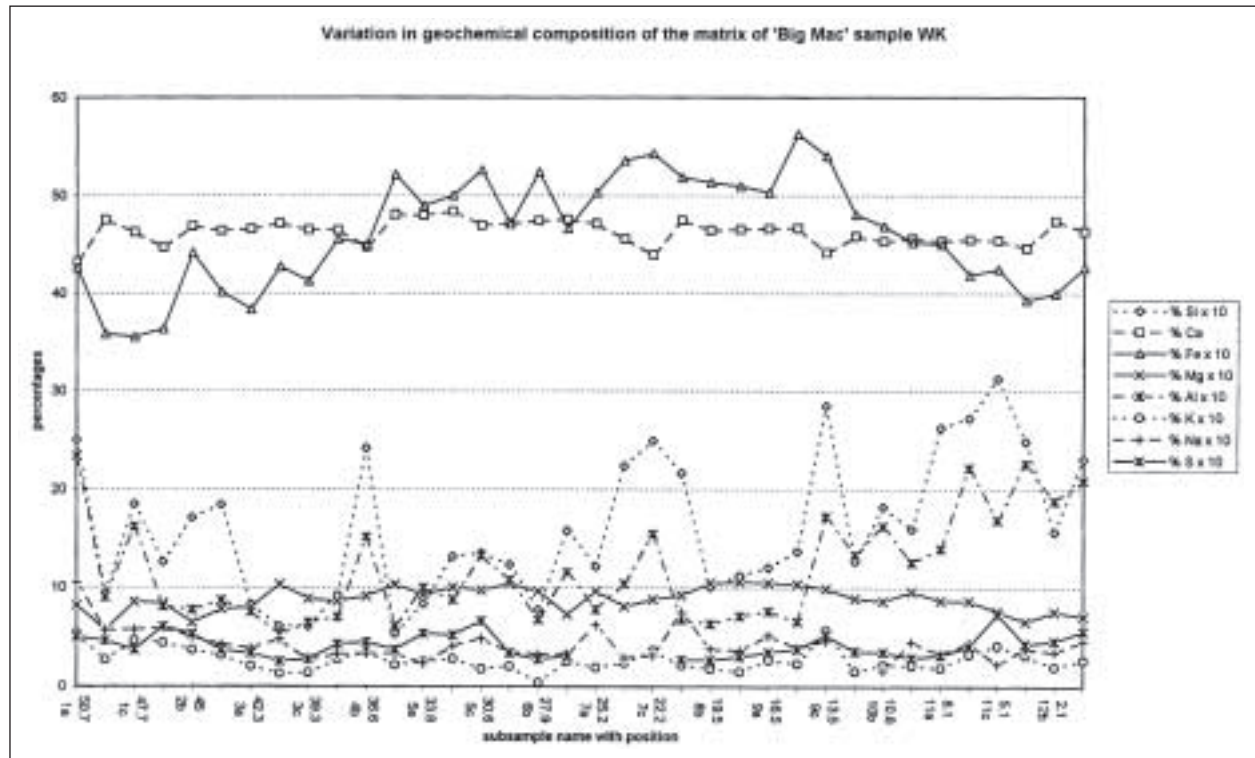


Figure 22. Variation in geochemical composition of the matrix within concretion WK.

Sample	Height or distance (cm)	$\delta^{13}\text{C}$ (‰ to the PDB)	$\delta^{18}\text{O}$ (‰ to the PDB)
WK1	49.50	-14.39	-1.85
WK2	45.00	-14.90	-2.33
WK3	40.00	-14.33	-0.91
WK4	36.00	-15.17	-0.90
WK5	27.00	-16.94	-0.33
WK6	22.00	-16.90	-0.59
WK7	16.00	-17.00	-0.77
WK8	8.00	-15.47	-0.22
WK9	0.50	-13.75	-1.57
WHc1	0.50	-20.02	-0.99
WHc2	1.00	-19.88	-0.69
WHc3	2.00	-17.76	-0.57
WHc4	3.50	-21.53	-3.27
WHc5	First formed (burrow)	-18.70	-1.04
WHc6	Last formed (meteoric? cement)	-5.74	-1.04

Table 2. Stable isotope composition in concretion WK (samples WK1-WK9; total height of samples is 51 cm, listed in descending order), in the rim of concretion WHc (samples WHc1-WHc4; distance to rim in cm; WHc3 in bioturbation) and in a calcite vein in the core of concretion WHc (WHc5 and WHc6 are spaced 3 mm from one another, taken in the growth direction of the calcite cement).

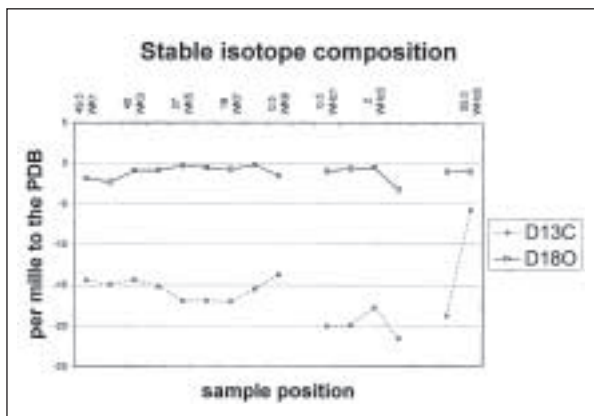


Figure 23. Variation in stable isotope composition of the matrix within concretion WK (left part of diagram) and of the matrix within the outer rim and a burrow and a vein within concretion WHc (right part of diagram).

4.5.2. Carbon and oxygen isotopes

The stable isotope compositions of the carbonate from the Wintham 'Big Mac' concretions are presented in table 2. A bottom-to-top transect in concretion WK is shown in Fig. 23. From concretion WHc, only a small outer rim of 5 cm was analysed, apart of the cement occurring in a burrow and in a calcite vein (Fig. 23, right end of diagram).

Concretion WK shows a range of $\delta^{13}\text{C}$ -values between -17 ‰ and -13.75 ‰, and $\delta^{18}\text{O}$ between -0.33 ‰ and -2.33 ‰ PDB. Centre-to-margin changes in this concretion show a trend towards less depleted $\delta^{13}\text{C}$ -values but somewhat more depleted $\delta^{18}\text{O}$ -values, commonly observed in calcite concretions (Mozley & Burns, 1993). The WHc rim shows a $\delta^{13}\text{C}$ range from -21.53 ‰ at 2 cm to -20.02 ‰ at 0.5 cm from the margin, while the $\delta^{18}\text{O}$ ranges along the same concretion interval from -3.27 ‰ to -0.99 ‰. As in concretion WK, also a negative relationship has been found. The burrow has higher $\delta^{13}\text{C}$ - and $\delta^{18}\text{O}$ -values than the cement sampled outside the burrow between the sand components. The $\delta^{13}\text{C}$ of the cement in the crack ranges over a vertical distance of 3 mm from -18.70 ‰ to -5.74 ‰, but in both samples the $\delta^{18}\text{O}$ equals values of -1.04 ‰.

5. Discussion

5.1. Stratigraphy and depositional setting

Grain-size analyses, organic-walled microfossils (De Coninck, 1999), geometrical arguments and comparison with the Niel and Hingene-Wintham well descriptions (Gulinck, 1967) suggest that the Wintham 'Big Mac' concretions occur in the upper part of the Ruisbroek Member (upper part of the Niel Formation), probably close to the

boundary with the Belsele-Waas Member. The Ruisbroek Member is a fine sand, while the base of the overlying Belsele-Waas Member is a sandy, clayey silt.

Dinoflagellate biostratigraphy suggests the same age for the sediment enveloping the 'Big Mac' concretions as for the Ruisbroek Member. Small differences in microfossil associations between the Ruisbroek and the overlying Belsele-Waas Members indicate the presence of a small hiatus, that was also described in Sint-Niklaas (Steurbaut, 1986, 1992). The Waasmunster concretions were formerly considered to occur at the base of the Niel Formation. According to recent biostratigraphical investigations by J. De Coninck (pers. comm.), these concretions might have the same age as the Wintham 'Big Macs' that occur at the same stratigraphic level.

It is therefore concluded that in the study area, a regionally important concretion level was present as a kind of 'lag' deposit. Originally these concretions could have been formed in the upper part of the Ruisbroek Member during a late sea-level highstand. They probably were positioned at preferential levels of pronounced lithological difference (similar to the septaria concretions which occur in the overlying Boom Clay). The concretions rather reflect a lag deposit, caused by an erosional episode affecting the upper part of the Ruisbroek Member as a consequence of the relative sea-level fall at the end of the Lower Oligocene eustatic cycle. Strong but short-lived erosion events eroded and collected all concretions of significant volume down to local base level as all concretion specimens lack marks of mechanical transport. During a renewed relative sea-level rise, deposition of the transgressive Belsele-Waas Member progressively covered the entire concretion horizon.

The Cruziana ichnofacies present in the concretions refers to bioturbation in a subtidal shallow-marine environment with low or medium energy, including estuaries, bays, lagoons and tidal flats (Frey & Pemberton, 1984; Pemberton *et al.*, 1992), supporting earlier bioecological interpretations of biostratigraphical data (Gaemers, 1984; Steurbaut, 1986). Burrows in a sandy sediment can easily be destroyed. Their good preservation within the concretions points towards reinforcement of their walls, probably by smaller sediment particles and organic material. Afterwards, the burrows have been filled with silt and sand.

5.2. Paragenesis

The 'Big Mac' concretions formed by diagenetic differentiation processes in the sand of the Ruisbroek Member (Niel Formation). Bioturbation, with associated clay infiltration, was an important post-depositional process as evidenced by the omnipresence of burrows in the central portion of the concretions (Fig. 11).

In the paragenesis history of the concretions three stages can be distinguished: (1) the early diagenetic stage corresponds to the formation of pyrite and to the growth of the

main concretion bodies, prior to appreciable compaction; (2) the second stage is represented by pre-compactional concretion growth; (3) the late syn-compactional stage with crack development and subsequent calcite cementation.

During early diagenesis, pyrite is formed by the activity of sulphate-reducing bacteria which utilise seawater sulphate to metabolise organic matter, and in doing so they produce dissolved sulphide. Reactions between Fe released from detrital iron minerals and dissolved sulphide ultimately generates pyrite, although a variety of reaction pathways is possible (Goldhaber & Kaplan, 1974). This process takes place during shallow burial of the sediment and requires an oxygen-poor environment in which anaerobic bacteria can initiate the sulphate reduction process. Anaerobic micro-environments are present in microfossil tests, in shells and at places where organic material is buried (Berner, 1980), leading to pyrite crystallisation in bioturbations, in shells and in microfossil tests.

The diagenetic process responsible for the concretion formation caused redistribution of the material present in the original sediment. Based on the high density of burrows in the concretions, it is likely that nucleation was initiated in a highly but very finely bioturbated zone with easy migration of building components, that later became the observed central indentation zone of 'Big Macs'. The nucleation of calcite cement could be a consequence of difference in solubility between carbonate fossils (possibly aragonite and high-Mg calcite) and calcite cement. The concentration of dissolved calcite in the pore water 'in equilibrium' with unstable fossils may exceed the critical supersaturation necessary to precipitate calcite cement (Bjorkum & Walderhaug, 1990). Precipitation of calcite is associated with instability of chert and quartz (Walker, 1962), occurring when the pH of the depositional environment exceeds 7.8. Sulphate reduction will raise the pH to 8.5, a value at which feldspars, clay minerals and quartz become soluble, which explains the corrosive grain edges and the partial replacement of these detritals by secondary calcite (Dapples, 1979). In all concretions, the calcium concentration in the matrix decreases from the centre to the edge. This is caused by the growing relative contribution of non-carbonate cement phases due to compaction. The cement of the concretions not only consists of pure CaCO_3 : iron/manganese and magnesium also became incorporated. The availability of iron/manganese is the result of the reduction of detrital iron/manganese oxy/hydroxides (both can coat clay particles). The association of iron with organic matter, particularly humic acids (Irwin, 1980), and the breakdown of glauconite also form a possible iron source. Potential sources of magnesium are: dissolution of high-Mg calcite, exchange reactions involving clay minerals, seawater trapped in the sediment, and possible organic matter (magnesium is a constituent of chlorophyll) (Irwin, 1980). Breakdown of detrital sediment minerals can also supply magnesium and iron (Curtis *et al.*, 1986).

In concretion WK, the decrease of magnesium and iron concentrations probably reflects the decrease cement content. In concretions Wha, Whc en WM however, iron increases from the centre to the margins, indicating an increase through time. In diagenetic environments characterised by H_2S production (sulphate reduction SR zone), Fe^{2+} -activities are maintained at very low levels due to rapid precipitation of very insoluble iron sulphides (Curtis *et al.*, 1986). When sulphate reduction diminishes, there will be less hydrogen sulphide present and iron can build up in the interstitial solutions to become incorporated in the carbonate (Irwin, 1980). Assuming that the contribution of detritals to the total iron content is homogeneous, the increase of iron content with concretion growth causes a decreasing luminescence intensity. This feature can be used to differentiate between carbonate cements: the precipitation of micrite thus preceded the microsparite and sparite, while the sparite in septarian cracks formed later in the concretion history. The tendency towards coarser fabrics with progressive crystallisation may be related to lowering of the calcium in the precipitating solutions (Bathurst, 1971), but could also be caused by recrystallisation.

5.3. Stable isotopes

Also the stable isotope composition suggests the concretions grew from center to edge. The range of $\delta^{13}\text{C}$ -values in the 'Big Macs' indicates that sulphate reduction was an important source of bicarbonate (Irwin, 1980). The occurrence of framboidal pyrite within the concretions confirms sulphate-reduction reactions to be an important processes. As assumed by Coleman & Raiswell (1981), an additional source of relatively heavy carbon is needed to adjust the cement values from those typically expected from sulphate reduction ($\delta^{13}\text{C}$ of -24 ‰) to the observed values between -17 and -13 ‰. The concretion cement probably represents a mixture of several carbon sources related to a number of processes such as: sulphate reduction ($\delta^{13}\text{C}$ of -24 ‰), fermentation (incl. methanogenesis) (typically between -24 and +15 ‰ or less) and marine-related processes $\delta^{13}\text{C}$ varying around 0 ‰. Unfortunately, it is impossible to calculate from the available evidence the amount of carbonate contributed by each of these sources.

The most depleted $\delta^{13}\text{C}$ -values in the WK concretion are found in the center, with less depleted values occurring at the margins. The negative values indicate a major contribution from sulphate reduction (SR) with some dilution by marine-derived bicarbonate with an average $\delta^{13}\text{C}$ of 0 ‰. Thus concretion nucleation might have occurred at the interface between sulphate reduction and the sea-bottom. While growing, the contribution from below of less depleted carbon derived from methanogenesis increased, explaining the less depleted values, which were recorded at the margins. This happened while burial compaction started to affect the sediments, also explaining the increase

in SiO_2 , Al_2O_3 and K_2O values in concretion borders. Similar observations were made in the septarian concretions studied by De Craen *et al.* (1999a, 1999b).

In the oxygen isotopes, $\delta^{18}\text{O}$ -values decreasing with growth can be observed in concretion WK. This is a common phenomenon in marine carbonate concretions (Mozley & Burns, 1993). As seawater has a $\delta^{18}\text{O}$ -value of +1.5 ‰ at the start of the Oligocene (Crowley & North, 1991; De Craen *et al.*, 1999a), concretionary calcite $\delta^{18}\text{O}$ -values are apparently not consistent with supporting $\delta^{13}\text{C}$ -data. This discrepancy between evidence for early, shallow burial formation of many carbonate concretions and apparently contradictory $\delta^{18}\text{O}$ -values has already been mentioned in previous studies (Mozley & Burns, 1993). This trend of systematic lowering $\delta^{18}\text{O}$ -values points to a continuously evolving composition of the water out of which the calcite precipitated. Interactions between the sediment and the water, combined with the presence of

more evolved compaction waters originating from adjacent clays, could cause this evolution (Sass *et al.*, 1991). Also, the diffusion degree of seawater decreases with sediment burial. Two strongly deviating values are present: -2.33 ‰ (WK2) and -3.27 ‰ (WHc4). The latter might relate to alteration/recrystallisation due to the interaction with meteoric water in a near-surface setting.

5.4. Growth conditions

Because carbonate cement could have replaced part of the original sediment, it is not possible to retrace the absolute porosity of the sediment at the time of cementation (Raiswell, 1971). However, petrological characteristics of the concretions point towards initial high porosity and permeability, and concretionary growth during shallow burial. The cementation process prevented further compaction. The higher compaction degree of the outer con-

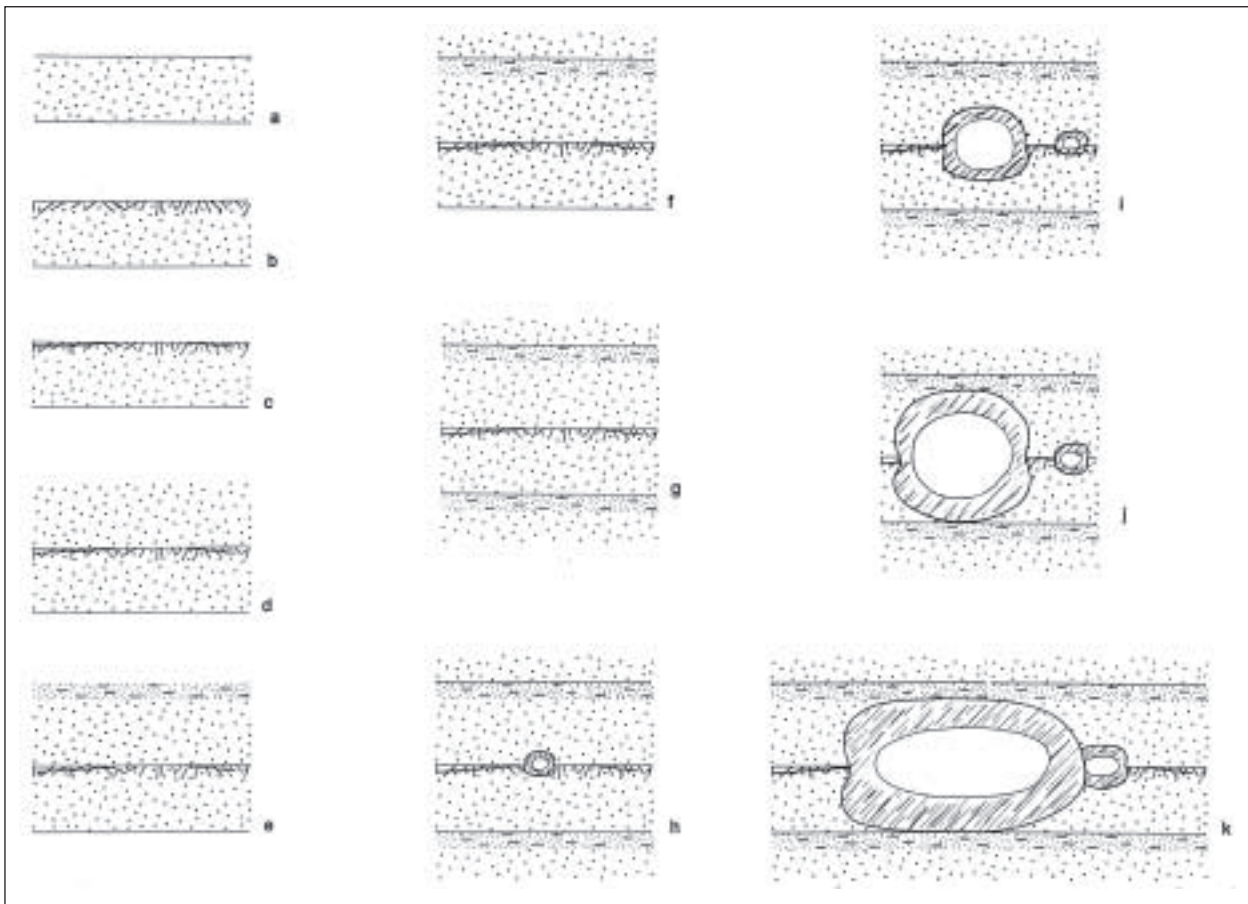


Figure 24. Conceptual model for the enveloping sediment deposition and calcarenite concretion growth. Evolutionary stages through time: a) deposition of water-logged sands; b) vertical bioturbation at sediment-water interface; c) horizontal bioturbation at sediment-water interface; d) resumed deposition of water-logged sands; e) gradual deposition of sandy clays or clayey sands; f) deposition of water-logged sands covering sandy clays or clayey sands; g) complete depositional cycle of bioturbated permeable sands sandwiched between two horizons of less permeable clayey sands or sandy clays; h) initiation of concentric spherical concretion growth at bioturbated horizon; i) isotropic concretion growth with central indentation at bioturbated horizon; j) isotropic concentric concretion growth completed in permeable sands; k) anisotropic lateral concretion growth with consequent overgrowth and coalescence of smaller but spherical concretions.

cretion parts indicates concentric accretion. It is therefore likely that concentric growth was rather rapid, because central parts of concretions were almost completely cemented during this early stage of diagenesis.

Concretion morphology provides some clues to their origin: in general, spherical 'Big Macs' tend to be smaller than the circular but flattened specimens. Obviously the former types are the result of a more isotropic growth process, while the latter must originate from an anisotropic growth process with a dominant horizontal factor, regarding their rather small vertical/horizontal dimension ratio. Field observations indicated the overgrowth and coalescence of large ellipsoidal types on much smaller spherical ones, suggesting that all concretions were originally spherical with initial concentric growth characterised by isotropic migration of building components. Such conditions are fulfilled in highly bioturbated sands that act as active fluid flow conduits or aquifers. The thickness of these sand packages of high permeability forms the limiting factor to isotropic concentric growth: once growing concretions touch a less permeable underlying or overlying clayey sand or sandy clay horizon, their growth is no longer isotropic, but governed by the dominant horizontal ground-water flow (Fig. 24). This mechanism might explain why concretions evolve from spherical to flat during their growth. Hudson (1978) and Gluyas (1984) mention that spherical concretions probably grew in permeable sands, while flat concretions grew in sediments where the vertical permeability is less important than the horizontal permeability (clay and mud). For the more flattened concretions it seems likely that a more permeable central layer existed allowing faster growth in horizontal direction.

5.5. Late evolution

Apparently, post-compactional, but still shallow burial, concretion growth seemed not very important as most cementation occurred earlier. Only the very outer parts of the concretions are characterised by a higher compaction degree and a higher incorporation of elements related to an increasing contribution of detritals.

During subsequent shallow but slowly increasing sediment burial after concretion cementation, septarian cracks developed due to progressing sediment load. Their creation is not completely clear: theories trying to explain this crack pattern mostly deal with concretions in clayey sediments (Lippman, 1955; Raiswell, 1971; Astin, 1986; Wetzel, 1992; De Craen *et al.*, 1999a, 1999b). The cracks were filled with a late-diagenetic sparite cement with high Fe²⁺-content and low luminescence intensity. Also the stable-isotope composition of the crack cement depleted in C indicates that it has formed late in the diagenetic history of the concretion, most likely from meteoric water. However, it is apparent that these cracks were also cemented during shallow burial, indicating the concretions never passed through deep diagenetic zones, since maximal burial was in the order of 150m.

All concretions are concentrated in a kind of lag deposit between the Niel and the Boom Formation. Within our concept of concretionary growth during late stage of sea-level high stand, sedimentation rates were low during cementation. Most probably, the not-cemented enveloping sediment was eroded shortly after concretion formation. Small amounts of iron oxides which precipitated in small veins, might have been formed once the concretions were submitted to oxidising conditions of the shallow subsurface or when eroded and laying on the sea bottom. However, a short subaerial exposure during rapid relative sea-level fall is another possibility.

6. Conclusions

In the area of Wintham and Waasmunster (NW Belgium), an important calcarenite concretion horizon occurs in the top of the Ruisbroek Member, close to the boundary with the overlying Boom Formation (Lower Oligocene). Stratigraphically these 'Big Mac' concretions belong to the Niel Formation, and originated through diagenetic processes that occurred in the shallow marine sandy deposits of the Ruisbroek Member at the end of the Niel Formation period. The sediments in which the concretions formed, were bioturbated by ichnofossils belonging to the *Cruziana* ichnofacies. After bioturbation, early framboidal pyrite was formed by reduction of seawater sulphate throughout the sediment, especially at places where organic material was present (like burrows, microfossil tests, ...).

The 'Big Mac' calcarenite concretions clearly preserve petrographical and geochemical evidence for their early-diagenetic origin. The concretions formed during shallow burial of the sediment during a period characterised by slow sedimentation rates. Their formation relates to diagenetic processes, causing redistribution of the material present in the sediment. Carbon stable-isotope values indicate that the calcite (mainly micrite and minor microsparite and sparite) precipitated from pore waters in which bacterial sulphate reduction was the dominant process. Bacterial organic matter reactions that occurred during early diagenesis provided abundant carbonate precipitation. Also solution of primary carbonate played an important role. Oxygen stable-isotope signature shows that the calcite was formed in a marine environment. Most of the values are slightly more negative than might be expected for precipitation from Oligocene seawater or from shallow-burial pore waters. Of the various possible explanations, interactions between the sediment and the water, combined with the presence of more evolved pore water are probably the more likely. Other influences are the decreasing diffusion degree of sea water with sediment burial and sub-recent alteration/recrystallisation in contact with meteoric water.

Variations in stable isotope and element composition reflect changes in pore-water chemistry during growth. The

contribution of bicarbonate, originating from sulphate-reduction reactions, relatively decreased while bicarbonate derived from methanogenesis gradually increased. Fe²⁺ is distributed between carbonates and sulphides, depending from SO₄²⁻-availability in the deposition waters. When sulphate reduction decreases, less pyrite is formed and Fe²⁺ is incorporated in the carbonate cement. Indeed, the concentration of Fe²⁺ in the cement increases from the concretion centre to the rims, assuming an homogeneous iron contribution from the host sediment. In other concretions, concentrations of Ca, Fe and Mg decrease from centre to margin, caused by a decreasing input in the pore water and the increase in contribution of detrital constituents in the matrix due to compaction.

It is suggested that all concretions were originally spherical and growth was initially concentric with isotropic migration of building components. Due to differential (large horizontal versus small vertical) permeabilities in sandy aquifers, 'Big Mac' concretions grew faster in horizontal direction. Some concretions grew together (overgrowth and coalescence). Most concretions developed a crack pattern similar to that in calcitite concretions ('septaria') described from the overlying Boom Clay Formation, due to slowly increasing sediment loading. Until now, most compaction-related theories trying to explain this crack pattern showed only valid for clayey concretions.

All concretions were concentrated in a lag deposit between the Niel and the Boom Formations, interpreted in terms of submarine erosion subsequent to the late stage of sea-level highstand with subsequent erosion during sea-level lowering. This also suggests low sedimentation rates during cementation. Thus shortly after concretion formation, the not-cemented part of the enveloping sediment was eroded during relative sea-level fall due to strong but short-lived erosion events, eroding and collecting all concretions down to local base level. Small amounts of iron oxides which precipitated in small veins, might have been formed when the concretions were submitted to the oxidising conditions of short subaerial exposure during this rapid sea-level fall or when laying on the sea bottom. During consequent sea-level rise, deposition by the Belsele-Waas Member transgressed over the entire concretion horizon. Possibly the iron oxides also could relate to sub-recent subsurficial alteration.

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