Flint and flint generation in the Cretaceous Chalk and Danian Limestone

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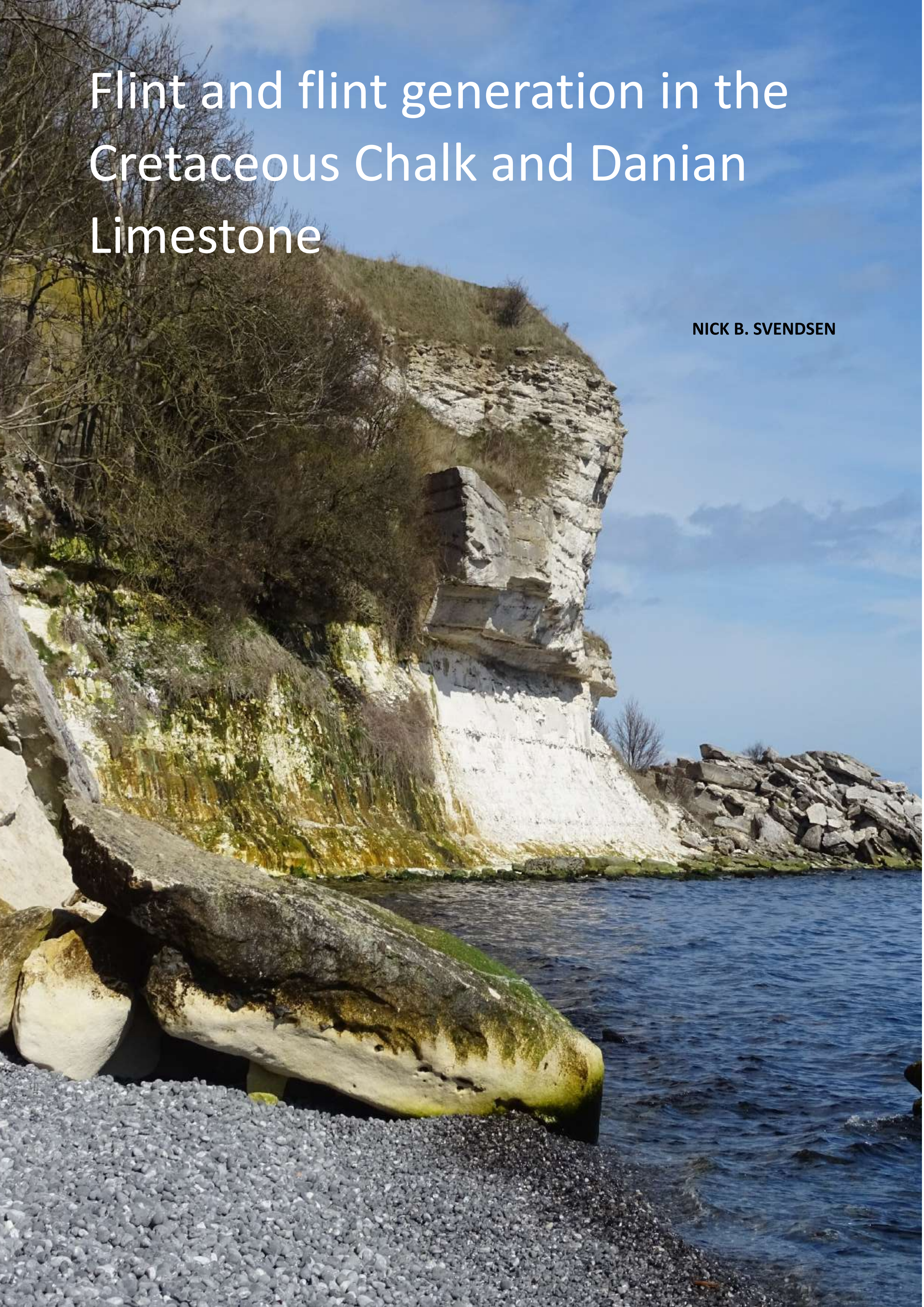


Abstract

This paper reviews the current state of knowledge for flint generation as well as demonstrate that there are several possible sources for the silica in the flint beds such as diffusion from seawater, detrital clay and clay beds (volcanic ash beds), and finally biological derived silica. It is illustrated by examples from Stevns Cliff and from Danish North Sea core material. The numerous and generally thick Danian flint beds is tied to the volcanic eruptions associated with the opening of the North Atlantic Ocean some 65 to 62 million years ago which increased the influx of silica via volcanic ash into the sea. The cyclic flint beds are explained as the result of episodic upwelling in the basin related to climatic changes (Milanković-cycles), which would explain the regular occurrence of flint layers and sequence stratigraphic subdivision of the chalk both Danian and Maastrichtian. A sequence of events is proposed for the formation of flint. This note is a summary of my book on the same subject published in Danish (Svendsen 2021).

Introduction

If you are walking in the Danish nature, especially at the beach and in the gravel pits, you are walking mostly on flintstones.
Archaeologists and historians are very interested in flint, especially those who work with antiquity, where humans used flint for their tools and weapons. There are therefore several books with a description of flint, flint tools and the manufacture of flint tools, but there is a lack of a broader geological foundation for the understanding of flint formation.

Where does the flint come from and how is it formed?

The author has collected information on flint and flint formation from a predominantly geological perspective with detours into archeology, which have been published in Svendsen (2021), and which constitutes the basis for this note.
The study is based on observations at Stevns Cliff Denmark at the famous Højerup profile near the centre of the cliff. Furthermore, Danian and Maastrichtian core material from the Danish North Sea has been studied.

Chapter 1 - Maastrichtian and Danian limestones

In Denmark, flint is present in limestone formations from the Maastrichtian and Danian Stages. These layers are present in the Danish subsoil as well as at the surface in some parts of Denmark. Stevns Cliff in eastern Denmark has been selected for the study of flint (Fig 1) as it exhibits a good outcrop of the two formations.

The thickness of the two limestone layers is between 200 and 2100 m. They are most thick in the Danish Basin (Kattegat and Sjælland) and thin on the Ringkøbing-Fyn High (Lolland, Falster og South Jutland) (Fig 2).

Onshore the limestone is outcropping and, in Kattegat, it is buried to a depth of approx. 300 m, while in the North Sea it occurs at depths of 2,000 to 3,000 m.

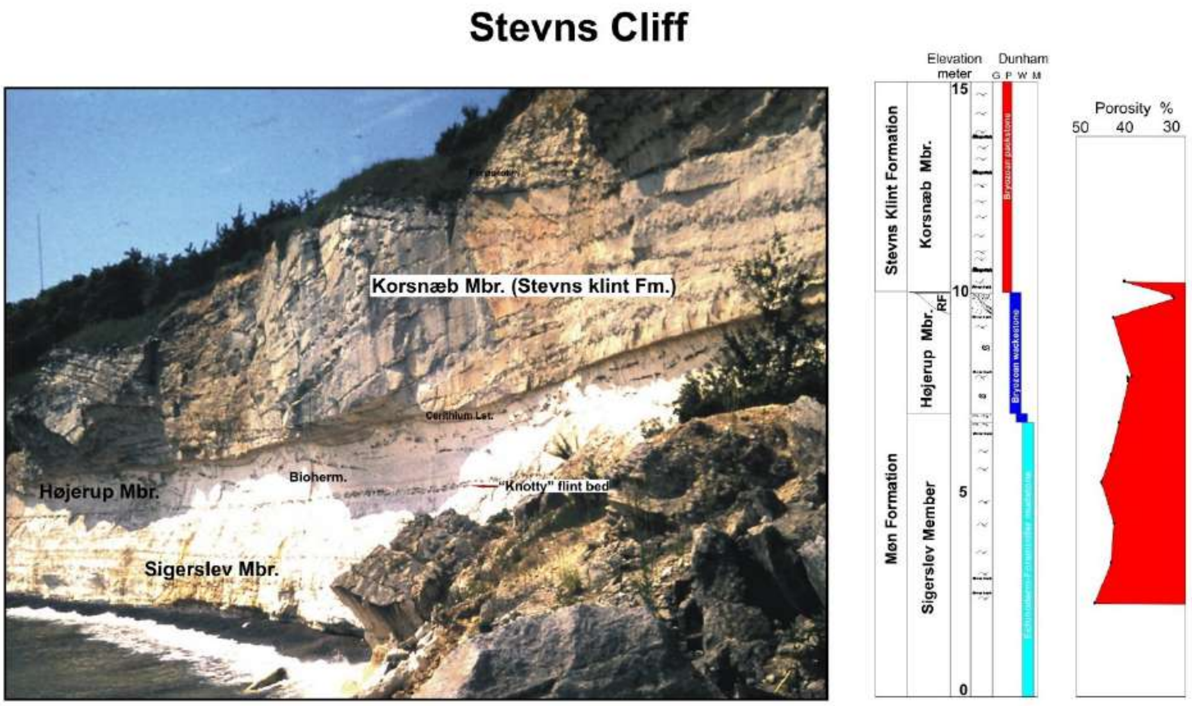
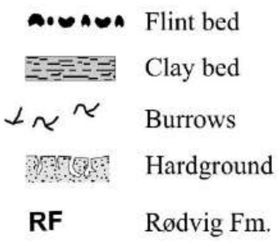


Fig. 1 - Stevns Cliff. Standard section at the cliff near Højerup with the new stratigraphic nomenclature. The sedimentological profile is based on Svendsen (1975) and later work.



During the Maastrichtian and Danian, large parts of Europe were covered by a sea that connected the North Sea area with the central part of Russia all the way to the Black Sea and the Arabian Gulf (Fig. 3). The climate was hot and dry.

Limestone sedimentation is widespread in the Arabian Gulf today, reminiscent of the Cretaceous in northern Europe.
The low relief of the landscape and the dry climate led to the rivers carrying only little and generally only fine material to the sea. Sea level was high, so large parts of the continents were flooded by the sea. In the sea, lime mud was deposited and in the nearby coastal areas' sandstone or fossil-rich limestone (Fig 4 and 5).
The water depth in the sea around Denmark, during the Maastrichtian and Danian times is estimated to vary between 200 and 400 m (Surlyk and Lykke-Andersen 2007). Modern limestone deposits with bryozoans are known offshore northern Australia, at water depths between 100 and 250 m.

The limestone consists predominantly of coccolith mud with varying amount of other fossil debris. The finer fraction of the limestone is predominantly microscopic grains that are so small that it requires an electron microscope to study. They are predominantly between 1 and 3 microns in size (1 micron is 1/1000 mm). Occasionally they are arranged in "wheels" (Fig. 6).

These "wheels" are skeletal remains of coccoliths (single celled planktonic algae). The coccoliths have been arranged in spheres called cocospheres, where the algae cell was inside the rim of the cocospheres. The climatic conditions, during the Cretaceous, led to a significant flourishing of the cocosphere algae; the sea was presumably at times white from these algae.

The lime mud was originally mixed with organic material derived from the remains of the soft parts (organic tissues) of the coccospheres. As mentioned, the rivers, from the surrounding land areas, did not carry much clay and sand into the sea, therefore the limestone is very clean.

The Maastrichtian limestone generally contains less than 3% clay, the Danian limestone contain much more clay, due to presence of numerous marl beds.

The Cretaceous limestone was deposited as a type of sediment found today only in the deep sea, ie. at water depths from 1,000 to 4,500 m and at shallow water in the Arabian Gulf.

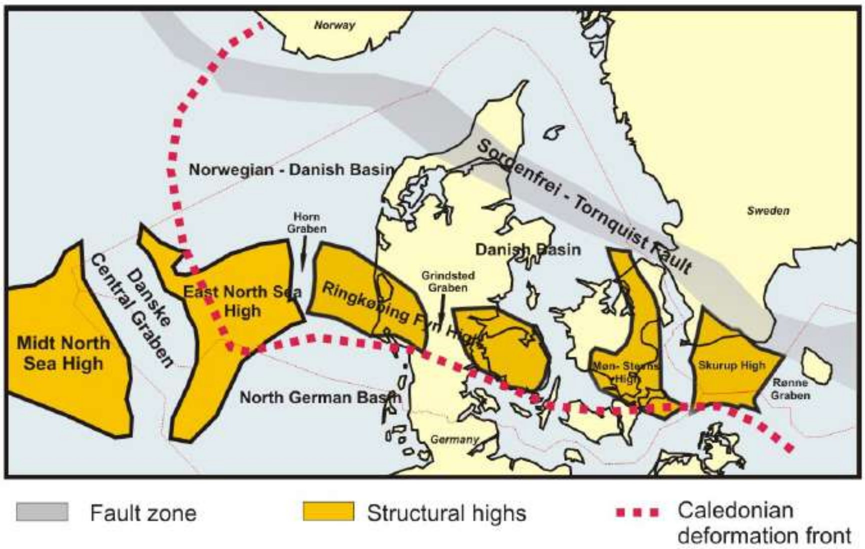


Fig. 2 - Struktural elements in the subsoil of Denmark.

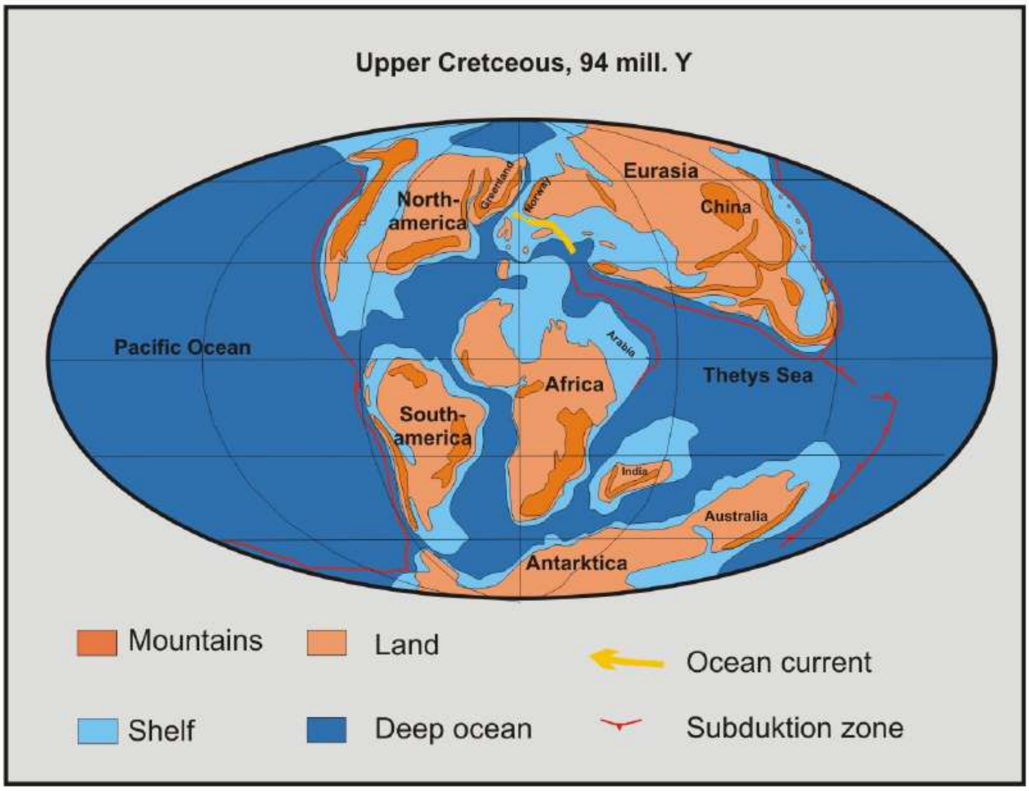


Fig. 3 - U. Cretaceous, platetektonik reconstruktion. Most of Europe was covered by the sea with a water depth less than 400 m. The sea towards the east, between Eurasia, Africa and Australia, is called the Thetys Sea (deep sea), it is the forrunner of the Indian Ocean. The ocean current from the Thetys Sea could be an analog to the present day Golfstream.

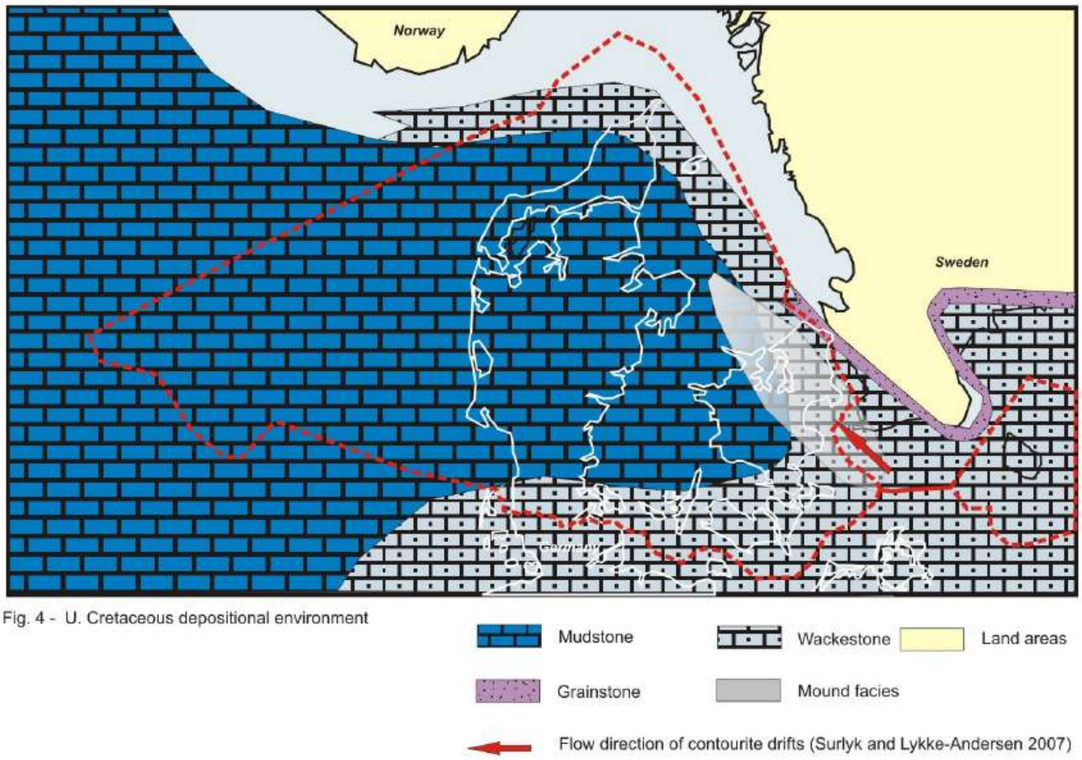


Fig. 4 - U. Cretaceous depositional environment

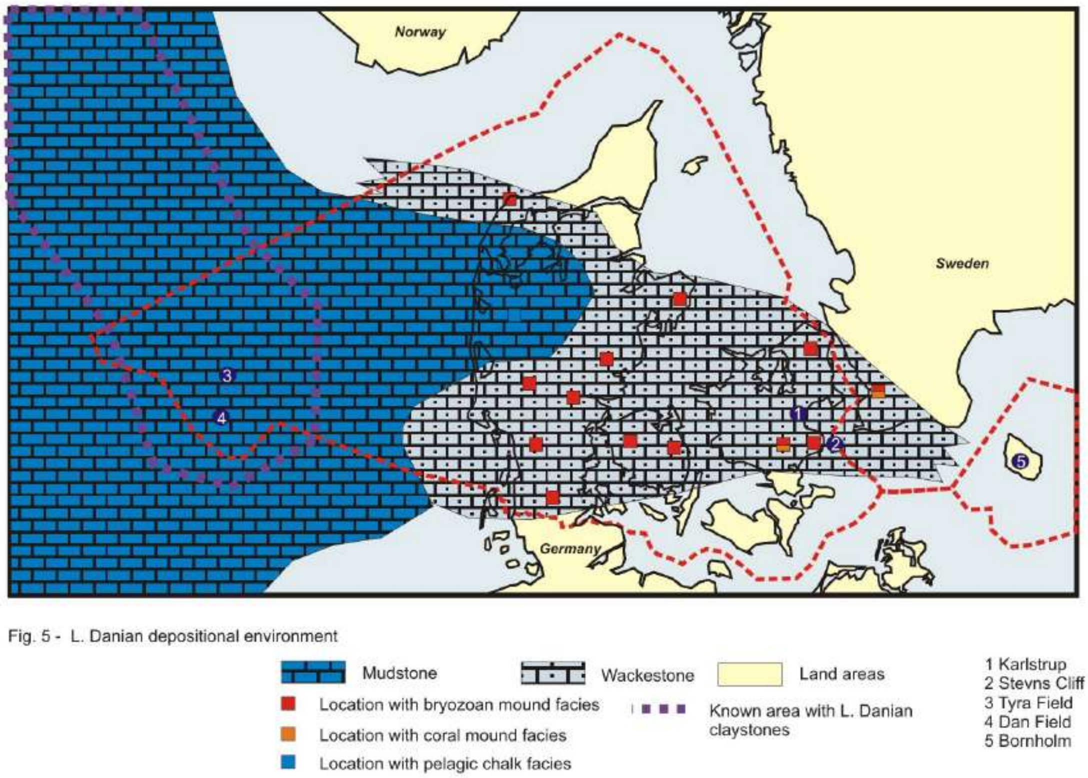


Fig. 5 - L. Danian depositional environment

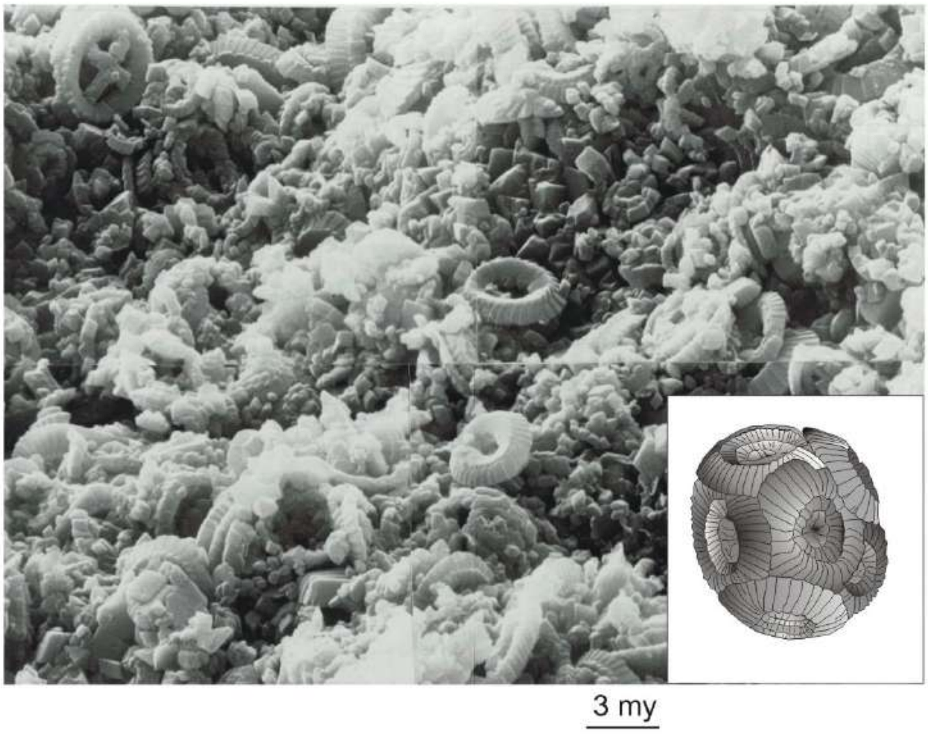


Fig. 6 - Elektronmicroscope-picture of the North Sea chalk, Tyra E-1x borehole from 2058 m depth.
Note the cocoliths ("mill wheels").
6000 x magnification. Indsert drawing of a cocosphere approx. same magnification.

Stevns Cliff

At Stevns Cliff, the Maastrichtian limestone is divided into two members, at the base the Sigerslev Member and at the top the Højerup Member (Fig 1). The Sigerslev Member consists predominantly of coccolithic mudstone with a few larger fossils, while the Højerup Member is a bryozoan wackestone. The bryozoan was growing in small mounds which due to sea currents from the south were migrating to the south towards the nutrient rich water that was feeding the bryozoans.

The Danian Limestone is also called the Korsnæb Member. The member consists of bryozoan packstone. In the same way as for the Højerup Member, the bryozoans formed mounds which were migrating towards south.

Between the Højerup and Korsnæb Members is the thin Fish clay member and above that the Cerithium Limestone Member. These two members are included in the Rødvig Formation. The base of the Fish clay constitutes the boundary between the Maastrichtian and the Danian Stages hence also the Cretaceous/Tertiary boundary.

Tabel 1 - Summary of the physical properties of the members

Stratigraphy	Sigerslev Mbr.	Højerup Mbr.	Cerithium Lst., Fish Clay and cemented part of the Højerup Mbr.	Korsnæb Mbr.	Copenhagen Limestone
Sediment	White chalk	Grey chalk	Hardground and clay	Bryozoan limestone	White lst.
Classifikation	Mudstone	Wackestone	Wackestone	Pack- to grainestone	Mudstone
Porosity%	40 - 45	39 - 42	30	40	40
Estimated water depth in m	200 - 400	100 -200	50 - 100	100 - 200	200 - 400
Clay content %	2 - 3	2 - 3	2 - 3	10 - 30	10 - 30

The water depth is based on Surlyk and Lykke-Andersen (2007).
The Copenhagen limestone member is only present at Stevns as a remnant. It is a younger formation than the Korsnæb Member and is well developed to the north. The stratigraphy is summarized in Fig. 7.

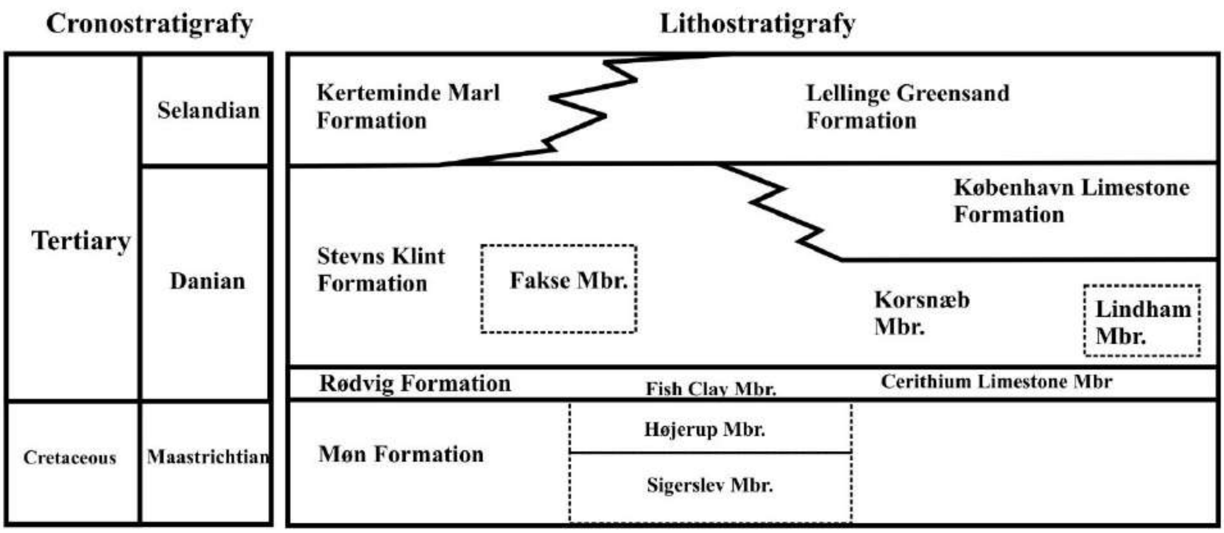


Fig. 7 - Danian-Maastrichtian stratigraphy in east Denmark, Zealand.

Flint layers occur in all these limestone layers.

Chapter 2 - Flint appearance and physical properties

Flint (Fig 8) is a hard and dense rock. It is harder than a steel pocket knife. It is black, white or grey in color, and consists almost exclusively of the mineral quartz in the form of α-quartz (SiO_2) and opal (SiO_2 - nH_2O).
X-ray analyzes show that the Danian flint consists of 98.2% SiO_2 with a crystal grain size of 2 - 30 microns, while the Maastrichtian flint consists of 99.2% SiO_2 (Appendix A). The grain size of the grey Danian flint is on average slightly larger than the grain size of the black Maastrichtian flint, where the grains have an average size of 7.5 microns (Fig.10).
The Danian flint contains 0.18% clay and the Maastrichtian flint 0.1% clay.
The flint has a conchoidal fracture typical of dense rocks and glass. At the same time, the edge of the fracture surface is sharp as a knife. This is what has made flint suitable as a tool for the Stone Age people.
The flint layers are silicious concretions, i.e., formed by chemical precipitation of silica (SiO_2) in the limestone, where silica replaced the limestone that was dissolved in this process.
The flint often contains fossil remains (Fig. 8C), which supports that silica has replaced the limestone after it was deposited.
The surface of the flint is often knotted and irregular (Fig. 9). It shows how the growth of silica on the flint took place by small protrusions on the surface when the flint was formed.

Flint is a Nordic term synonymous with the English term chert (Petittijohn 1956), and mostly used for the silica concretions in the Cretaceous chalk and the Danian limestone in Northern Europe for example Stevns Cliff (Fig. 1). There is no equivalent term for chert in the Nordic languages, which only have the term flint for silicious sediments and concretions.

The color of the flint.

The color of the Maastrichtian flint varies between black (Fig. 8A) and white (Fig. 8B). The flint can be porcelain-like (porcelainite). The color variation is interpreted (Madsen 2009; Madsen and Stemmerik 2010) as a result of increasing degree of silicification, where the black flint constitutes pure α-quartz and the white flint a mixture of opal and α-quartz.

The Danien flint varies between black, gray and white colors (Fig. 8D, F and 12), sometimes yellowish color. At Stevns Cliff, the Maastricht flint is black, while the basal two Danien flint layers on Stevns Cliff are black to dark grey, while the upper flint layers on the cliff are grey.
It is possible that it is a combination of the clay, as well as the slightly larger grain size of the Danien flint, that is the reason for the grey color of the Danien flint.
The black color of the Maastricht flint may be due to the smaller clay content and the smaller grain size of the flint crystals.

The color of the flint is not always uniform, but stained and variegated. Upon closer inspection (Fig. 11), it turns out that the " black spots" are the shadows of sediment structures that were in the limestone before it was silicified. This means that small variations in the trace elements in the lime mud have an effect on the color of the flint.

Fig. 8A - Black flint from Maastrichtian with a white crust. Sharp edges. 15 cm wide. Stevns.

Fig. 8B - Black flint from Maastrichtian with a white crust. 10 cm wide.

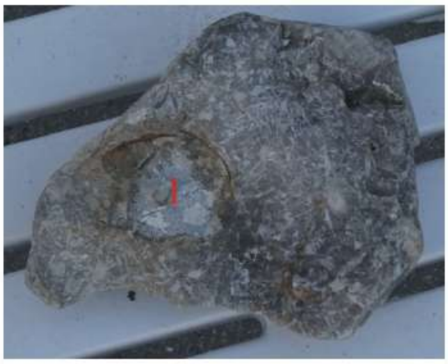


Fig. 8C - Grey/transparant Danian flint from the island Fyn. This flint contains abundant bryozoans.
1- imprint of sea urchin.
15 cm wide.

Fig. 8D - Grey varigated Danian flint from Stevns. In the middle a burrow, that has not been silicified.
40 cm wide.

Fig 8 - Flint types

The white crust on the flint.

The flint, in the outcrops on land (ex. Stevns Cliff), has in the surface almost always a thin crust, with a thickness from less than one millimeter to occasionally up to 2 millimeters and sometimes even more (Fig 8 A).
We must distinguish between two types of crust, the crust found on the flint while it is still in the limestone (ex Stevns Cliff (Fig.8F) and the island Møn), here referred to as the primary crust, and the white crust found on flint, which has been processed by humans and has been exposed to seawater or groundwater, here referred to as secondary crust.

Fig. 8E - Black Danian flint with white crust and whitedots. 10 cm wide. Karlstrup quarry.

Fig 8F - Grey Danian flint bed with white crust and white center. Varigated. Flint bed still in place. 20x60 cm, Stevns Klint.

Fig 8 - Flint types

Stone age flint artefacts, e.g., flint axes, have in some instances developed a (secondary) white crust.
Michelsen (1966) demonstrated that the white crust on the flint is α-quartz and the result of a "looser" structure of the quartz crystals, where water has diffused into the fissures between the crystals, thereby changing the optical properties of the flint.
It is possible that the penetrating water becomes part of the crystal structure (opalization), but most of it is probably just present in the fissures.
The crust is only developed in areas where the formation water in the flint-bearing formation has become fresh, i.e., the areas affected by the Qaternary glaciers.

Fig. 9 - The surface of the flint is very irregular which may reflect the solution of the chalk and the precipitation of the silica. Similar pattern kan be observed on the surface of eratic flint blocks in Quaternary tills. Dan Field wellbore ME-1 at 7167.6 ft.

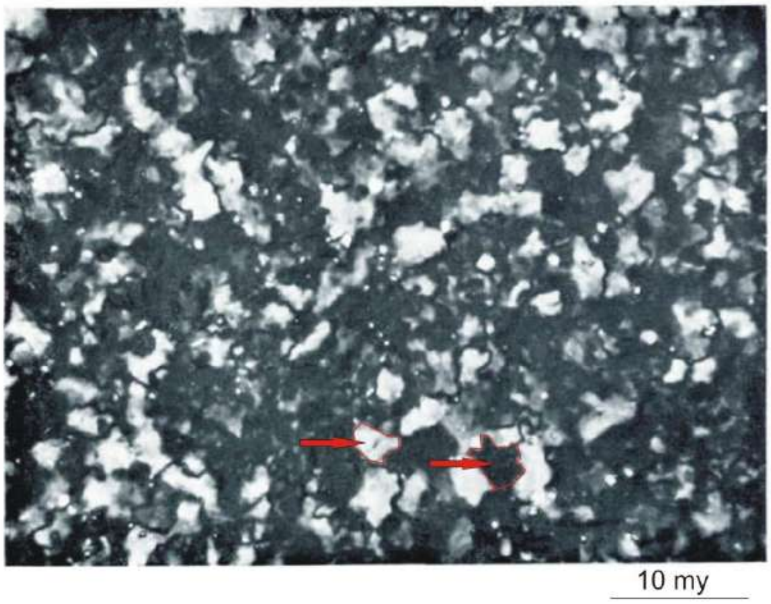


Fig. 10 - Mikroskope picture of thinsection of flint showing the silica crystals in the flint (Michelsen 1966). Crossed Nicol. The red arrows show eksamples of single crystals.

In the North Sea where the formations never have been exposed at the surface, the flint has no crust (Fig. 12).

In summary, the crust of the flint, primary and secondary, is thus due to the penetration of water into the fissures between the crystals, and can therefore be classified as a weathering phenomenon.

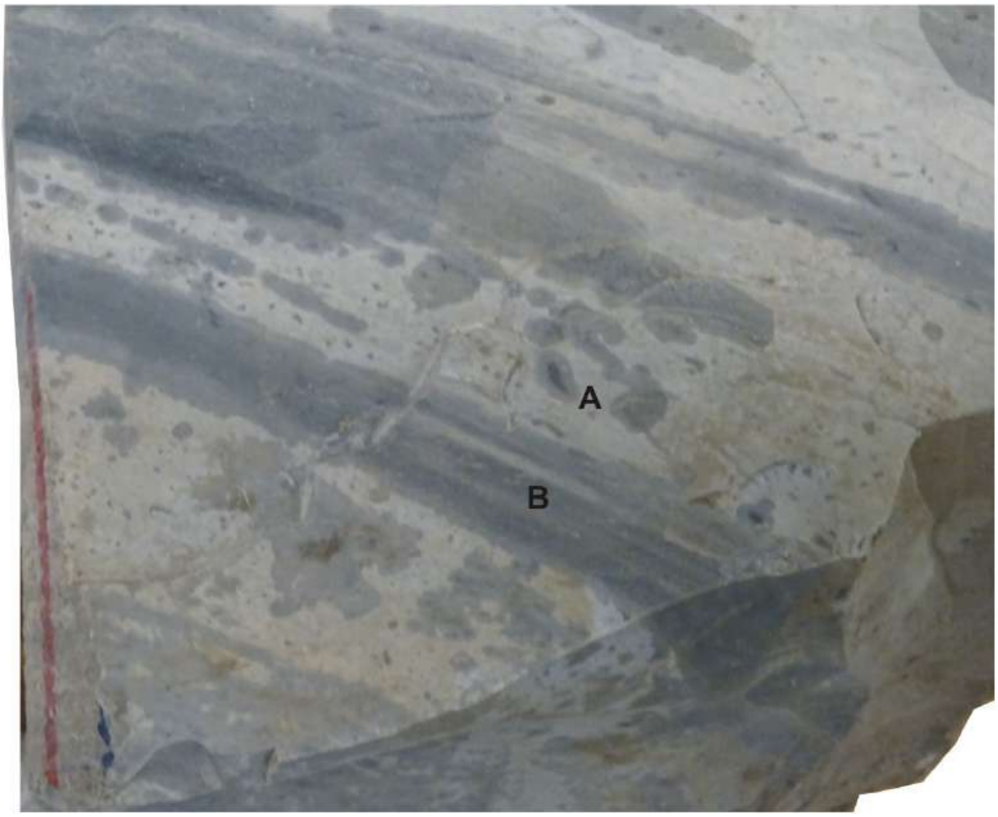


Fig. 11 - A massive flint bed from the North Sea Dan field, which can be followed beween several boreholes (Fig x).
The flint is grey and white with geyish burrows (A) and layering (B).
The flint vary between non-bioturbated and bioturbated layers.
The flint is a porcelanit.
ME-1 borehole 7213 ft (2383,75 m), Maastrichtian limestone of the Tor Formationen.
20 cm wide.

Patination.

Erratic flint blocks often have a reddish-brown to yellow color (Fig. 13). The stone has been colored (patinated) by groundwater with dissolved iron oxide (Ocher, Fe_2O_3).
Often the patinated flints have a diffuse transition from the reddish-brown exterior to the black interior flint. It shows how the penetrating water has deposited iron oxide in the fissures between the silica crystals (2 - 30 microns).
Patination is mostly a surface phenomenon.
X-ray examinations have shown a higher iron concentration in the patinated samples (Appendix A).
All the sampled flint examined had a small amount of iron (average Fe for Danian 165 ppm and for Maastricht 65 ppm, while patinated flint has 3762 ppm).
Unfortunately, there is no analysis of Fe from the North Sea.
The patination may also be black, presumably colored by humic acid, perhaps in some instances from seaweed (Vang-Petersen 2007).

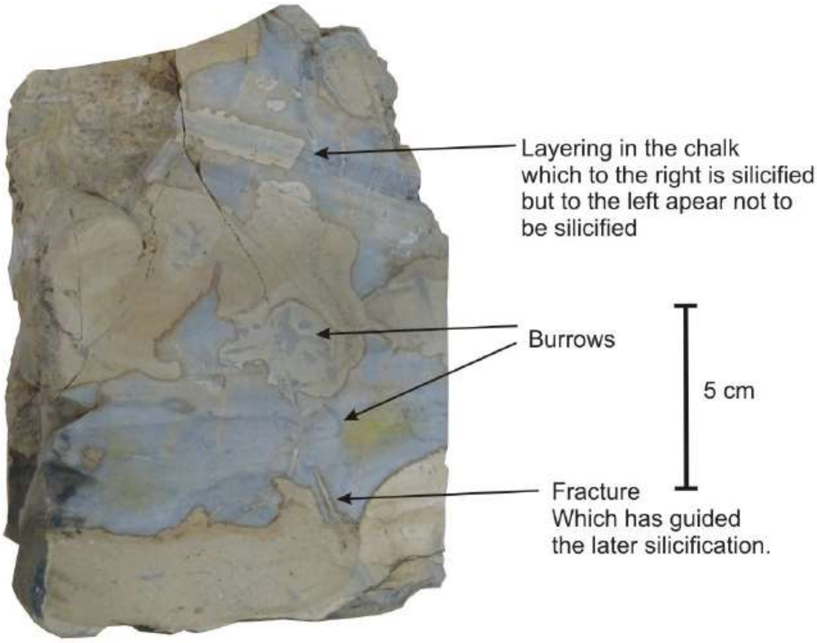


Fig.12 - The flint has a very irregular surface which are also observed on Fig. 25. Note that the silicification seems to have continued along a fracture. Although the burrows have had an influence on the silicification the primary bedding seems to have guided the proces also. Tyra E-4 at 6586 ft, Ekofisk formation.

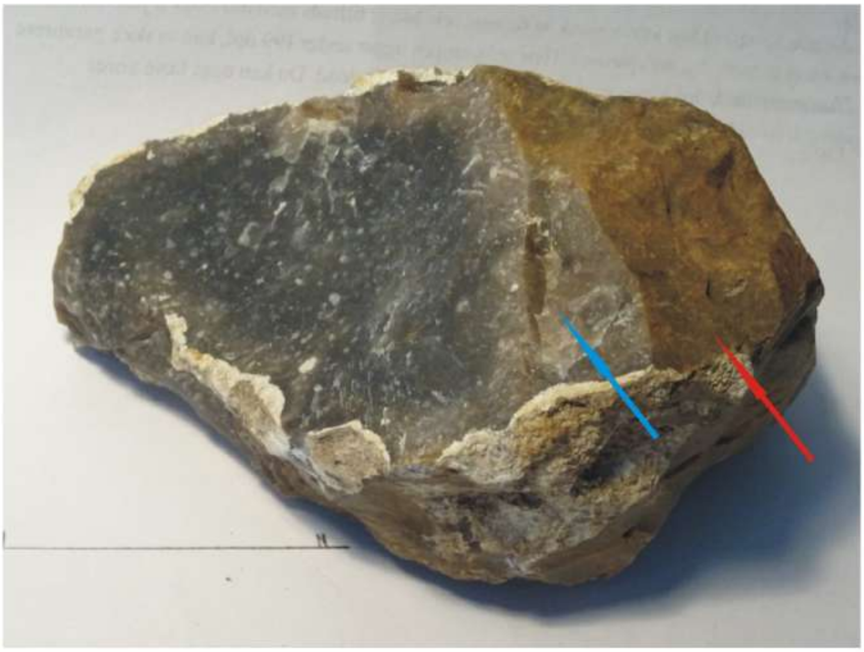


Fig. 13 - Patinated Danian flint from Karlstrup Quarry. The surface is ocher coloured by iron oxide (red arrow).
Inside the nodule the red colouration is gradually reduced untill the flint is grey (blue arrow). This demonstrate how the iron oxide has slowly difused into the flint nodule. 10 cm wide.

The shape of the flint beds.

The flint beds can have many different shapes such as oblong, almost tubular or tuberous, but the elongated sausage, or phallos-shaped, is common, as the flint has taken shape after borrows, (Figs. 14 and 15).

In some cases, flint layers are plate-shaped. Often the flint layers are developed as separate flint nodules, and are not a solid layer. This is especially true of the Maastrichtian flint, while the Danian flint layers are mostly massive coherent beds (Fig. 15).

Fig. 14 - Flint knodule formed around a Thalassinoides burrow.
Fallosformed knodule, Hasselø Falster (island), southern Denmark.
14 cm wide.

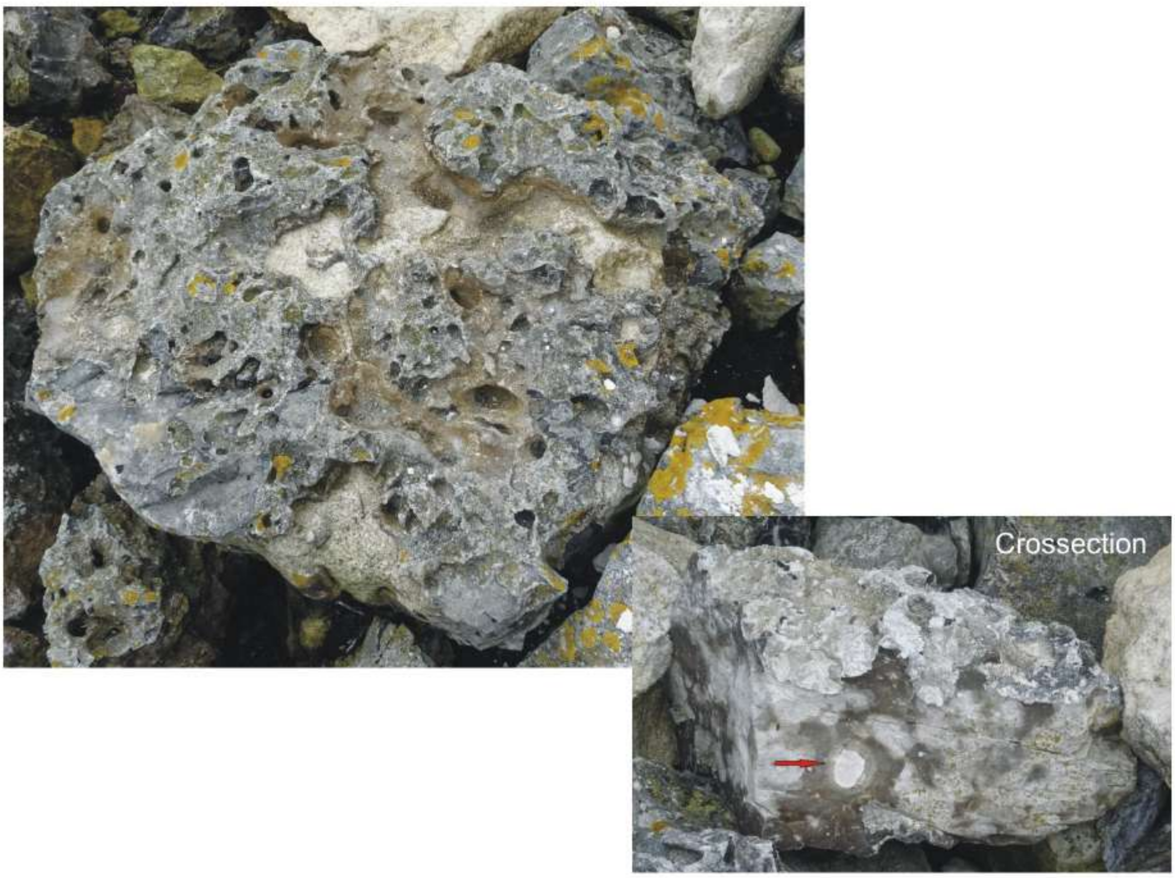


Fig. 15 - Massive flint bed in the Korsnæb Member at Holtug, Stevns Klint.
The irregular surface shows that the silicification has commenced in the walls of the burrows and thereafter grown into the surrounding limestone.
On the surface and in the crossection it is evident that some of the burrows have not been filled with silica (red arrow).
The flint bed is a fragment of a flint bed which has fallen down from the cliff to the beach.
Size ca 75x75 cm and crossection ca. 20 cm thick.

Chapter 3 - The origin of the silica

Most books and scientific articles mention that the silica of flint originates from fossil remains, ie. fossils that had a skeleton of opal. The question is whether it is the only source of silica.

The author envisages that there are 3 possible sources of silica (Fig. 16):

1 Sea water.
2 Biological debris (fossils).
3 Volcanic ashes.

Sea water

During the hot and humid climate of the Cretaceous, bauxite and laterite soil were formed inland by weathering processes. Such soils are rich in iron and aluminum, but poor in silica, which was carried out into the sea as quartz sand and dissolved in the water of the rivers.

The silica content of the seawater in the Cretaceous and Danian times is unknown, but is assumed to have the same variation as today, i.e., higher concentrations close to river outlets and higher concentrations in the cold bottom water of the sea.
The present-day seawater (as an example) contains about 2.5 g dissolved SiO_2 pr ton water and in rivers up to 10 times more (Gyldendal 2015).

The solubility in the seawater of silica decreases with decreasing temperature. Therefore, the undersaturated surface seawater that cools and sinks to the bottom of the ocean, will gradually increase its saturation with silica until it becomes saturated. In the North Pacific the deep water is supersaturated with silica (Kastner 1979). In situations of "upwelling" of cold bottom water from the deep ocean that floods the continental shelf, the bottom water will be saturated with silica. It allows diffusion into the sediment, from the intruding cold water.
Hoyez (2013) links flint formation with periods of "upwelling".

The Cretaceous Sea was connected to the Thetis Ocean by a sea way through central Russia (Fig. 3) (Surlyk and Lykke-Andersen 2007).
It is not envisaged that the ocean current from the southeast, across Denmark, resulted in periods of "upwelling". However, climatic conditions may have played a role and affected the oceanographic conditions, and at times stopped the ocean current from the southeast and thus the production of coccoliths.

A possibility is the enrichment of the seawater of silica from submarine hydrothermal (volcanic) activity, as indicated for Jurassic flint from Poland. There has been no subsea volcanic activity to the south in the central part of Russia, but the opening of the Atlantic Ocean, just at this time (Fig. 17), could provide an enrichment of the sea water, of silica in ocean currents from the north in the form of “upwelling”.

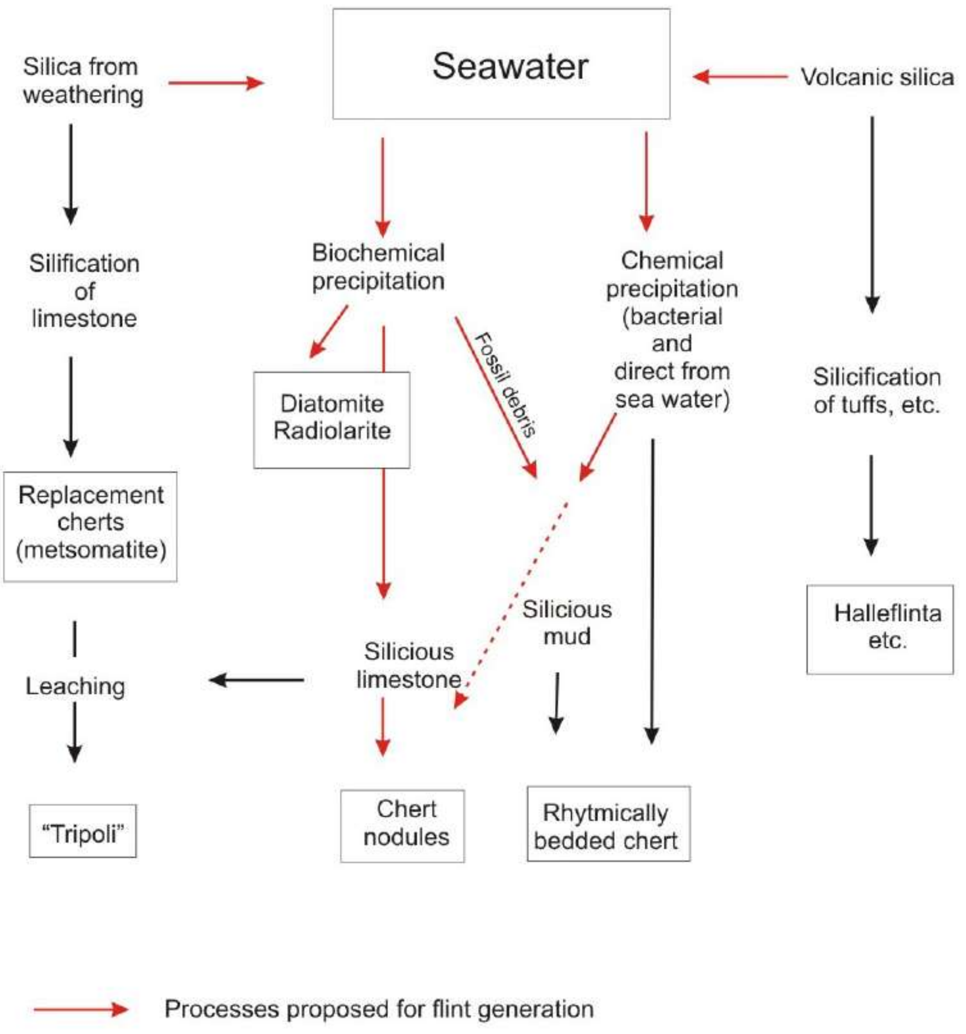


Fig. 16 - Provenance of chert and other silicious sediments. Modified after Petijohn 1956

This process, with influence directly from the seawater of silica, is very difficult to detect and must at present be considered as a hypothesis.

The biological source

In his classic textbook, in the chapter on silicious sediments, Pettijohn (1956) shows an illustrative diagram of "origin of chert (flint) and silicious sediments" (Fig. 16), in which he suggests that the source of silica is erosional products that were carried to the sea by rivers or are of volcanic origin (volcanic ash, lava, etc.).

It appears from his diagram that silica is extracted from the seawater through biological processes, i.e., that the organisms use silica to form a skeleton, which later, after the organism died and was buried, supplied silica to the formation water in the limestone sediments. The buried and dissolved silica was then precipitated in the lime mud as flint concretions. - Many authors, as well as data from the deep-sea drilling project, have since confirmed that this is an important process (Madsen 2009).

Madsen and Stemmerik (2010) mention that the seawater is undersaturated with respect to silica, and that the silica skeletons are unstable in such an environment and will dissolve.

However, there is ample indication that at least some of the silica skeletons (e.g., needles from sea sponges) were buried in the sediment (Fig. 19). This suggests that the seawater was not necessarily always undersaturated, or that the rate of deposition was so high that the needles were buried before they were dissolved. In addition, an increased silica content of the seawater may have caused the blooming of radiolarians and diatoms, thereby increasing the silica content of the sediment when they died and their shells were deposited on the sea floor.

The sedimentation rate for the Maastrichtian period varies between 3 and 15 cm per 1000 years or 0.5 to 1.5 mm per 10 years. This means that fungal needles located at the sediment-water interface may have been exposed to seawater for at least 10 years.
The question is how large a proportion of them survived such a long exposure if the seawater was always undersaturated.

Quartz is usually said to consist of silica, and it does not usually dissolve in water, but opal (SiO_2 - nH_2O), which is not crystalline, can be dissolved in water under reduced conditions (anoxic).
The sea sponges, the radiolaria and the skeletons of the diatoms consist of opal. After they died and their skeletal remains were buried, their skeletons were dissolved in the anoxic zone.
Opal is then present in the formation water of the lime mud. The biogenic silica is mostly recycled and only 1 - 2 % enters the geological record (Kastner 1979).

Volcanic ash
A third possible source is volcanic ash. At the end of the Cretaceous and Danien Stages,
a "rift" formed between Europe and Greenland. The North Atlantic was formed in this new rift valley (Fig. 17).
Such a plate tectonic event means increased volcanic activity, remnants of which have been found in Greenland and the Shetland Islands. Volcanism is still taking place in Iceland, among other places. The ash from the volcanoes spread across the surrounding continents and oceans.
We find several layers of marl in the limestone from the Danien Stage both on land and out in the North Sea (Fig. 18). Mineralogical studies have shown that the marl was originally volcanic ash. After the ash was deposited on the seabed, the ash was slowly converted to clay (montmorillonite - $Al_2[(OH)_2/Si_4O_{10}]\bullet nH_2O$)
In that process, silica is released, which is then included in the formation of flint (Simonsen and Toft 2006).

A model of flint formation
We know the end product, flint, based on analyzes and observations, but we do not know the process from the starting point to the final product, flint.
The following are the author's proposals for a flint formation model based on Clayton's (1983) and Madsen's (2009) proposed models:

At the time of deposition, the limestone contained organic material (Fig. 20) derived from the organic tissue of the cocospheres. After the deposition, the organic material was degraded by aerobic bacteria, in the upper 20 to 50 cm of the sediment, the bacteria using the oxygen present.

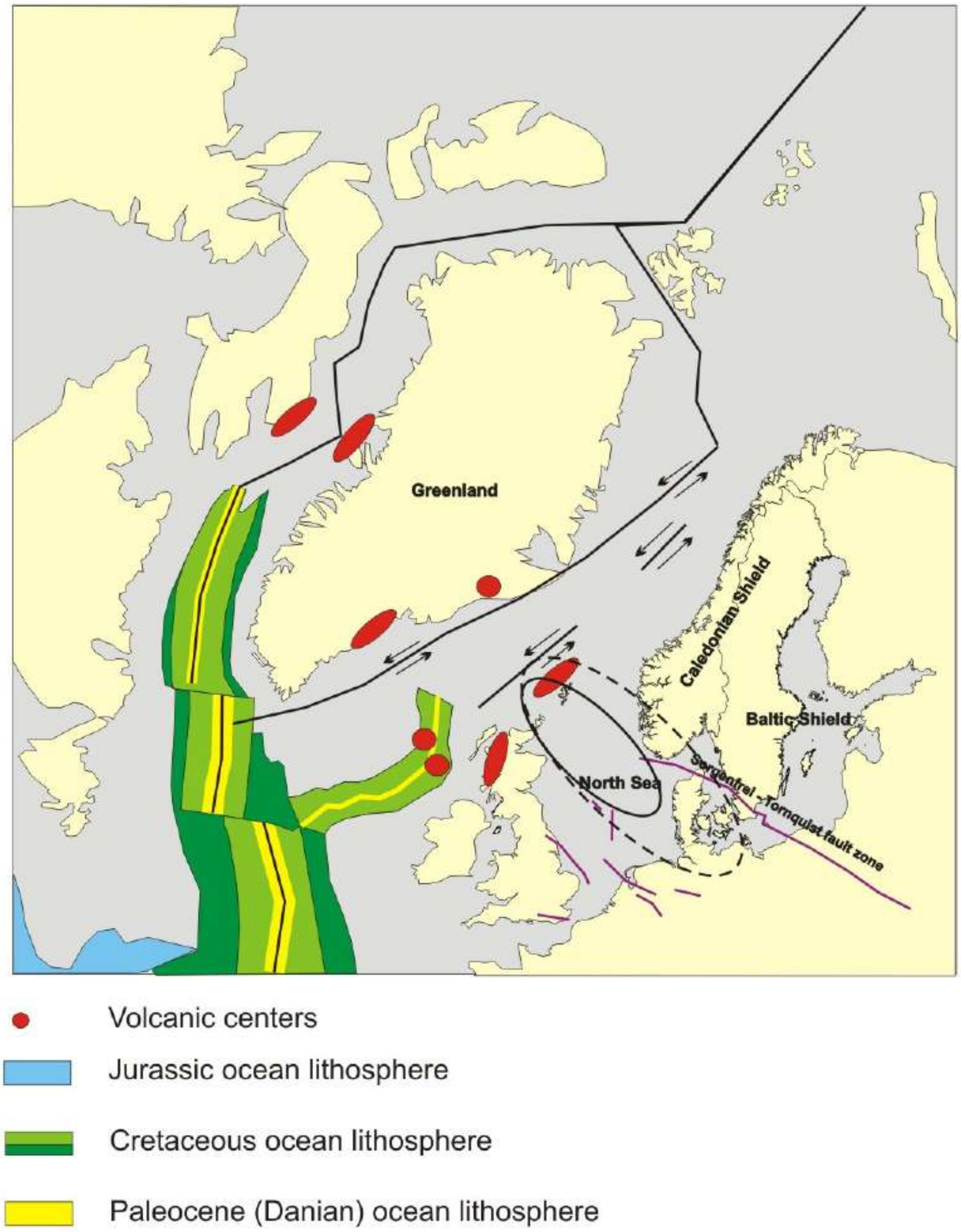


Fig 17 - Plate reconstruction 62 million years ago. Based on Ramberg et al. 2006 and Nielsen et al 2008. The volcanic centers are the possible sources for the Lower Danian clay beds and detrital clay content. The Britis Tertiary ignious provinces have yielded ages between 65 and 62 Ma (Saunders et al 1997). The cirkel area is the minimum area which have bee influenced by the early Danian volcanic activity. The dotted cirkel indicate the maximum area for the volcanic influence. The marl beds in the Karlstrup limestone quarry is possibly the effect of major eruptions. The volcanic ash beds of the Eocene rocks have a similar source as the Danian and can be traced far down in Europe.

Below the oxic zone, sulfite-reducing bacteria take over the work of degrading the organic material. In this process, hydrogen sulfide (H_2S) is formed, which diffuses up to the boundary between the oxic and anoxic zone in its liquid form HS^-. At this border, sulfide-oxidizing bacteria convert the hydrogen sulfide creating an acidic environment. This boundary is called “the hydrogen sulfide front”.

Biogenic opal, in the anoxic zone (sponge spicules, shells of diatoms, etc.), dissolves in pore water, undersaturated with respect to amorphous silica (Clayton 1983). The pore water is then strongly saturated with crystalline silica (opal CT). This solution is only metastable and silica precipitates as a gel at the oxic/anoxic boundary (30 to 50 cm below the sediment-seawater interface, the hydrogen sulfide front).

If the sedimentation of limestone stops, this layer of silica gel grows, and becomes "protoflint" (see following examples). The gel formation possibly started where there was silica skeletal remains close to the hydrogen sulfide front, which acted as crystal nuclei.

At the time the coccoliths were deposited, the sediment was originally a "soup", with a porosity of 50 to 70%. Below this sediment soup, of 3 - 4 cm, the sediment was compacted (Håkansson et al. 1974). Thus, there was no restriction in the top 3 to 4 cm of the sediment, in terms of contact with seawater and oxygen.
Burrows (Thalssinoides type), however, created a more efficient contact, between the anoxic layer in the sediment and the seawater (Fig. 21). This may have provided an additional supply of silica, directly from the seawater, especially during periods of "upwelling", with seawater supersaturated with silica.

The gel hardened relatively quickly to opal ("protoflint") which may be the same as the industrial product called silica gel (which are amorf silica grains). The burrow itself was only silicified after it had been filled up with lime sediment (Fig. 24).
The formation of opal continued after the deposition of the lime, with silica (Simonsen and Toft, 2006) coming from the volcanic ash. The ash was slowly converted to clay and free silica (microquartz). This is especially the case for the Danian limestone.
The conversion of the amorf opal to α-quartz is a lengthy process which only started after the flint had been buried and which may still be in progress.

An example - the border between the Sigerslev and Højerup Members

At Stevns Cliff, there is a prominent flint bed about 30 cm below the boundary between the Sigerslev Member and Højerup Member (the white and the grey chalk). This flint bed has a knotty and rugged shape and in places seems to have taken shape after the burrows (mostly Thalssinoides type).
The boundary between the two members consists of two hardgrounds ca. 20 cm apart (named SHH 1 & 2 in Fig. 21). These two hardgrounds are not completely cemented as the Danian Maastrichtian hardground (Svendsen, 1975, Surlyk 1979 and many other authors). The two incipient hardgrounds correspond to a hiatus in the sedimentation. Burrows at the hardground surface extend down to the flint bed. These burrows were open and filled with seawater.

In the chalk below the flint bed, we can observe Thalassinoides burrows that are cut by Zoophycos burrows (Fig. 22) which suggest that the Thalassinoides burrows were filled with sediment shortly after they were burrowed and there was no time for the precursor flint to be generated. This points to a different depositional environment than above the flint bed.
The Thalassinoides burrows at the hardgrounds were open during the period of non-deposition, hence allowed continuous contact between the seawater and the hydrogen sulphide boundary, which was present where the flint bed now is situated. This was also the place where the proto flint was formed and grew from the initial seed (SiO_2 gel).

In the lower part of the Sigerslev Member at the outcrop at Højerup there is two flint beds with no observable omission surface above the flint. It is possible that the overlying omission surface is not visible. The omission surfaces in Højerup Member are especially visible because there is a slight color difference between the chalk above and below the omission surface. This is not the case in the white chalk of the Sigerslev Member. Sometimes it is possible to observe a bedding plane may be corresponding to a short hiatus. The shape of the lower flint beds clearly indicates that the silicification took place around burrows of the Thalassinoides type.

At Rødvig in the Southern part of the Stevns Cliff we find open burrows in the hardground between the Korsnæb Member and the Rødvig Formation that are lined with flint (Fig. 23). This flint tube may be an example of a precursor flint where the silica gel generation stopped at an early stage and later hardened into flint.
After the initial silicification at the edge of the burrows the silica grew out in the surrounding sediment (Fig. 24). When the burrows later were filled with sediment the fill of the burrow was also silicified.

The Højerup Member (Grey Chalk) is developed as asymmetrical bryozoan bioherms (Fig. 1) (Svendsen, 1975, Surlyk, 1979 and many others) with the steep flank towards south. The bryozoans on the top of the bioherm acted as a baffle catching the fine cocolith debris which came from the south, which later slided down on the southern flank. The bioherms was therefore growing towards the south with a higher sedimentation rate on this flank. The northern flank developed as an omission surface. The flint beds in the Højerup Member are parallel to the omission surfaces (Fig. 1).
The flint beds in the Danian bryozoan limestone are generally massive and much more frequent compared to the Maastrichtian flint beds. The bryozoan limestone is a packstone, which had a much higher permeability than the chalk, possibly a factor 100, which facilitated that the seawater may have contributed as a silica source by diffusion (Toxværd 2011). Most of the Danian flint beds have no observable omission surface above the flint beds.

Bromley and Ekdale (1983) mentions that it often is possible to recognize several phases of flint generation.
The flint bed in the Højerup Member (Grey Chalk) often has tabular flint layers, which follows the bedding planes on the southern flank of the bioherms and is seen as a direct extension of the main flint bed. This is probably also a late stage silicification.

Another example – the North Sea

The author has described the cores from the chalk section from two Tyra Field wells (E1x and E4) (Fig. 25) (Kunzendorf et al. 1986), as well as cores from four Dan Field wells in the Danish North Sea (M-1x, M-2x, MD-1 and ME-1) (Fig. 26). A comparison of the flint beds in the core material with onshore outcrops is difficult due to the limited thickness of the cores (20 cm). An additional issue is that the wells are situated several kilometers apart. It is therefore difficult to accurately demonstrate the lateral distribution and correlation of the flint layers.

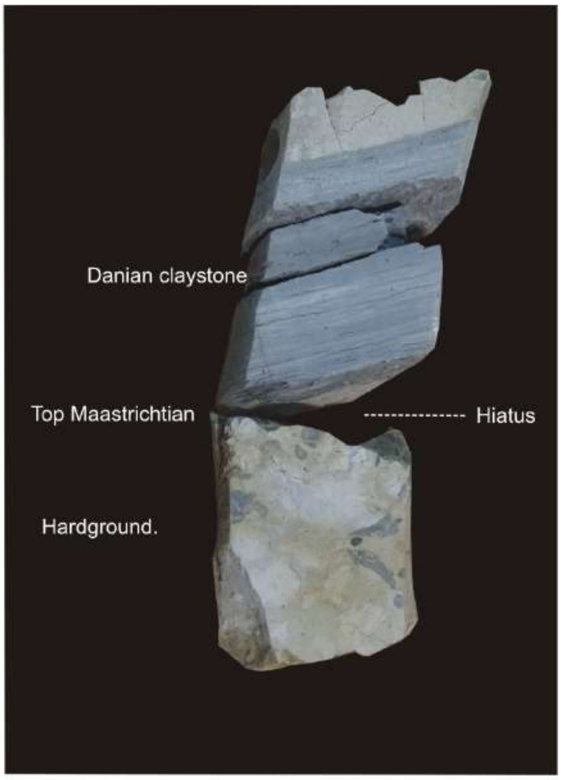


Fig. 18 - The Danien-Maastrichtan boundary in the Dan Field well ME-1 at 6961.5 ft. The claystone above the hardground is 15 cm thick. It is not equivalent to the Fish Clay because paleo data indicate, that there is a hiatus between the claystone and the hardground time equivalent to the Fish Clay and the overlying Cerithium Limestone on Stevns Cliff (F. Surlyk personal information 2016 and others). This amounts to a time gap of 0.7 to1.0 mill y.

Core analysis

The advantage of looking at the North Sea cores is that the cores have been analyzed (sedimentological description, porosity, permeability, clay content, etc.), which gives a more detailed picture of the physical properties of the Maastricht and Danien limestones (Fig. 25) (Kunzendorf et al. 1986). Thereby it is possible to get an idea of the properties of the limestone at the time of the formation of the flint (Table 1).

Unfortunately, no similar studies (apart from sedimentological descriptions) have been systematically performed on the limestone outcrops from Stevns, Møn and other exposures on land. However, the author has done some porosity analyzes on the Maastricht limestone on Stevns Klint (Fig.1) and some analyzes of the clay content (acid residue) in Danien and Maastricht - the limestone on Stevns Klint, Nye Kløv in Jutland and Karlstrup limestone quarry near Copenhagen (Kunzendorf et al. 1986). - The latter analyzes support the analyzes from the North Sea.

Appearance

The flint beds in the North Sea core material are black to grey white and speckled by the original sedimentary structures (Fig. 11 and 12) in the same way as observed in the outcrops. If we use the definition of Madsen and Stemmerik (2010) the flint is porcellanite or flint with a black core. There does not appear to be any color difference between Maastrichtian and Danian flint. In the onshore outcrops, the Danian flint is grey (mostly porcellanite) compared to the black flint of the Maastrichtian (Reinicke, 2012). In some cases, the flint beds are associated with burrows, and in others, they appear as tabular.

Marl Beds

There are also marl beds in the North Sea cores (Fig. 18), and even one at the border between the Danien and Maastricht formations. However, the layer is not time equivalent to Fish Clay. It is younger (900.000 years).

In general, the Danian limestone contains much more clay than the Maastrichtian limestone, up to 10 times more (Fig. 24).

Microscopy studies have revealed that the clay montmorillonite was generated from transformed volcanic ash (Simonsen and Toft 2006). The ash is in places only partly transformed.

Frequency of the flint beds

The flint beds in the Sigerslev Member can be followed along the entire Stevns Cliff, a total of 10 km. There are reports of some flint layers in England extending over a distance of at least 100 km. This means that the conditions for flint formation have apparently extended over large areas, with areal size of 100 to 10,000 km^2. The flint beds in the Højerup and Korsnæb Members cannot immediately be correlated from one bryozoan mound to the next mound, but each flint layer probably represents same periods of widespread flint formation.

The flint beds on Stevns Klint in the Korsnæb Member are located at an interval of approx. 1 meter while the Maastrichtian flint beds are separated by 2-meter intervals of limestone. The flint beds in the Maastrichtian limestone on Møn has a fequncy of just over a meter.

Compared with the limestone on land, the number of flint beds in the North Sea are significantly lower. In the North Sea the frequency is approx. 20 meters between the Maastrichtian flint beds and 3 to 10 meters between the Danien flint beds.

Compared to the outcrops at Stevns Cliff (Fig. 1) and Møns Cliff, the number of flint beds in the Dan Field and Tyra Field cores (Figs 25 and 26) are significantly lower. However, comparing Danian to Maastrichtian, the former is more abundant in all locations compared to those in the Maastrichtian.

Table 2 demonstrates a comparison of flint bed frequency between the Danian and Maastrichtian at several locations both onshore and the North Sea.

Fig. 19 - Scanning elektron mikroskope photo from the Danian-Maastrichtian hardground at Stevns Cliff with casts of sponge spicules.

Tabel 2 - Flint bed frequency

	Dan Field	Tyra Field	Stevns cliff	Møns cliff
Danian	6,7	3,3	1	
Maastrichtian	11	33	2	1,2

The frequency is given as average vertical distance between the flint beds in meter.
The data from Møn (only Maastrichtian) is based on Håkansson et al (1974), Stevns on Svendsen (1975) and the North Sea by own count. The lower frequency of flint beds in the offshore wells may be due to that only the most massive flint beds are recovered in the cores. The well bore can easily miss a nodular flint bed by drilling between the nodules.

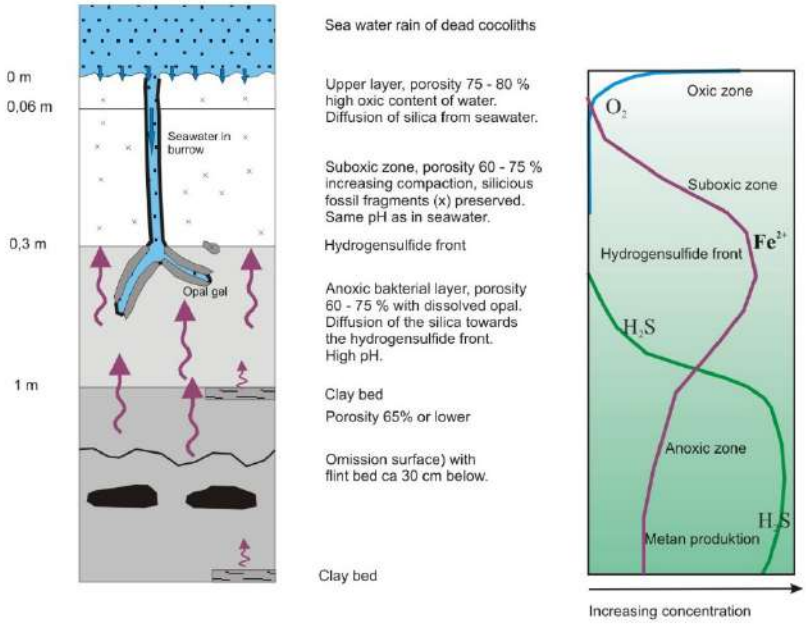


Fig. 20 - The layering in the upper meter of the chalk at the time of deposition. Note that thickness is not linear. When the flint bed looses contact to the seawater influx, the silicification continues presumably until the dissolved silica has been used. The model suggest that the silicification is tied to the chalk sequences in the same way as in the Limburg area and Northern France. In the Danian bryozoan limestone the permeability of the sediment is higher and porosity lower all the way to the surface. In this environment there will also be seawater which perculates down outside the burrows. This effect and the increased silica content of the seawater during the Danian may explaine the thick flint beds of that period at Stevns Cliff. Released silica from the clay beds and detrital clay from volcanic ash contribute to the dissolved silica.

The chalk in the North Sea has many allochtonous features with sedimentary structures such as slumps, debris flows and submarine erosional channels (Gennaro and Wonham, 2014). Some of these sedimentary structures can be recognized in the cores, which the oil companies have in abundance whereas erosional channels and larger moats requires seismic in order to recognize (Surlyk and Lykke-Andersen, 2007). Such a depositional environment results in a variable but high sedimentation rate. The Maastrichtian flint beds in the Dan Field wells seems to be present over distances of some 4 km. The correlation has been enabled using a wire line log marker, the MHS log marker (Fig. 26), which is probably a hardground and is well expressed on the sonic log. There are two massive flint beds situated below the log marker. The Dan Field has a radius of some 4 km.

In contrast, there is only one flint bed in the Maastrichtian of the Tyra Field (Fig. 25). This may due to the fact, that the Tyra structure is an inverted depo centre whereas the Dan Field is a salt structure with growth during the deposition. The chalk in the Maastrichtian of the Tyra Field is in many places alloctonous with possibly high rate of deposition.

The flint beds in the lower part of the Danian Ekofisk Formation (D2 Member) may have a wider distribution. The log profile for the D2 Member is fairly constant in the Tyra, Gorm and Dan Fields as well as various exploration wells nearby. This suggests that the D2 lithology is relatively constant in a large area of the southern part of the Danish North Sea (Svendsen 1979), and this translates to a constant flint bed distribution (Simonsen and Toft 2006). The Danian flint beds is therefore expected can be correlated over large distances.

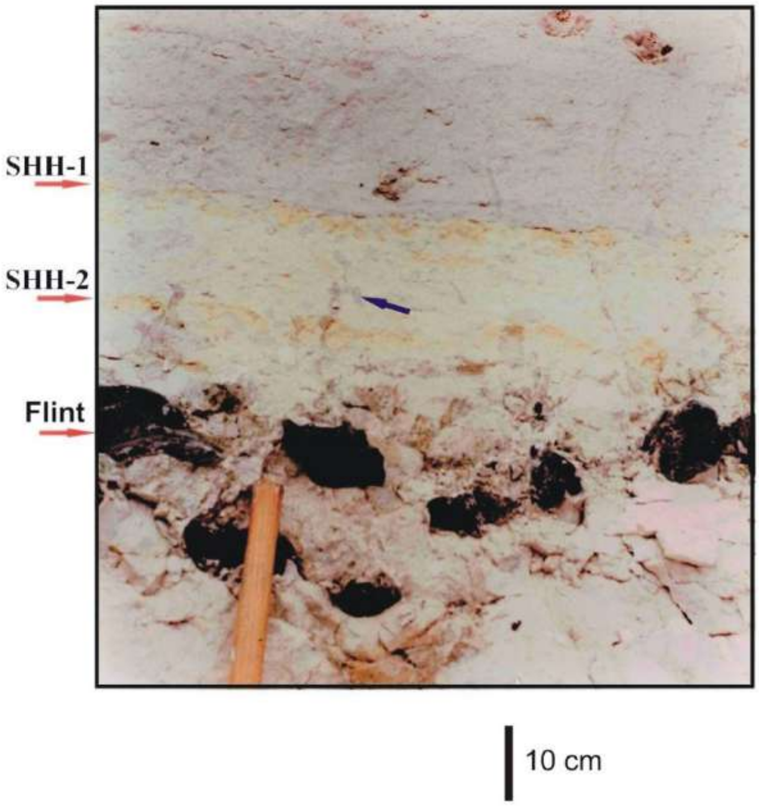


Fig. 21 - The border between the white Sigerslev Mbr. (SHH-1) and the grey Højerup Mbr. The redbrown (ochre) coloured parts are possibly remains of pyrite. There has been two stops in sedimntation resulting in two incipient hardgrounds SHH-1 og SHH-2.

10 centimeter below SHH-2 is the knotty flint bed which can be followed along the entire cliff, a distance of some 15 km.
The hydrogen sulfide front was situated where the flint bed is now.
Grey patches (blue arrow) is burrows.

Diagenesis

Most data suggest that the flint is not of sedimentary origin but is diagenetic, i.e., formed after the limestone was deposited, although flint formation began shortly after the sediment was deposited. Furthermore, it is not clear when the opal gel was transformed to flint (α quartz). Hoyàs (2013) shows an example from Etretat, in northern France, with flint nodules in a brecciated zone (Fig. 37). The brecciated zone is formed shortly after the deposition of the limestone, in connection with slumping, and the flint is broken, which shows that it had become solid at the time of slumping. Similarly, Stenestad (1976, his Figure 22) shows a picture of a flint layer from the Copenhagen limestone in the Copenhagen area, where the flint is fractured and the fractures which are not tectonically induced, is filled with lime mud.
Ie. the flint hardened early prior to fracturing.

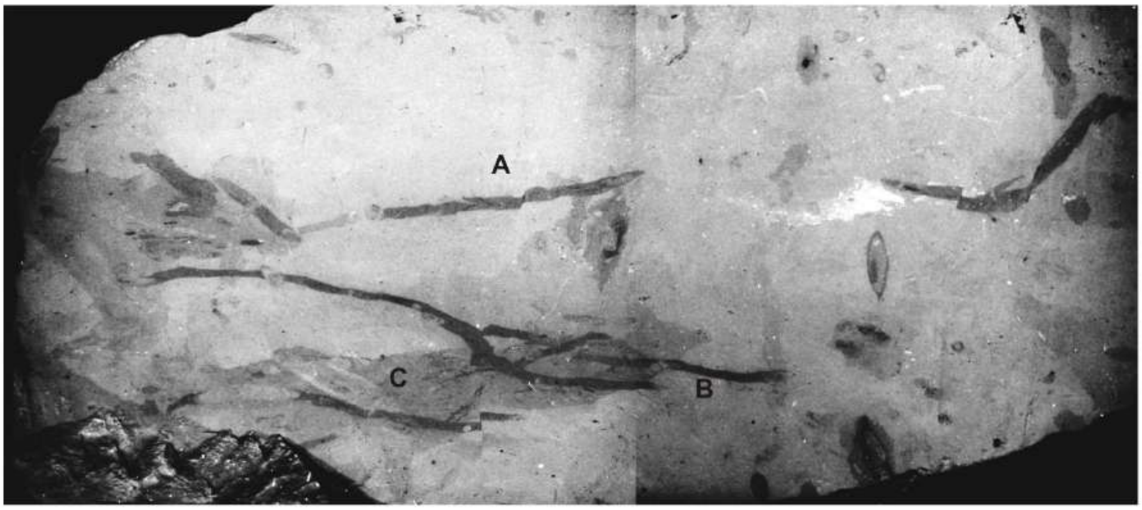


Fig. 22 - Compiled UV photography of vertical surface in the white chalk of Stevns Cliff. Small scale faults, A, caused by compaction, cuts Zoophycos spreite. The irregular grey patches are Thalassinoides burrows, C. which are reburrowed by the Zoophycos spreiten, B. Hence the Zoophycos spreiten postdate the Thallassinoides burrows but were made before the compaction (Håkansson et al. 1974, Svendsen 1975).

Clayton's flint formation model gives us an explanation of the presence of the flint beds we observe in the limestone. We know the end result, but not all processes from the "protoflint" (gel) to the flint of today, which consists of α quartz.
The question is whether the transformation to α quartz took place early or only long after the limestone was buried by younger sediments.
This question is most relevant for the flint formations in eastern Denmark, where the flint and limestone have not been buried very deep by younger sediments, no more than 250 m during the Tertiary period, and if we include the Quaternary period perhaps another 450 m (the weight of a 2000 m thick glacier).
Remains of a flint conglomerate have been found in Jutland, in the glacial sediments. The flint bolders are cemented together by sandstone. The sandstone contains plant fossils from the most recent part of the Miocene. That is, the flint was formed and hard at the end of the Miocene.

The examples from Etretat and Copenhagen with intraformational brecciated flint, show that the flint was solid at an early stage.
The limestone in northern France has been buried in the Tertiary period and exposed to alpine folding, so it is difficult to compare with eastern Denmark.
The conversion of opal to α quartz requires activation energy and time. Low temperature: long time. High temperature: short time. With the known geothermal gradient and knowledge of the temperature development of the Tertiary period, the limestone in Eastern Denmark has not been exposed to temperatures higher than 25 g C. The conversion to α quartz has therefore taken place during the Tertiary period. The opal must therefore have been solid early, as in northern France, and have replaced the limestone before it was buried.

In the first proposed flint formation models (Shepard 1972) it was suggested that the flint beds are formed long after the limestone was deposited. It simply does not explain why the flint layers are

Fig. 23 - Photo of flint tube from the Danian Maastrichtian hardground at Rødvig, Stevns Cliff.

Fig. 24 - Flint nodule formed around a Thalassinoides burrow. The original shape of the burrow can still be distinguished. The flint constitute much more than the burrow, which confirms that the silicification continued outside the burrow.

situated as they do, why they are formed in connection with burrows and why the Danien flint beds are very massive compared to the Maastricht Flint.

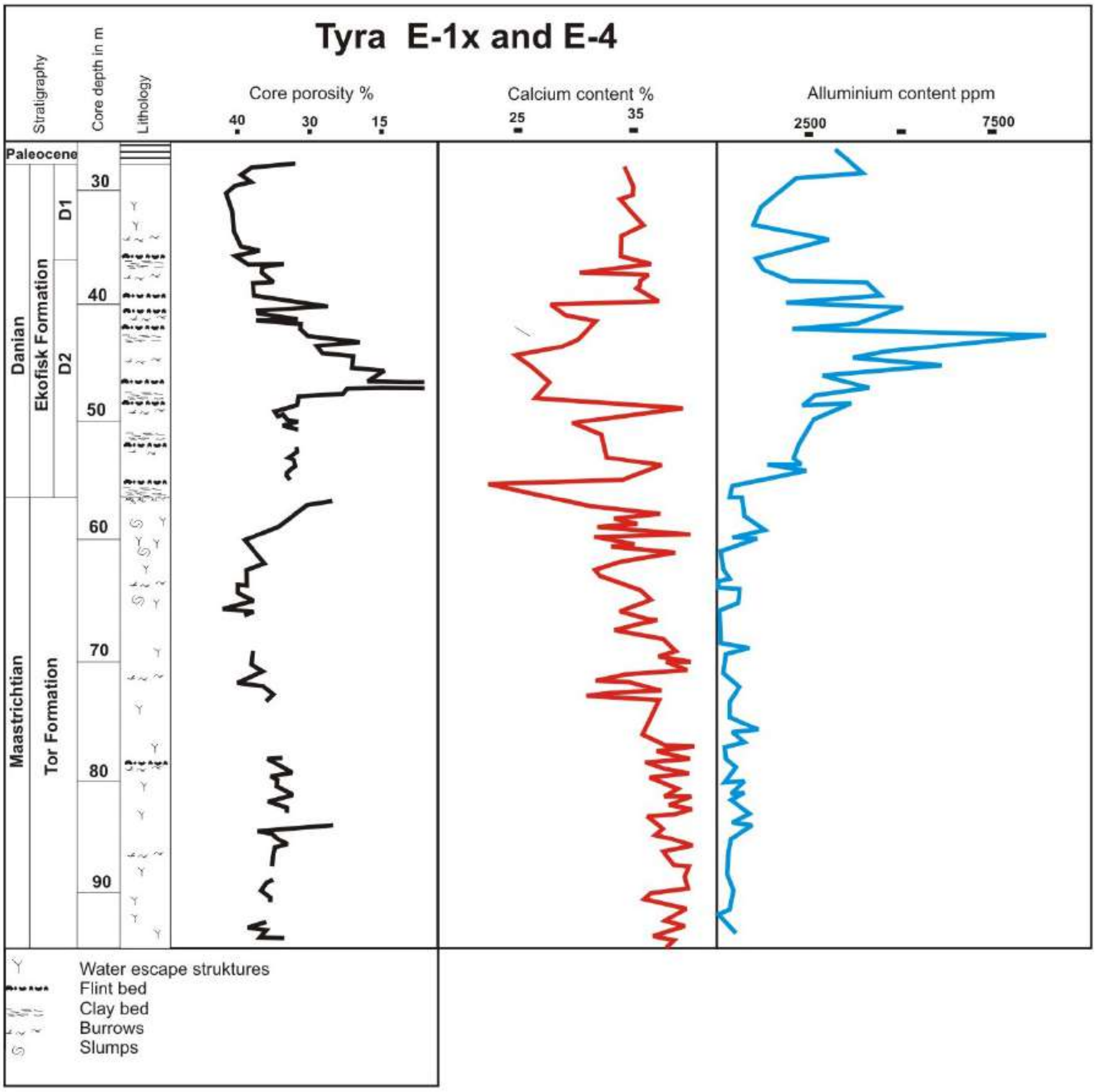


Fig. 25 - Well profile with core recovery over the Ekofisk Formation and the upper part of the Tor Formation compiled from two Tyra wells, E-1x and E-4. The Ekofisk D1 is from E-1x whereas the rest is from E-4.
Modified from Kunzendorf et al. (1986). E-1 and E-4 are situated ca. 3 km apart. The Maastrichtian chalk has numerous water escape structures suggesting fairly high rate of deposition. The aluminium content is a proxy for the clay content.

The two examples (Hoyas 2013 and Stenestad 1976) suggest that the silica gel hardened very early to opal.

In the Coniacian Arnager limestone on the island Bornholm, and in the Danien deposits near Mariager in eastern Jutland, there are no flint layers, but the silica is found scattered in the limestone in the form of lepispheres, i.e., microscopic spheres of silica (Opal-CT), approx. 5 microns in diameter.

Dan Field in the Danish North Sea

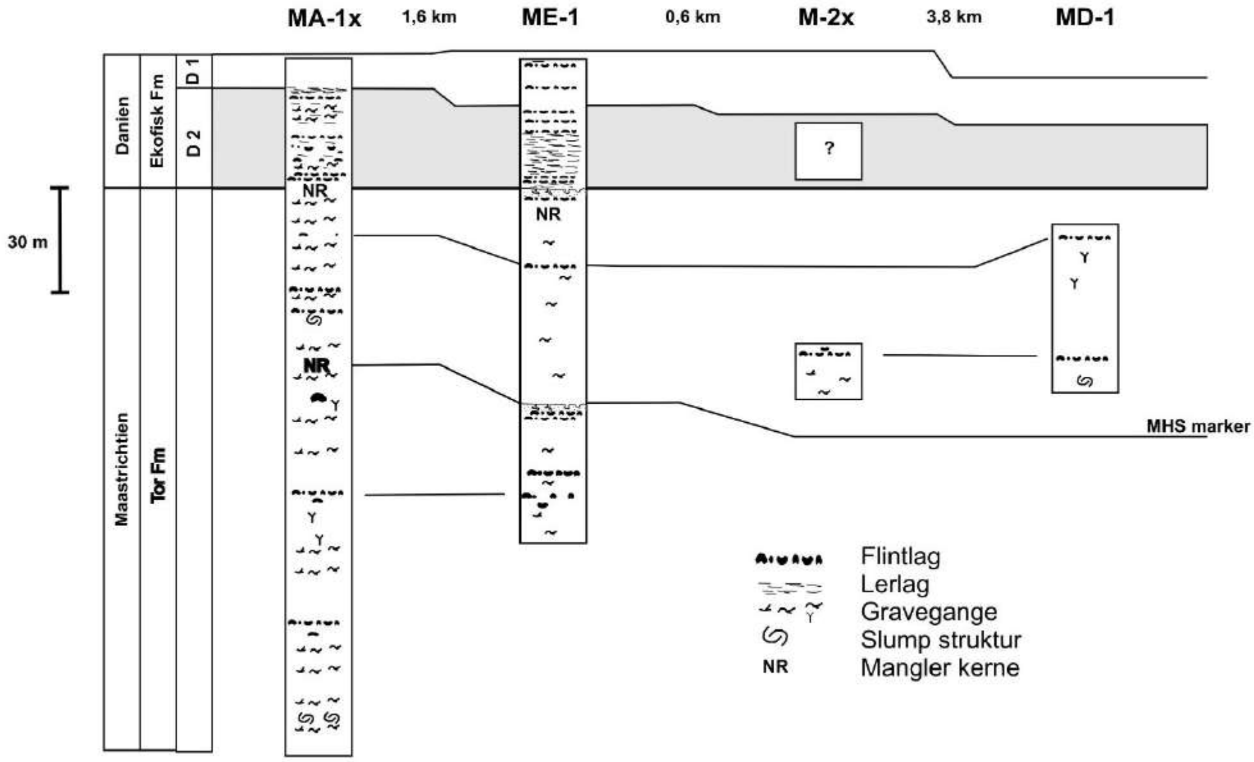


Fig 26 – Dan Field wells with coring in the Chalk. The sedimentological profile only covers the cored section of the wells. An attempt has been made to correlate the flint beds in the wells using the wireline logs as guide.

In the middle of Denmark at Mariager, in Jutland, the opal CT lepispheres constitute up to 40% of the limestone. The limestone is relatively homogeneous, and there are indications that the sedimentation has been continuous, without interruptions, so that the formation of the silica gel, and therefore the flint beds, has not been able to take place, as previously outlined.

The lepispheres are formed at a temperature of 17° C (the Arnager limestone), which means that they are formed late after the limestone had been buried to a depth of perhaps 250 m.

Summary

If we summarize, the flint in Northern Europe is a product of many factors:

- The silica has at least 3 sources: diffusion directly from the seawater, buried silica skeletal remains and volcanic ash.

- The flint beds in the Maastrichtian may be related to the fact that a dominant ocean current from the southeast of the Cretaceous Sea was interrupted for periods, which reduced the coccolith production and therefore the limestone sedimentation rate. An omission surface/ hardground was formed. Thereby the hydrogen sulfide horizon was locked in the same position and the silica gel was formed and could grow. - Perhaps these periods are caused by climate change, related to volcanic activity in the South Atlantic, formed by the separation of South America and Africa during the early Cretaceous. During these cold periods, cold water, enriched with silica, was flooded (upwelling) into the chalk seas of northern Europe.

- The silica in the Maastrichtian limestone originates mainly from silica skeletal residues and diffusion from seawater.

- In the Danian, it is the same processes as well as volcanism, now from the opening of the North Atlantic, that come into play. The increased volcanism brought large amounts of volcanic ash over Denmark and the North Sea, from the newly formed North Atlantic Ocean. This increased the amount of silica in the limestone and the seawater during this period, which increased the silicification of the limestone, the formation of the flint beds and their later growth.

- The conversion of the early hardened opal to α quartz is a process that took place after the limestone was buried and over a period that extended far into the Tertiary period. Perhaps the variation between white and black flint reflects this process, as suggested by Madsen (2009). This means that the transformation is still taking place.

Chapter 4 - Earlier theories of flint formation

Earlier theories

Over years, there have been several theories about the formation of flint.

1 - Syngenetic, simultaneous precipitation of silica, in the sediment (1000 - 10,000 years). Clayton (1983).

2 - Late generation, i.e., formed long after sedimentation. More than 100,000 years. Simonsen and Toft (2004).

3 - Deposition of silica gel directly on the seabed. Owen (1850), Lindgren and Jacobsen (2012).

4 - Liesegang theory. Seepage of silica from surface water. Liesegang (1913), Shepard (1972).

The first two theories have been discussed in the text. It is the author's opinion that Nos. 1 and 2 constitute the most plausible explanations for flint formation.
Lindgreen and Jakobsen (2012) (3) suggested that a silica gel was deposited as a layer before it was transformed into flint. The gel was supposed to originate from a blooming of radiolaria, as a consequence of massive volcanism (i.e., acidification of the sea and heavy supply of silica to the seawater). The layer of silica gel was reworked by burrowing organisms while the sediment was still soft.
They use an example from a core in the Danish Gorm field (the N22 borehole).

The author has similar observations in the drill cores of the Tyra field (Fig. 12) and in exposures from Stevns Cliff and Faxe Quarry. The filling in the burrows were the last to be silicified while the silica gel was being generated and before the burrows were filled with sediment.
A two-dimensional section through a flint layer may possibly show what appears to be a burrow inside the flint stone, while in a three-dimensional view a complicated silicification process emerges that continued after the limestone was buried (Fig. 12).
There is no evidence that flint was formed as a sedimentary formation, but the flint formation may have been increased by extra-large supply of silica skeletons.

The Liesegang theory (4) has been reviewed in the section on striped flint (see later), but was also used to explain the presence of flint layers in the English chalk. In this explanation, the infiltrating groundwater, with elevated silica content, forms the flint layers, in the form of a liesegang process, where the flint layers form the liesegang bands. This explanatory model has long since been abandoned.

Modern studies

There are many publications, which discuss the provenance, generation and the cyclicity of the flint beds in the Cretaceous Chalk and Paleocene Danian Limestone in Northern Europe. Gry and Søndergaard (1958) did a detailed petrographic study on several types of flint from both Maastrichtian and Danian where the white opal rim of the flint was detailed studied. H. Michelsen in 1966 described the mineralogy of the flint of the Maastrichtian chalk at Stevns Cliff in Denmark. In 2009, Håkansson et al. (1974) presented both chemical and sedimentological observations on flint generation. They mention that the aspect of the cyclicity of flint beds, is not resolved. Smed (1988) and later, Toxværd (2011) described the chemical process involved in flint generation without discussing the sedimentological processes. Clayton (1983) and Madsen (2010) proposed that bacterial activities and the sedimentation rate in the sediment is important processes in the silicification process. Felder (1983) describes the rhythmicity (depositional sequences) in the chalk of the Gulpen Formation in the Limburg area, whereas Bromley and Ekdale (1983) and Hoyaz (2013) discuss the Cretaceous Limestone of Northern France with its flint beds. Madsen et al. (2010) describe the silicified Arnager Limestone on Bornholm.

A widely accepted view of the provenance of the silica was from fossils which originally had silica-based skeletons i.e., sponges, diatoms etc., (Håkansson et al. 1974, Maliva et al. 1989). However, Toxværd (2011) in his note on the flint beds from Stevns Cliff proposed that the silica originates entirely from seawater.
It has been commonly accepted (e.g., Bromley and Ekdale, 1983) that burrows are a significant factor in flint generation and in most cases directly shapes the irregular formed flint layers. The paramoudra flint in the UK is a special example of this (Clayton 1983).

Fig 27 - Paramoudra-flint also known as barrel flint (Evelyn Simak).

Chapter 5 - Types of flint

Paramoudra flint (barrel flint)

In the Campanian and Maastrichtian limestones, some strange barrel-shaped flint knots (Fig. 27) occur. They are typically 30 to 40 cm in diameter and 60 to 80 cm high. The walls are 10 to 15 cm thick. They are best known from England, but have also been observed in Denmark, including western Jutland, although in a smaller size. These "barrels" are silcified burrows. They have been named Batichnus paramoudrae, which means something like "sea pears" in Gaelic. Several barrels are often found on top of each other, so that they form a several meter high pipe. It is not known which creature made these burrows. - According to the various proposals for the formation of paramoudra, the "barrel" was formed along a vertical burrow, several meters deep, which bent the hydrogen sulphide front downwards, around the tube (Thomsen 2000). Thereby, the flint formation was focused around the burrow (Fig. 27). The fact is, however, that it is not known which animal made the burrow, nor whether the barrels were made simultaneously, on top of each other or sequentially. It is possible that the paramoudra burrow was several meters deep, but this does not mean that the ordinary flint beds were formed at several meters' depth below the seabed. As described earlier, the beginning of the flint formation of the ordinary flint beds has taken place at a depth of 30 to 50 cm below the seabed.

Silicified fossils

One often finds fossils that are silicified and form a flint nodule. Sea urchins are a well-known type of silicified fossil. Most common is Echinochorys. The sea urchins are from 2 to 5 cm in diameter. When they lived, the shell covered a cavity containing the soft parts. When the animal died, the soft parts went into decay and the cavity was filled with lime sediment. This created a "mini" seabed with a hydrogen sulfide zone along the shell, where the rotten organic material was located. The fossil was now the focus of silica gel formation, and the cavity was slowly filled with flint. - What we find is a “steinkern” sometimes with the shell still preserved.
Another example is spherical flint nodules, which is not formed as an erosional product, but is the steinkern of a type of sea spongy, called Plinthosella resonance.
The silica needles in the skeleton have served as a focus for flint formation. They are especially known from Møens cliff.
It is not clear whether these silicified fossils are found by chance in the limestone or are associated with a flint layer, and thus have been in the hydrogen sulfide front of the flint bed.

Sheet flint

Plate-shaped flint nodules are present in the limestone and are clearly formed in connection with fractures. Fractures are usually formed long after the limestone was formed and was buried by younger sediments. When the fracture opened, formation water, enriched with silica, seeped into the fissure and flint was formed (Fig. 12).

Sheet flint is common in deep-sea limestone from the Jurassic period, and is found in the Mediterranean, Greece and Albania. These flint layers are not formed in connection with fractures, but follow the bedding surface, and are perhaps formed in the same way as described for the Danien and Maastrichtian flint. The deep-sea flint is not formed around burrows which are not present in the limestone.

Banded flint

Banded or striped flint is most frequent on the island Falster (Vang Petersen (2007), Fig. 28), and is therefore Maastrichtian flint. The flint appears with white and dark stripes, which may be variation between opal and α-quartz. It resembles the striped Jurassic Krzemionki flint (Fig. 29).
The question is how the stripes was formed. One possible explanation is that it is formed in a liesegang process.
Liesegang rings are a chemical phenomenon in which a salt diffuses through a gel, or a dense formation, and forms concentric rings. An example is iron oxide dissolved in groundwater. When the solution seeps through cracks in a dense formation, the salt crystallizes out in concentric rings, where every other ring has a high salt concentration and subsequently a ring with less salt concentration (Fig. 28A).

The question is whether the banded flint was formed by a liesegang process while the flint was still a gel. In this case the banded flint was formed by the diffusion of silica into the silica gel. The light bands constitute opal (higher H_2O concentration) and the dark bands α-quartz (higher silica concentration) (Figs. 28B and 29).

Vang Petersen (2007) shows a piece of Falster Flint (his Fig. 7, no. 2), where the white opal stripes show a diffuse outer edge and a sharp inner edge, towards the center of the flint, and towards the next opal stripe. The thickness of the stripes increases towards the center of the flint stone and becomes more diffuse.
It could indicate diffusion of silica, from the edge of the flint stone, towards the center.

Liesegang rings of iron oxide are often observed in dense (low permeable) formations of lime / marble (Fig. 28A) or sandstone, where groundwater has seeped through the formation and where the iron oxide is precipitated with varying concentration in rings. It is a process that occurs long after the formation of the dense rocks. A beautiful example can be seen at the Danish National Museum in Copenhagen, in the Stone Age collection. In the display case with flint axes there is also a large unworked flint block with rings of ocher.

We do not know exactly how the liesegang process works and whether the banded flint is formed by a liesegang process. No modern scientific analyzes have been made that bring us closer to an explanation, but it is a possibility.
Nor has a systematic collection of striped flint been made in Denmark, which makes it difficult to better understand the formation and occurrence of striped flint. The band occurs elsewhere than on Falster. Madsen (2009) shows flint with liesegang rings from Stevns Cliff.

Fig. 28 - Liesgang rings in marble (A): The fluid with ironoxide has diffused into fissures in the marble and have generated Liesegang rings. Banded flint from the island Fyn (B).

Fig 29 - Krzemionki flint from Poland (Wikipedia).

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Appendiks A – X-Ray analyzes

The X-ray fluorescence analyzes shown here are from Högsberg et al (2012) and Michelsen (1966). Both authors analyzed for 9 elements, Al_2O_3, SiO_2, SO_3, Cl, K_2O, CaO, Ti, Mn and Fe. Only 4 elements Al_2O_2, SiO_2, Cl and Fe are selected here. - The analyzes are made on flint pieces that have not been patinated as far as possible. - Högsberg also made an analysis of patinated flint pieces, showing that the patinated surface is affected by penetrating salts, iron and clay (Al_2O_3). Kunzendorf et al. (1986) made his analyzes on limestone samples from the North Sea's Tyra boreholes, including a single sample of flint. The analyzes on the limestone are shown in Fig. 23 and the analysis of the flint in the table above. Kunzendorf's analyzes were performed with Neutron Activation technique at the Danish Risø Research Laboratory. The purpose was to investigate the trace elements of the limestone. In this context, Al_2O_3, Cl and CaO have been extracted from his analyzes. Unfortunately, no analysis was made for SiO_2.

Maastrichtian Flint

Type	**Lokality**	**Age**	**Al_2O_3 %**	**SiO_2 %**	**CaO %**	**Cl ppm**	**Fe ppm**	
Falster	Hasselø	Maast	0,069	99,66	0,11	0	60	Högsberg 2012
Falster	Hasselø	Maast	0,077	99,60	0,15	36	66	Högsberg 2012
Scandinavisk	Rørdal	Maast	0,088	99,62	0,14	81	64	Högsberg 2012
Senonian	Ellidshøj	Maast	0,067	99,20	0,17	62	57	Högsberg 2012
Senonian	Ellidshøj	Maast	0,173	99,41	0,16	NA	88	Högsberg 2012
Senonian	Ellidshøj	Maast	0,143	99,57	0,12	30	100	Högsberg 2012
Senonian	Ellidshøj	Maast	0,206	99,17	0,21	102	46	Högsberg 2012
Senonian	Ellidshøj	Maast	0,123	99,42	0,21	109	57	Högsberg 2012
Rügen	Jasmund	Maast	0,054	98,76	1,08	66	62	Högsberg 2012
Rügen	Jasmund	Maast	0,107	98,36	1,31	81	47	Högsberg 2012
Black Maastricht	Stevns	Maast	0,032	98,44	0,09	NA	70	Michelsen 1966
	Maast. middle		0,104	99,2	0,34		65,2	
	Maast. median		0,088	99,41	0,16		62,0	

Danien Flint

Type	Lokality	Age	Al_2O_3 %	SiO_2 %	CaO %	Cl ppm	Fe ppm	
Light grey chert	Tyra Feltet	Dan	0,159	NA	0,48	4760	NA	Kunz 1986
Bryozoan	Klintholm	Dan	0,340	99,00	0,27	139	135,0	Högsb2012
Bryozoan	Klintholm	Dan	0,406	98,91	0,295	115	143,0	Högsb2012
Bryozoan	Klintholm	Dan	0,238	98,83	0,39	123	113,0	Högsb2012
Bryozoan	Klintholm	Dan	0,315	99,00	0,36	129	128,0	Högsb2012
Bryozoan	Klintholm	Dan	0,109	99,45	0,21	108	133,0	Högsb2012
Grey Band Danian	Kølbygaard	Dan	0,221	99,09	0,50	123	116,0	Högsb2012
Grey Band Danian	Sevel	Dan	0,135	94,18	5,35	106	466,0	Högsb2012
Grey Band Danian	Sevel	Dan	0,154	93,82	5,57	93	441,0	Högsb2012
Grey Band Danian	Mønsted	Dan	0,126	97,69	1,64	178	178,0	Högsb2012
Grey Band Danian	Mønsted	Dan	0,210	97,06	1,95	305	171,0	Högsb2012
Red-Brown Bryozoan	Odby*	Dan	0,000	99,55	0,26	123	60,0	Högsb2012
Red-Brown Bryozoan	Odby*	Dan	0,119	99,32	0,28	60	62,0	Högsb2012
Red-Brown Bryozoan	Bjerge by*	Dan	0,264	98,97	0,30	94	97,0	Högsb2012
Red-Brown Bryozoan	Helligkilde*	Dan	0,120	98,73	1,06	23	105,0	Högsb2012
Brown Bryozoan	Fakse	Dan	0,130	99,41	0,30	93	56,0	Högsb2012
Brown Bryozoan	Vokslev	Dan	0,000	99,59	0,25	61	62,0	Högsb2012
	Dan middle		0,179	98,29	1,19		154,1	
	Dan mean		0,154	98,99	0,33		122,0	

* Lokality on salthorst

Kristianstadflint

Type	Lokality	Age	Al_2O_3 %	SiO_2 %	CaO %	Cl ppm	Fe ppm	
Kristianstad, black	Hanaskog	Maast	0,778	97,88	0,46		1737,0	Högsb2012
Kristianstad, black	Hanaskog	Maast	0,415	98,61	0,34		1661,0	Högsb2012
Kristianstad, black	Hanaskog	Maast	0,231	98,34	1,01		1097,0	Högsb2012
	Hanaskog Middle		0,475	98,28	0,602		1498,3	

Ordovisian flint

Type	Lokality	Age	Al_2O_3 %	SiO_2 %	CaO %	Cl ppm	Fe ppm	
Ordovician	Öland	Ordo.	1,17	81,40	15,90		7118	Högsb2012
Kinnekulle	Kinnekulle	Ordo.	0,50	98,33	0,41		441	Högsb2012

Paramoudra flint

Paramoudra	England	Camp.	0,027				150	Clayton1983
Paramoudra	England	Camp.	0,025				1000	Clayton1983

Patineret flint

Patinated flint		1,72	96,82	0,04		3763	Högsb2012
Unpatinated flint		0,14	99,31	0,37		118	Högsb2012