

Early diagenetic silica precipitation, in relation to redox boundaries and bacterial metabolism, in late cretaceous chalk of the Maastrichtian type locality

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Received 11 September 1987; accepted 28 September 1987

Abstract

Silica concretions, known as chert, flint or silex, are common in Late Cretaceous chalks of the Maastrichtian type locality (Maastricht, the Netherlands). They show differences in shape, size and distribution that can be related to depositional structure and texture of the carbonates. It is suggested that the source of the silica was biogenic opal (diatoms), dissolving in the sediment after deposition. Precipitation of dissolved opal started during early diagenesis, at the boundary between oxidizing and reducing sediment. Anaerobic decomposition of organic matter by archaeobacteria lowered the hydrogen ion concentration in pore fluids. The alkaline conditions at the boundary between oxidizing and reducing sediment, caused dissolved biogenic silica to polymerize and precipitate. Later, during further burial, a high concentration of primary silica precipitates enhanced further precipitation. The concentration gradient that was generated in this way, forced dissolved silica to diffuse from the surrounding sediment towards the sites of primary high silica precipitation. After all biogenic opal had been dissolved to nourish the growing 'protonodules', further precipitation resulted in the lowering of dissolved silica in pore fluids below the saturation level of the new polymorph. Then this polymorph started to dissolve and precipitated as a lesser soluble and more ordered polymorph at the most dense parts of the 'protonodule'. This process, resulting in the generation of dense, sharp rimmed nodules, ended when all silica was precipitated as stable quartz.

Silica concretions in chalks can be used to determine palaeoredox zones and the depositional and early diagenetic conditions of the chalks.

Introduction

This paper describes silica concretions in the very pure, marine carbonate sediments of the Maastrichtian stratotype (Limburg, the Netherlands) and it explains how they may have been formed.

Silica concretions, known as chert nodules or flint, are common in pelagic and hemipelagic carbonate mudstones of various ages. 'In relatively young sediments, chert nodules consist of a central crystalline quartz core and a several mm thick rim.

This rim consists of isotropic quartz (cristobalite and cryptocrystalline chalcedony) and is surrounded by a zone in which inter/intra granular pores of the host rock are filled with cristobalite lepispheres' (Wise & Weaver, 1974).

The origin and genesis of the concretions has been frequently discussed by oceanographers, sedimentologists and geochemists. For summaries of previous investigations and results, the reader is referred to Calvert (1974), Bromley et al. (1975), Williams et al. (1985).

The problem of growth of silica concretions is summarized in three questions: (1) what was the source of the silica?; (2) when were the concretions formed?; and (3) which factors controlled shape, size and distribution of the concretions?

In the marine sediments of the area under discussion, no conclusive evidence for the source of the silica was found. However, in recent marine environments, 70–90% of the suspended silica in surface waters can consist of diatoms (phytoplankton), whereas in deeper waters radiolarians (zooplankton) form a larger portion of the suspended silica. Diatomaceous opal can form up to 70% of the sediment (Calvert, 1974). As there also seems to be a relation between the volume percentage of the silica concretions and the amount of pelagic carbonate micrite within the host rock, there is reason to believe that the silica is derived from biogenic opal that is present in siliceous plankton.

Also, no conclusive evidence was found to determine the moment the silica concretions started to grow. However, an early diagenetic origin is suggested by several observations. The carbonates contain abundant early diagenetic precipitates like calcite cement, glauconite, smectite, phosphate and pyrite. Excellently preserved silicified plant remains (seagrasses and driftwood) have been found. Furthermore, volume, shape and distribution of silica concretions are specific for different lithological units and the distribution is related to primary depositional structure and texture of the host rock (Felder, P.J., 1960). Silica concretion layers have been used for lithostratigraphic correlation over several kilometres distance (Felder, W.M., 1975). There is thus reason to believe that silica concretions started to grow, just after deposition, during early diagenesis.

On the assumption, that the silica was derived from diatoms which dissolved within the sediment and that precipitation occurred during early diagenesis, a model is proposed that explains shape and distribution of silica concretions within carbonates of the Maastrichtian stratotype. The value of the model presented, however, does not lie in solving the problems of source and timing of silica precipitation and nodule growth, but in the fact that it enables us to understand the primary depositional

conditions that controlled the sedimentation of chalk.

Geological setting of the Maastrichtian type locality

During the Campanian and the Maastrichtian (Late Cretaceous), large parts of NW-Europe were drowned (Fig. 1). After a long period of only minor tectonic activity, land masses were flat, low lying and deeply weathered. In the sea mainly hemipelagic coccolithic mudstones accumulated, resulting in a deposit known as chalk. It crops out in the countries that border the present North Sea.

An approximately 130 m thick chalk sequence, reflecting a Campanian deepening and a Maastrichtian shallowing is exposed in the Dutch-German-Belgian borderland (Fig. 2). Block-faulted Paleozoic rocks of the Ardennes and Brabant Massifs form the basement. The base of the Cretaceous succession consists of coastal siliciclastic sands of the Aken Formation and shallow marine glauconitic sands and clays of the Vaals Formation, derived from Paleozoic rocks during the Early Campanian. Chalk was deposited on the glauconitic, mainly siliciclastic sediments, reflecting deepening of the basin during the Campanian. The shallowing during the Maastrichtian, is represented by the upper part of the Gulpen Chalk and the Maastricht Chalk. This part of the sequence consists of pure bioclastic carbonates, and it is characterized by a gradually coarsening upwards from calcilutites into micritic calcisiltites and finally into fine- and coarse-grained calcarenites.

The regressive sequence is represented by the Maastrichtian Type Section (Dumont, 1849), that is exposed in the E.N.C.I. quarry (Fig. 3). The 70 m thick succession of carbonates shows a coarsening upwards of sorted calcisiltites and calcarenites with decreasing micrite content. Fossil assemblages change from light-independent echinoids, crinoids, ophiurids etc. at the base, towards light-dependent large foraminifera, anthozoa, algae, seagrasses etc. at the top.

LATE CRETACEOUS PALAEOGEOGRAPHY OF NW-EUROPE

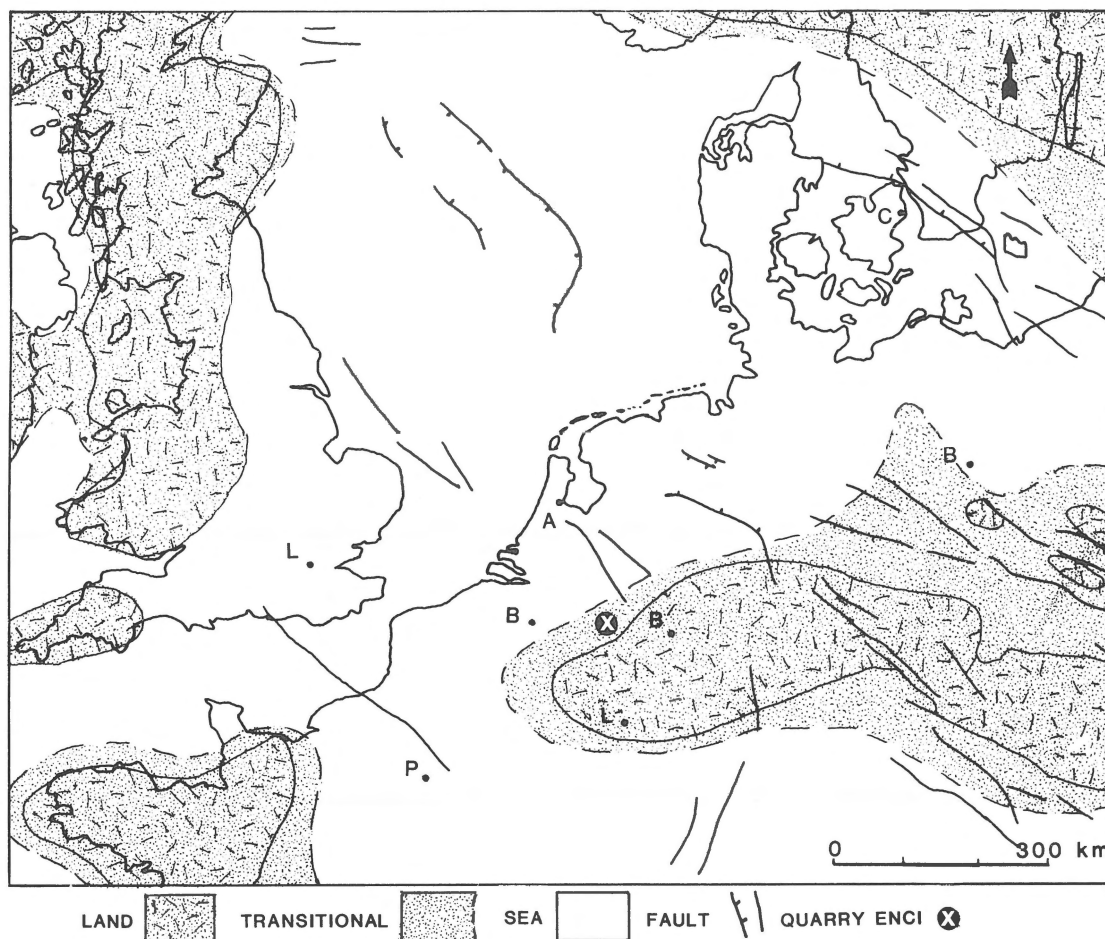


Fig. 1. Palaeogeographical reconstruction of North-western Europe during the Late Cretaceous and Early Tertiary (Cenomanian-Danian, after Ziegler, 1982). The area was characterized by flat, eroded land masses. These more or less stable highs were surrounded by shallow marine transitional zones with mixed carbonate/siliciclastic sedimentation. The open marine realm was characterised by accumulation of planctonic marine algae in faultcontrolled basins of several hundred metres depth.

Shape, volume, and distribution of silica concretions, in the type Maastrichtian chalks

In the coccolithic mudstones at the base of the Maastrichtian sequence (Fig. 2), small scattered silica concretions do occur. Higher in the sequence the calcilutite becomes more and more silty and the small concretions start to be arranged in faint horizontal layers. In the uppermost part of the Gulpen Chalk the concretions are large and occur in well traceable horizontal layers and they account for 22 percent of the sediment volume (Felder, P.J., 1960).

Sediments that belong to the uppermost part of the Gulpen Chalk form the base of the Maastrichtian type section in the E.N.C.I. quarry (Fig. 3). As we go upwards in this sequence silica concretions become less abundant and they are absent in the uppermost part.

Several types of concretions can be distinguished. They correlate with the primary texture and the structure of the limestones. Four main lithofacies types that contain silica concretions can be distinguished (Fig. 3), from the base to the top:

- Lithofacies A with large, irregular silica concre-

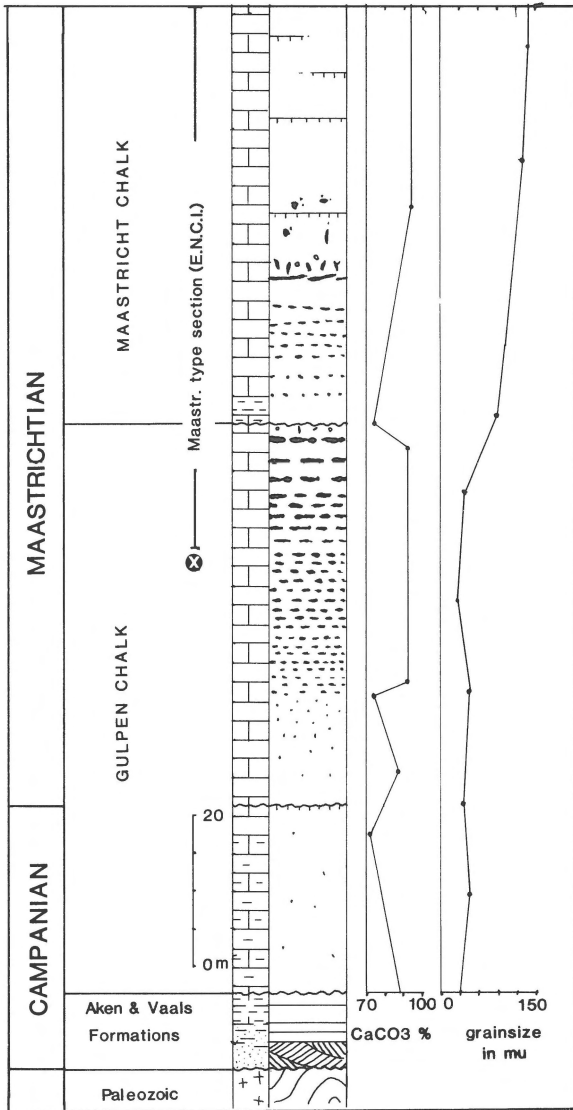


Fig. 2. Composite section of Campanian and Maastrichtian sediments, as they crop out in several quarries south of Maastricht, the Netherlands. Block-faulted Paleozoic basement is covered by siliciclastic sediments of the Vaals and Aken Formations. These are succeeded by coarsening upwards carbonates of the Gulpen and Maastricht Chalk Formations. Four disconformities are indicated by wavy lines. Hardgrounds occur at the Campanian/Maastrichtian boundary and in the top of the Maastricht Chalk. Silica concretions are indicated by black dots. Carbonate percentage and grainsize are derived from P.J. Felder (1975).

tions in horizontal layers. These layers are traceable over several kilometres. The limestone consists of structureless, bioturbated micritic calcisiltite

- Lithofacies B with small, irregular quartz concretions in gently dipping layers of restricted lateral extent. The limestone consists of large scale, low-angle, cross-laminated calcisiltite and fine-grained calcarenite with a low micrite content.
- Lithofacies C with large, platy and tubular silica concretions in gently dipping layers of very restricted lateral extent. The limestones form units with a truncated erosional base with coarse-grained calcarenite. Towards the top we find large scale, low-angle, cross-laminated fine-grained calcarenites with coarse sand sized micritic intraclasts and a low micritic matrix content.
- Lithofacies D with isolated large and irregularly shaped silica concretions. They occur in limestones that contain bioturbated, bored, mineralized and encrusted hardgrounds. The sediment consists of well sorted, large-scale, low-angle, cross-laminated fine-, medium- and coarse-grained calcarenite.

Although it is very difficult to describe and quantify the shape, volume and distribution of the above mentioned silica concretions, we can at least distinguish four basic types. They are characteristic for the successive different lithological units: irregular-shaped concretions in (sub)horizontal layers that contain locally ghost structures of bioturbation (Fig. 8-1); platy concretions in (sub)horizontal layers that show no sign of bioturbation (Fig. 8-2); tubular concretions, the result of quartz precipitation around burrows of *Thalassinoides* (Fig. 8-3); and finally, irregular shaped concretions that are scattered through the sediment and contain locally concentrations of coarse grained skeletal debris (Fig. 8-4).

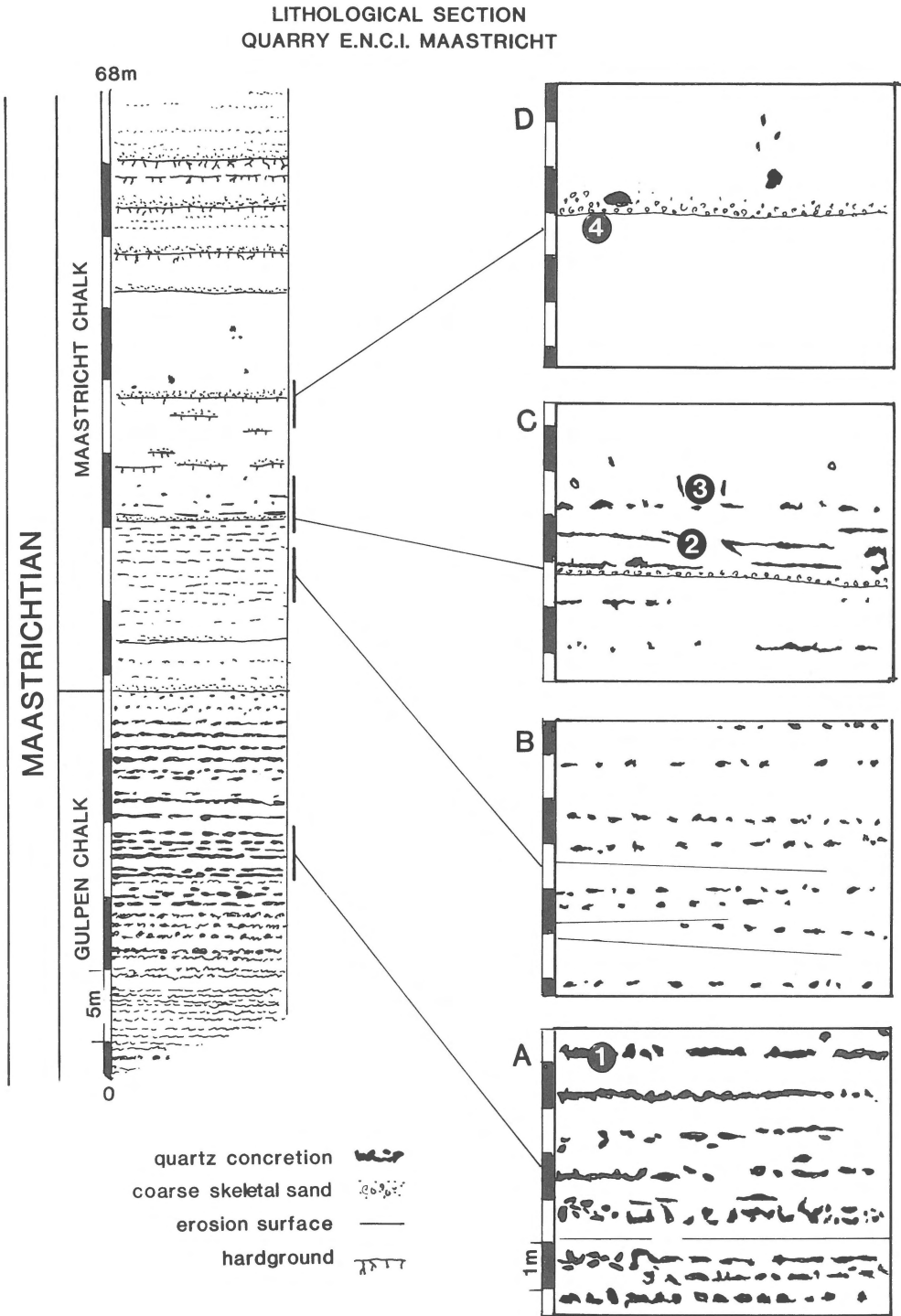


Fig. 3. Lithological section as exposed in the E.N.C.I. quarry (Maastricht). The section is equivalent to the Maastrichtian type section as defined by Dumont in 1849 which is exposed at the entrance of the quarry below the Lichtenberg farm (after W.M. Felder, 1975). Four detailed sections show the different types of silica concretions. Numbers 1-4 refer to the photographs 1-4 of fig. 8, that show four characteristic concretion types.

The relation between silica dissolution/precipitation and the hydrogen ion concentration in water

The concretions are without doubt the result of precipitation of silica from pore fluids within the sediment. Dissolution and precipitation of silica has been studied intensively by geochemists. The rate and magnitude of silica dissolution/precipitation in demineralized water depends on the hydrogen ion concentration, the crystallinity, the surface area exposed to the fluid, the temperature and the pressure.

At relatively high hydrogen ion concentrations ($\text{pH} < 9$), solid silica dissolves and silica molecules combine with two water molecules to form the monomeric acid H_4SiO_4 (Okamoto et al., 1957) (Fig. 4a). Reaction rate and saturation concentration are dependent on the magnitude of the above mentioned factors.

At relatively low hydrogen ion concentrations ($\text{pH} > 9$), the monomeric acid dissociates, while hydrogen ions are removed and negative complexes like H_3SiO_4^- and $\text{Si}_4\text{O}_6(\text{OH})_6^{2-}$ are formed (Baes & Mesmer, 1976). Because the solid silica has a strong negatively charged surface (Point of Zero Charge at $\text{pH} = 2$, Parks, 1967), negative silica complexes will not precipitate on the solid silica surface. Instead, the decrease in the concentration of monomeric acid complexes, while hydrogen ions are removed and negative complexes are formed, results in further dissolution of the solid silica. This leads, under alkaline conditions, to a fluid that contains the monomeric acid at saturation concentration and an additional concentration of negatively charged complexes (Fig. 4b).

The negatively charged complexes will polymerize in time and form oligomers and polymers (Iler, 1973, 1979). Large polymers, with a large surface and a low surface/volume ratio, will grow at the expense of smaller oligomers and polymers, with a small surface and a high surface/volume ratio. If the large polymers have a lower solubility than the initial, metastable solid (e.g. diatoms), then the initial solid continuously dissolves to contribute to the growth and precipitation of the large polymers (Williams et al., 1985).

The crystallinity or ordering of the initial solid is

of special importance for the magnitude of the saturation concentration of silica (Opal-A, 60–130 ppm; Opal-CT, 20–30 ppm; Quartz, 6–10 ppm; concentrations at 25° C and $\text{pH} 7$; Iler, 1979).

A large surface area, which leads to rapid dissolution, is characteristic of fine grained silica and especially of ornamented and porous diatoms (e.g. 258 m^2/g specific surface area for *Thalassiosira decipiens*, Kamatani & Riley, 1979).

Increase in temperature and pressure leads to an acceleration of reaction rates and a rise in saturation concentrations. However, within the early diagenetic realm, variations of these parameters are believed to be negligible.

The polymerization is retarded if salts are present (Iler, 1979) and the presence of multivalent metal ions, metal hydroxides and silicate minerals leads to complexation (Fournier & Marshall, 1983), absorption (Siever & Woodford, 1973) and neof ormation (Drever, 1982). As the discussed silica concretions occur in very pure carbonates, such complexities are neglected here. However, in less pure carbonates, it was observed that silica concretions are small and that they are often characterized by weakly silicified parts. In that case the silica has co-precipitated with Al-oxides and occurs also in glauconite and smectite.

Hydrogen ion concentration is believed to be the most important factor controlling dissolution/precipitation reactions in the sediment under consideration, a mixture of carbonate, silica, organic matter and water. Values of pH recorded in recent marine sediments, however, hardly exceed a value of 8 and significant polymerization and precipitation has been observed to occur at pH values larger than 9. Therefore, the presence of a catalyzing agent should be considered. Microbes that decompose organic matter are abundant in marine sediments and are the most suitable candidates. They create microenvironments within the pore fluids and locally control the concentration of hydrogen ions available to the silica complexes.

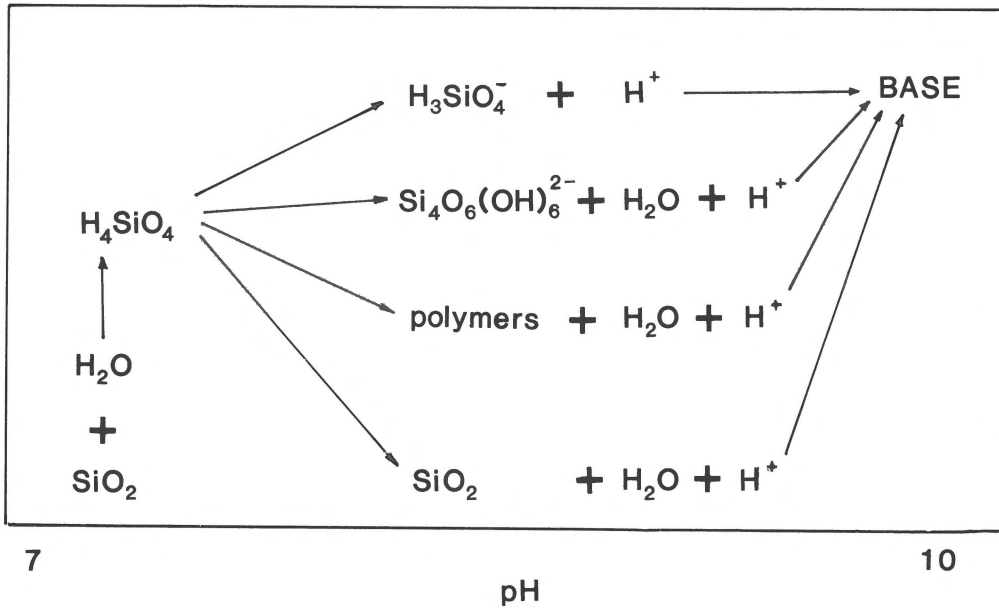


Fig. 4a. Dissolution of a silica polymorph and formation of the monomeric acid. With increasing pH, in the presence of a base, the monomeric acid dissociates while hydrogen ions are removed. Negative complexes polymerize and precipitate as a more stable silica polymorph. Reactions go on as long as the less stable polymorph is present and hydrogen ions are removed by the base.

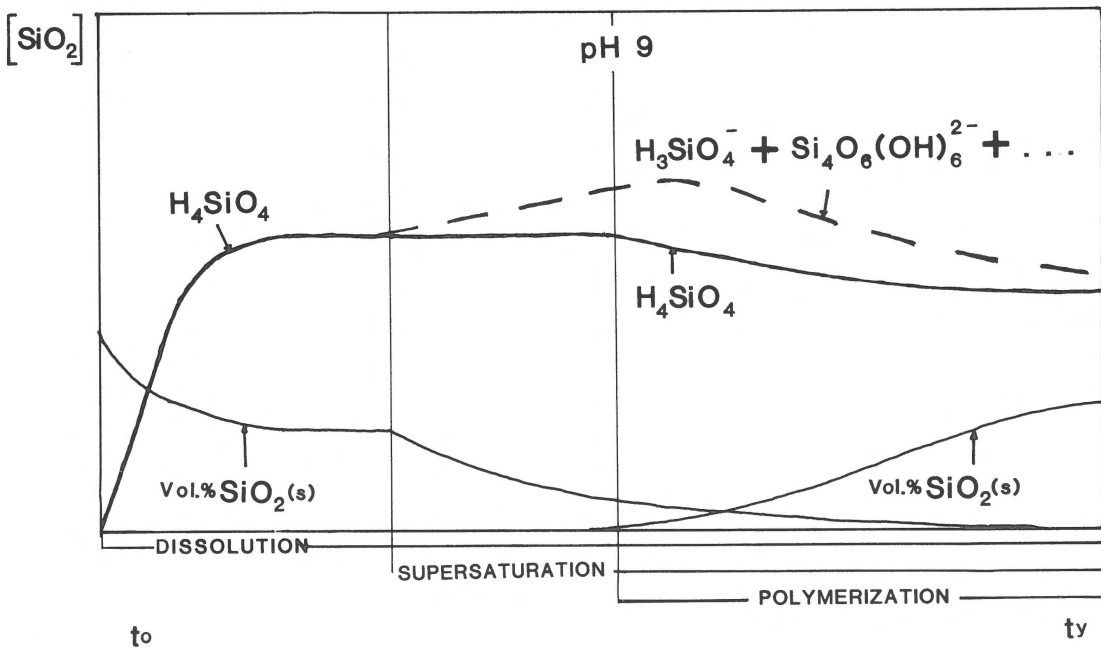


Fig. 4b. Variation in time (t_y - t_0) of solid silica volume and silica concentration as a result of dissolution, supersaturation and polymerization in a basic solution ($\text{pH} = 9$). Silica dissolves until the saturation concentration for the monomeric acid is reached. In the basic solution, negative complexes are formed due to the removal of hydrogen ions. Generation of negative complexes, without changing the saturation concentration of the monomeric acid, leads to supersaturation. In time the negative complexes polymerize into a more stable silica polymorph. The monomeric acid concentration is lowered towards the saturation concentration that is in accordance with the new solid.

Bacterial decomposition of organic matter controlling hydrogen ion distribution and silica precipitation

While accumulating, marine sediment passes through diagenetic zones, that are characterized by specific redox reactions. These reactions are, to a large extent, influenced by bacterial decomposition of organic matter. Below the sediment/water interface we can distinguish an upper zone of oxidation and a lower zone of reduction. In the oxygenated zone, oxygen is introduced by means of physical stirring, bioturbation and diffusion. The oxygen is removed from the pore fluid by bacteria for the decomposition of organic matter and oxides (i.e. SO_4^{--} , NO_3^- , CO_2) and hydrogen ions are produced (Fig. 5). Bacteria that are known to metabolize decaying organic matter and give off hydrogen as a waste product are the *Clostridia* (Woese, 1981).

During deposition and burial, the available oxygen is consumed, and the sediment passes from the oxidation zone into the zone of reduction. There, free oxygen is absent and bacteria remove oxygen from oxides to decompose organic matter. Hydrogen is removed from the pore fluid to form hydrides (i.e. H_2S , NH_3 , CH_4). Bacteria that are known to metabolize organic matter in the absence of oxygen, using CO_2 and hydrogen to produce CH_4 , are the *Methanogens* (Woese, 1981).

The hydrides that are produced in the reducing zone are gases. They can diffuse upwards and are oxidized in the zone of oxidation to form oxides and hydrogen ions again.

The overall result of bacterial activity in the sediment is a high concentration of hydrogen ions in the oxidizing zone and a low concentration in the reducing zone.

As demonstrated before, silica dissolution and precipitation are dependent on hydrogen ion concentration in the pore fluid. At relatively high hydrogen ion concentrations in the oxidizing zone, biogenic opal will dissolve until the saturation concentration for monomeric silica is reached. At relatively low hydrogen ion concentrations in the underlying reducing zone, archaeobacteria will act as a base and cause removal of hydrogen ions from

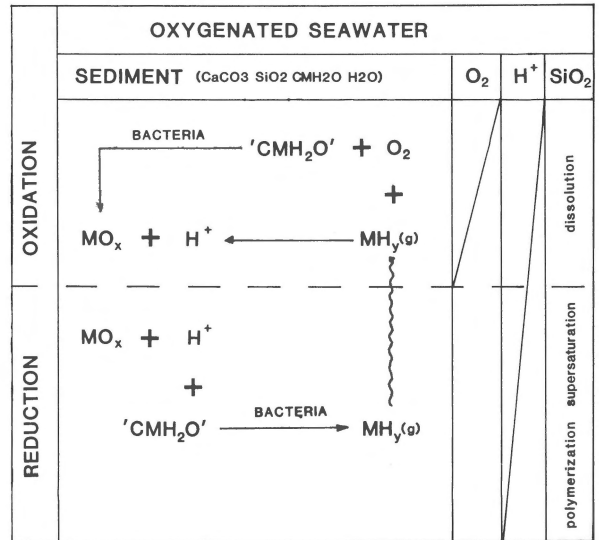


Fig. 5. Chemical reactions in the sediment controlled by bacterial decomposition of organic matter (' CMH_2O '). Consumption of oxygen in the zone of oxidation and production of hydrogen ions and oxides (MO_x i.e. SO_4^{--} , NO_3^- and CO_2). Consumption of oxides and hydrogen ions in the zone of reduction and production of hydrides (MH_y i.e. H_2S , NH_3 and CH_4). These are gases that diffuse upwards and are oxidized to oxides and hydrogen ions. Organic matter decomposition results in high concentrations of hydrogen ions in the zone of oxidation and low concentrations in the zone of reduction. This leads to silica dissolution in the zone of oxidation and silica supersaturation and subsequent polymerization in the zone of reduction.

monomeric silica complexes. The negative silica complexes so formed will raise the concentration of total silica in solution (supersaturation). The negative silica complexes will start to polymerize and precipitate from the supersaturated fluid. During polymerization, hydrogen ions are released and the subsequent rise of hydrogen ion concentration inhibits further dissolution and polymerization. However, in the presence of bacteria that cause removal of hydrogen ions, dissolution and supersaturation are maintained and polymers will continue to precipitate from solution.

In recent sediments, the concentration of dissolved silica in interstitial pore water, just below the sediment/water interface, is 7–20 ppm (Hurd, 1973). The concentration increases with depth, in the first 1–2 metres, towards a concentration of 35–60 ppm and subsequently decreases towards a constant value of 25 ppm (Bischoff & Sayles, 1972).

This is in accordance with the expected dissolution of biogenic opal towards a saturation concentration of 60–130 ppm and subsequent polymerization of the silica and precipitation as cristobalite with a saturation level of 20–30 ppm.

The fact, that measured concentrations of silica in pore fluids are lower than saturation concentrations measured under laboratory conditions, must be attributed to microenvironmental influences. For instance, in the oxidizing zone that is characterized by mainly dissolution, we may expect that locally supersaturation and polymerization will also occur. The overall tendency for either dissolution or supersaturation and polymerization will, however, be restricted to different zones within the sediment.

Thus, bacteria are able to control the hydrogen ion concentrations of the pore fluids, and are therefore also able to control the silica dissolution and precipitation within the sediment.

Preferential sites of early diagenetic silica precipitation and subsequent early to late diagenetic concretion growth

Silica, dissolved from biogenic opal, polymerizes and precipitates, in pore spaces at sites where the hydrogen ion concentration is lowest. These sites are created by hydrogen ion removing bacteria that occur at the boundary between oxidizing and reducing sediment. The bacteria cause supersaturation of the pore fluid and subsequent precipitation of polymers from solution. When the bacterial activity decreases and stops, the hydrogen ion concentration will rise, as hydrogen ions are released during polymerization. Supersaturation and precipitation of polymers from solution will then no longer occur. Instead, monomeric silica, dissolved from biogenic opal, will precipitate directly on the already precipitated polymers.

Thus we can expect the highest rate of polymerization and precipitation of silica at the boundary between oxidizing and reducing sediment. The longer this boundary is present within a certain site of the sediment, the larger is the concentration of precipitated polymers at this place. In this way, the

concentration of precipitated polymers, within a sequence, is dependent on the migration rate of the boundary and thus indirectly dependent on the sedimentation rate.

Newly formed silica polymorphs are always less soluble than the deposited biogenic opal. These polymorphs will not dissolve unless all biogenic opal has been dissolved.

The surface of the precipitated silica polymorphs acts as a precipitation site for monomeric silica. The more silica is precipitated, the larger the surface area becomes and the more silica is precipitated. Silica precipitation is autocatalytic (Krauskopf, 1959).

At the sites of highest primary silica precipitation (zones of supersaturation) the concentration of silica in solution is lowered fastest, due to the ever increasing surface of precipitation. As a result, a constant diffusion of silica from the rest of the sediment towards the sites of primary highest silica precipitation occurs.

After all biogenic opal has been dissolved from the sediment, to diffuse into the sites of primary high precipitation and to precipitate as the new polymorph, the concentration of silica in solution is lowered until the saturation level for the new polymorph is reached. At this moment, the new polymorph will start to dissolve at the sites of lowest concentration, to precipitate as another, lesser soluble polymorph, at the sites of highest concentration and largest precipitation surface.

In this way, there is continuous dissolution and precipitation of polymorphs (Fig. 6). The diffusely distributed silica in the sediment dissolves, and migrates into the sites of highest silica precipitate concentration. The process continues until all silica has been converted into the stable macrocrystalline quartz polymorph that is found in sharply bounded, dense concretions.

Thus, silica concretions in the Late Cretaceous carbonates of the Maastrichtian type locality, are situated at sites that have been boundaries between oxidizing and reducing sediment during deposition. These boundaries were fixed in place for longer periods and were characterized by continuous bacterial activity and precipitation of large quantities of polymers.

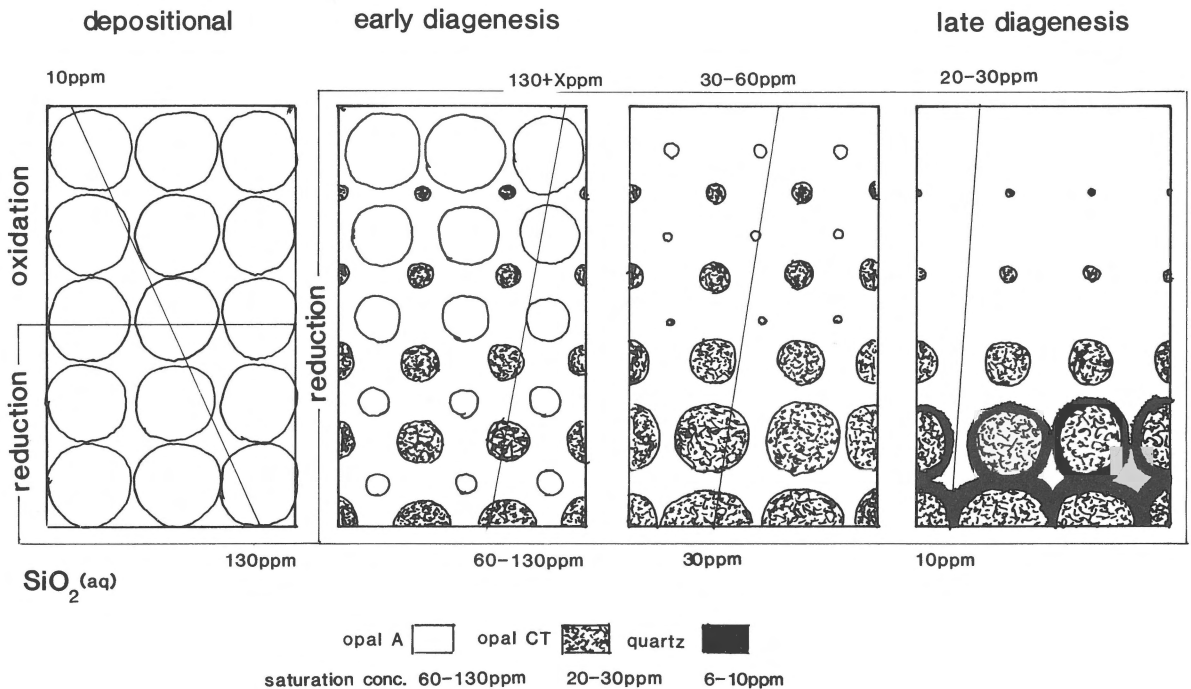


Fig. 6. Dissolution and precipitation of silica polymorphs and migration into the sites of highest primary silica precipitation. Just after deposition (left), biogenic opal (opal A) dissolves until the saturation concentration for monomeric acid is reached (130 ppm). Under reducing and alkaline conditions (early diagenesis) supersaturation (130 + X ppm), and subsequent polymerization and precipitation of cristobalite (opal CT) occurs (middle left). During diagenesis large cristobalite lepispheres grow at the expense of biogenic opal and small cristobalite lepispheres (middle right). While silica concentrations are lowered below 20 ppm, due to precipitation, quartz appears at the expense of dissolving cristobalite (late diagenesis, right).

In the surrounding sediment, biogenic opal and polymers that precipitated in low concentrations at moving boundaries, will dissolve during early diagenesis and the silica will diffuse towards the sites of primary highest polymer precipitation.

Discussion

The model allows the use of silica concretions for the determination of depositional conditions of chalk sedimentation and does, on the other hand, not exclude late diagenetic genesis of concretions. However, it will be difficult to find direct proof for the proposed succession of processes and their timing. During diagenesis information is altered and lost due to dissolution/precipitation reactions. Thus, at the moment the justification of the model lies in its application.

The four types of concretions that can be distinguished, can easily be explained with the mechanism of silica precipitation at the boundary between oxidizing and reducing sediment (Fig. 7).

Irregularly shaped concretions, arranged in (sub)horizontal layers and containing locally ghost structures of bioturbation were generated at the boundary between the upper zone of continuously bioturbated sediment and the underlying, no longer turbated sediment.

Platy concretions, arranged in (sub)horizontal layers and unaffected by bioturbation, were generated at the boundary between eroded, reduced sediment and the directly overlying, oxygen rich seawater.

Tubular concretions around burrows of *Thalassinoides*, were generated around the wall of open burrows, penetrating into reducing sediment, while oxygen rich seawater was in contact with the

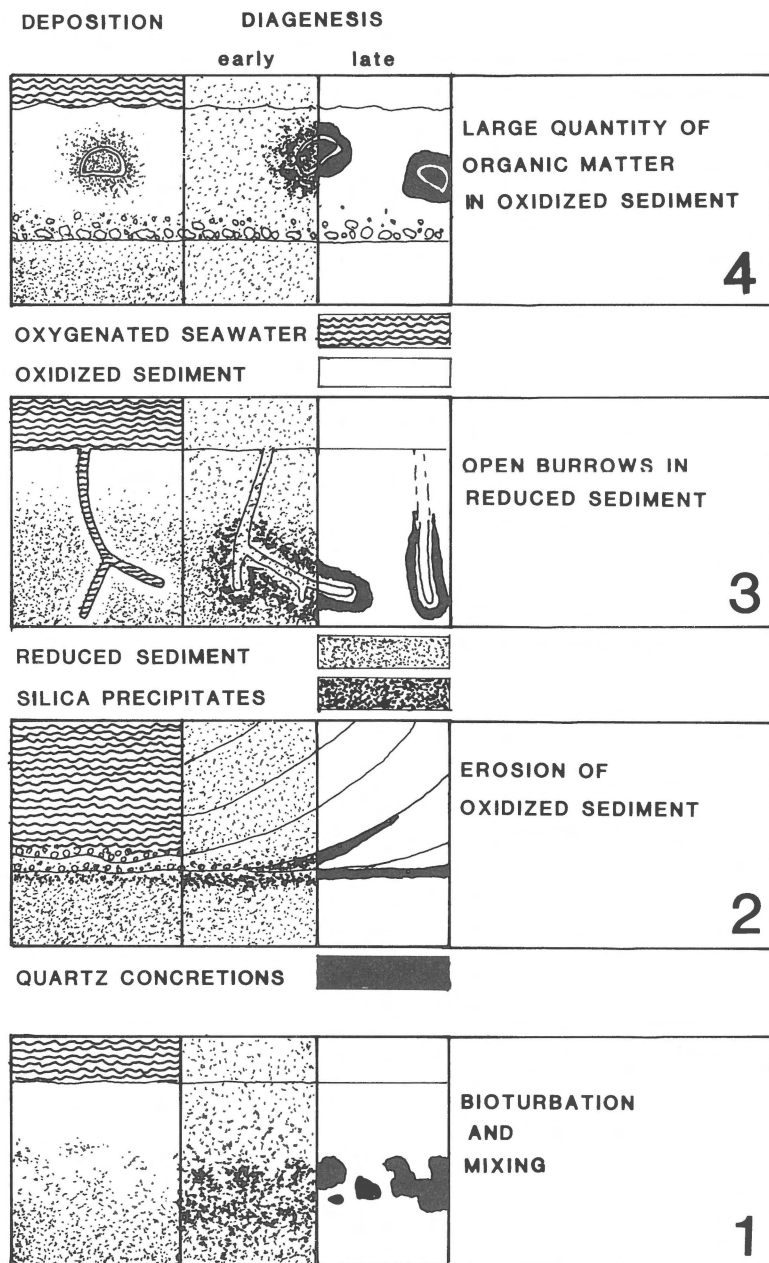


Fig. 7. Four types of boundaries between oxidizing and reducing sediment. Silica polymers precipitate at these boundaries during early diagenesis. During late diagenesis, all opal dissolves and silica diffuses into the sites of primary highest polymer precipitation. The resulting four nodule types (1-4) correspond with the four nodule types depicted in the photographs of figure 8.

reducing sediment of the burrow wall.

Finally, isolated, irregularly shaped concretions, that locally contain concentrations of coarse skeletal debris, were generated within the zone of oxidizing sediment, where reducing conditions were

created by the total consumption of oxygen through bacterial decomposition of relative large quantities of organic matter.

Although the sites of concretion growth were fixed during early diagenesis, it is not necessary

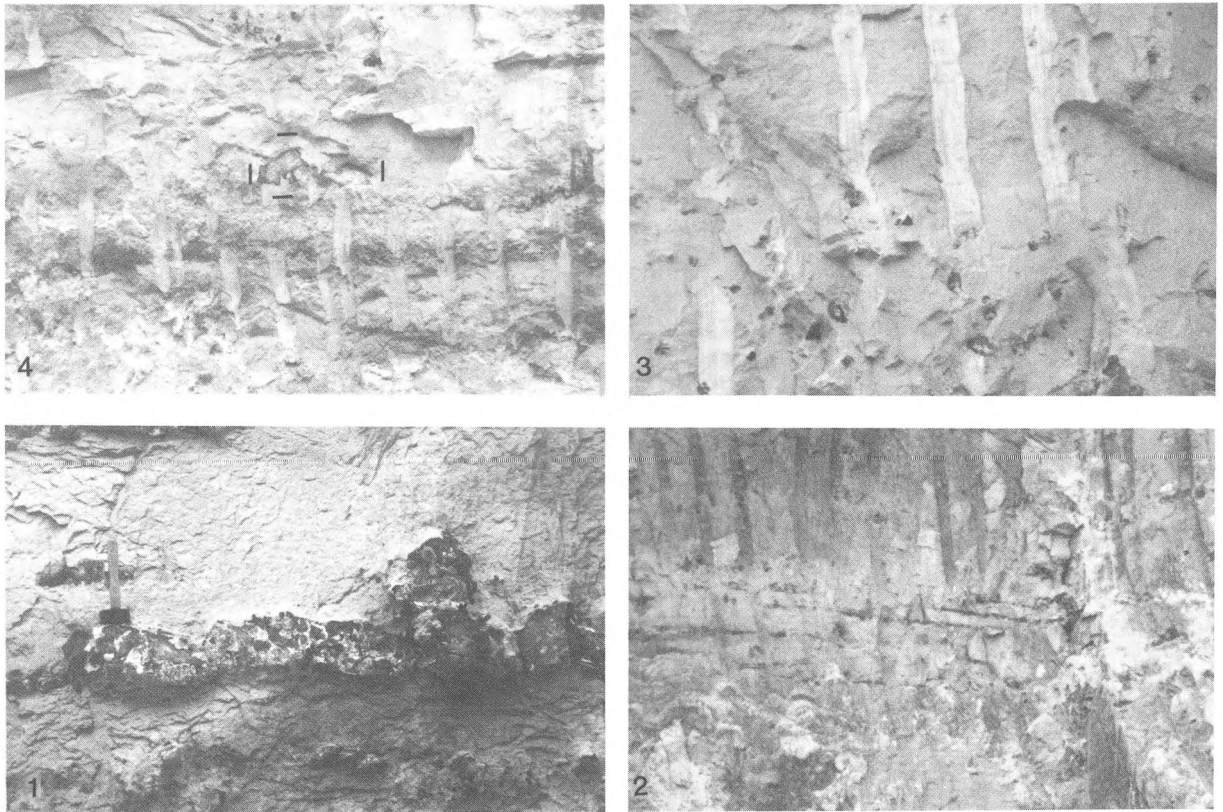


Fig. 8. Photo 1. – Large, irregular silica concretions with ghost structures of bioturbation. Concretions are embedded within light-grey, micritic calcisiltites. They are arranged in the upper part of the Gulpen Chalk, in horizontal layers that are traceable over several kilometres. (Width of photo is approx. 2 m).

Photo 2. – Platy silica concretions without traces of bioturbation. Concretions occur in yellowish, sorted, calcisiltite and fine grained calcarenite with micritic intraclasts and low micrite content. The concretions are underlain by a (sub)horizontal erosion plane, covered by coarse skeletal sand. Large scale, low-angle cross-lamination was observed within the limestones. (Width of photo approx. 7 m).

Photo 3. – Tubular silica concretions, around burrows of *Thallassinoides*. Concretions occur in yellowish, sorted, calcisiltite and fine grained calcarenite with low micrite content. (Width of photo is approx. 3 m).

Photo 4. – Large, isolated, irregular silica concretion. The concretion occurs above a hardground (Laumont horizon, Felder 1975). The carbonate consists of sorted, calcisiltite and fine grained calcarenite, containing coarse skeletal debris in lenses and pockets. (Width of photo is approx. 5 m).

that the total volume of precipitated silica originated from the directly adjacent sediment. Late diagenetic influx of compactional pore fluids from underlying sediments and even extrabasinal water influx could have introduced silica and contributed to concretion growth, as long as concentrations were not below the saturation concentration for the actually present polymorph.

According to the model presented, it seems reasonable to use silica concretions for identification of primary depositional environments of chalk sed-

imentation. On the basis of silica concretions it is possible to distinguish different lithological units within the chalk, which seldom contains distinctive sedimentary structures.

Conclusion

If we succeed in quantifying shape, volume and distribution of the silica concretions, and if it is possible to quantify the model, we should be able

to determine several parameters that govern primary depositional circumstances, such as the relative quantities of opal, water, organic matter and carbonate within the sediment. We also should be able to determine the migration rate of the boundary between oxidizing and reducing sediment, sedimentation rates and the temporal relationship between processes like sedimentation, bioturbation and erosion.

Acknowledgments

I thank Dr. P.L. de Boer, Prof. R.D. Schuiling and Dr. W.J.E. van de Graaff for discussion and critical reading of this manuscript, W.M. Felder and P.J. Felder for cooperation in the field, the E.N.C.I. Company for its hospitality and the Netherlands Organisation for the Advancements of Pure Research (ZWO) for financial support of project 751-356-015.

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