THE OCCURRENCE OF CLINOPTILOLITE-REPLACED FORAMINIFERA IN THE DANISH UPPER SELANDIAN NON-CALCAREOUS GREENSAND

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Evidence from clinoptilolite-replaced foraminifera shows that the Upper Selandian non-calcareous greensand must belong stratigraphically to the Paleocene. The presence of clinoptilolite-replaced foraminifera indicates that the low $CaC0_3$ content at least partially is caused by diagenetic changes in connection with precipitation of the clinoptilolite. The source of the solutions allowing clinoptilolite to precipitate is unknown but may be connected with early Tertiary volcanism. The formation of the clinoptilolite is autigenic.

Only a few authors have so far published information concerning the Upper Selandian non-calcareous deposits. As the boundary between the Paleocene and the Eocene was drawn on purely lithological evidence the present authors decided to investigate the Upper Selandian non-calcareous greensand for microfossils. Besides foraminifera small white spherical bodies were frequently found in the wash residues. Through the kindness of dr. phil. H. Gry, Danish Geological Survey, the authors hand opportunity to study Dr. Gry's thin sections of silicified nodules from the non-calcareous greensand from Rugaard. It was found that the white spheres were identical with what Gry in 1935 desribed as "radiolarian skeletons".

Locality and Fauna

The Upper Selandian non-calcareous greensand is known to crop out only in the coast cliff at Rugaard in Jutland (fig. 1). From borings in other parts of Denmark Grönwall (1908), Bøggild (1918) and Gry (1935) described the succession of the Selandian in ascending order as: Lower Selandian Greensand Marls (Lellinge Greensand) – Kerteminde Marl – Upper Selandian non-calcareous greensand – Upper Selandian non-calcareous clay (the last is known only from borings). The same succession is found in the cliff at Rugaard from north towards south. The Lower Selandian marls crop out in the northern part of the cliff at locality 1. These deposits and their fossil content have been described by Grönwall and Harder (1907) and by Franke (1927). The sediments are all glacial displaced blocks which today crop out as 2–3 m high sections along the coast. Kerteminde Marl crops out at locality 2 while the Upper Selandian non-calcareous greensand is found at locality 3. At locality 3 is seen a stratified, slightly disturbed series of about 3 m thickness. The sediment consists of quartz and glauconite grains in a predominantly clay matrix. Silicified nodules occur rather frequently in the upper part of the Selandian. In thin sections made of nodules from the non-calcareous greensand from Rugaard small white spheres ("radiolarian skeletons") constitute more than 1 % of the rock.

Gry (1935) mentioned as characteristic for the non-calcareous Upper Selandia rocks among other things the occurrence of the same type of "radiolarian skeletons", and of silicified beds and sponge spicules. He further stated that the non-calcareous greensand did not contain any fossils except for a few silicified foraminiferal shells.

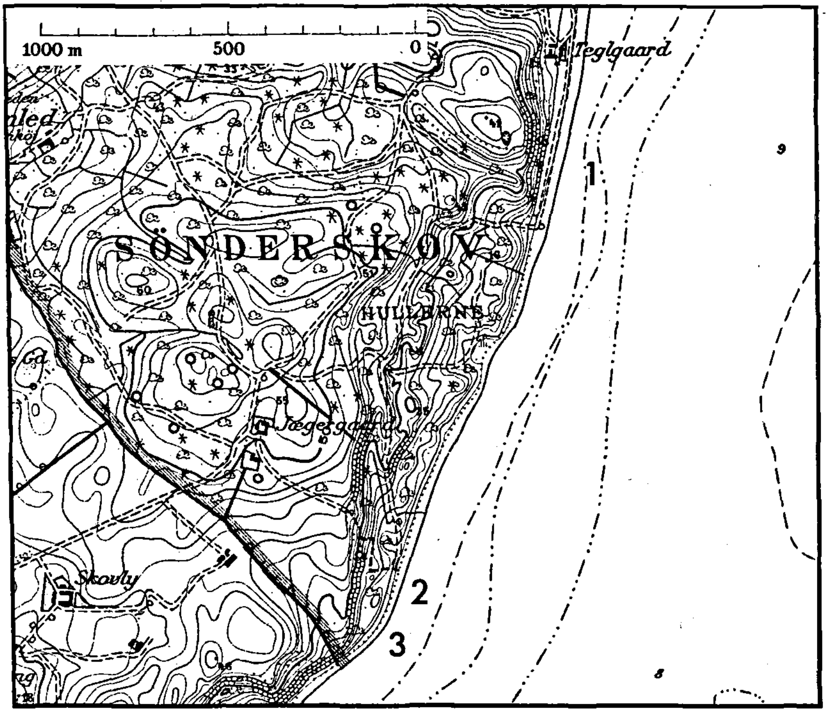

Fig. 1. Map of the coast cliff south of Rugaard, Central East Jutland. Locality 1: Lower Selandian greensand marl; Locality 2: Kerteminde Marl; Locality 3: Upper Selandian non-calcareous greensand.

An intensive search for foraminifera by the present authors revealed a restricted, but undoubtedly Paleocene fauna. In the non-calcareous greensand almost all shells have been replaced and are found in the wash residues together with white spheres.

The fauna is composed of the following species of which *Bulimina trigonalis* is the dominant:

Bulimina trigonalis Dam
Cibicidoides proprius Brotzen
Bulimina midwayensis Cushman & Parker
Gyroidinoides octocamerata Cushman & Hanna
Pullenia americana Cushman
Nodosaria latejugata Gümbel
Melonis nobilis Brotzen
Allomorphina halli Jennings
Lenticulina spp.

When the wash residues were treated with 10 % HCl the main part of the foraminifera and all the white spheres were left unaffected. It was therefore decided to investigate the shell material of the evidently replaced foraminifera. As, however, the chambers in most specimens were filled in with sediment of which they could not be freed, the white spheres were chosen for study instead as they were free of internal sediment impurities. The material of the white spheres had the same optical and physical properties as the wall material in the replaced foraminifera.

The white spheres

The shape of the spheres varies from globular to subglobular and may even attain a bean shape. Their largest diameter ranges from 60 to 150 μ.

Thin sections show that the spheres often posess a central cavity (pl. 1, fig. 1). The thickness of the wall is about 30 μ or less. It is penetrated by numerous channels with a diameter of about 2.5 μ. The wall between the channels is about 1.2 μ thick.

The central cavity is lined or in some cases filled in with material of the same composition as the sphere itself or by opal, but differs from the wall in not having channels.

The surface of the spheres is sculptured by the elevated terminations of the channels (pl. 1, fig. 2; pl. 2, figs 1 and 2).

In thin section the spheres appear colourless and transparent with a refractive index of 1.469 ± 0.002 and very low birefringence. The refractive index has been determined by the immersion method.

The spheres were not affected by boiling in 20 % HCl for 30 minutes (see Gilbert & McAndrews, 1948). A heulandite crystal from the collection of the Mineralogical Museum of the University of Copenhagen disintegrated in the course of 2 minutes during the same treatment.

X-ray diffractometry

The amount of material used here was less that 0.1 mg. It was cleaned by boiling in 20 % HCl for 15 minutes and later in demineralized water. The spheres were mounted on non-reflecting adhesive tape and were run in a Guinier camera for a period of 6 hours. The values of d(Å) obtained and the relative intensities compared to the corresponding values of a typical clinoptilolite and a typical heulandite (Mumpton, 1960) are recorded in table I.

The clinoptilolite spheres are constructed of crystal elements with a size ranging from 1.4 to 0.3 μ. A fractured sphere studied in scanning electron

Table I. Lattice spacings of clinoptilolite from Rugaard, Denmark, Hector, California (ASTM 13–304), and heulandite from Prospect Park, New Jersey.

Clinoptilolite Rugaard, Denmark		Clinoptilolite Hector, California		Heulandite Prospect Park, New Jersey	
d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0
8.96	10	9.00	10	8.90	10
7.92	10	7.94	4	7.94	2
6.78	2	6.77	3	6.80	1
6.64	2	6.64	2	6.63	1
–	–	5.91	1	5.92	1
–	–	–	–	5.58	1
5.24	4	5.24	3	5.24	1
5.12	8	5.11	1	5.09	1
–	–	–	–	4.89	1
4.65	6	4.69	2	4.69	2
–	–	4.48	2	4.45	2
4.32	6	4.34	2	4.36	1
3.96	10	3.96	10	3.97	2
3.90	8	3.90	8	3.89	3
3.84	2	3.83	1	3.83	1
3.70	2	3.73	1	3.71	1
3.55	6	3.55	2	3.56	1
–	–	3.46	2	3.47	1
3.42	8	3.42	6	3.40	2
3.13	3	3.12	3	3.12	1
3.07	4	3.07	2	3.07	1
3.03	2	3.04	2	3.03	1
2.97	6	2.97	5	2.97	4
–	–	2.87	1	–	–
–	–	2.82	3	–	–
2.80	6	2.80	1	2.80	1
–	–	2.73	1	2.72	1
–	–	2.72	1	–	–
–	–	2.68	1	2.67	1
–	–	2.44	1	2.48	1
–	–	2.42	1	2.43	1
–	–	2.38	1	2.35	1
–	–	2.29	1	2.28	2

Rugaard: X-ray pattern was made using Guinier technique with Cu-Kα radiation. Silicon served as internal standard. Time of exposure 6 hours. *Hector* and *Prospect Park* analyses after Mumpton (1960).

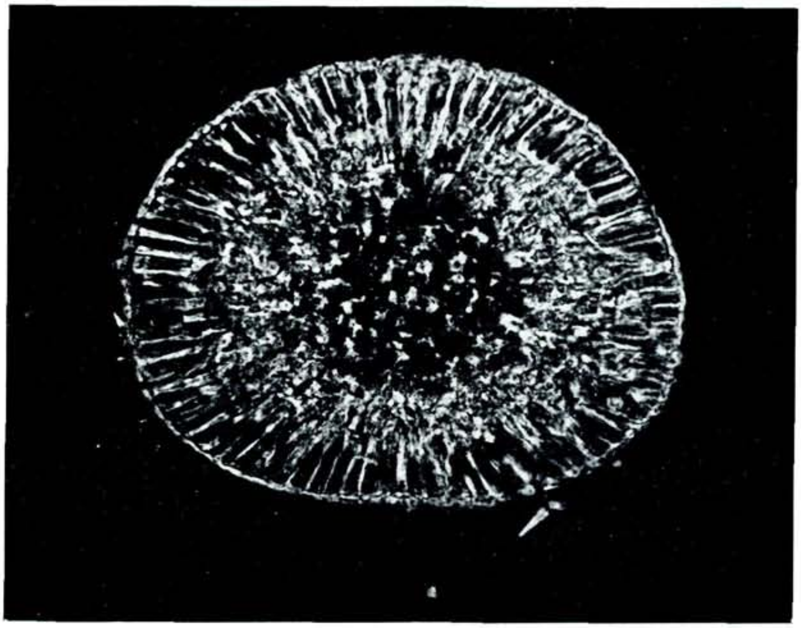

Fig. 1. Thin section of a clinoptilolite sphere. Transmitted light. Phase contrast. × 486. Locality 3, Rugaard.

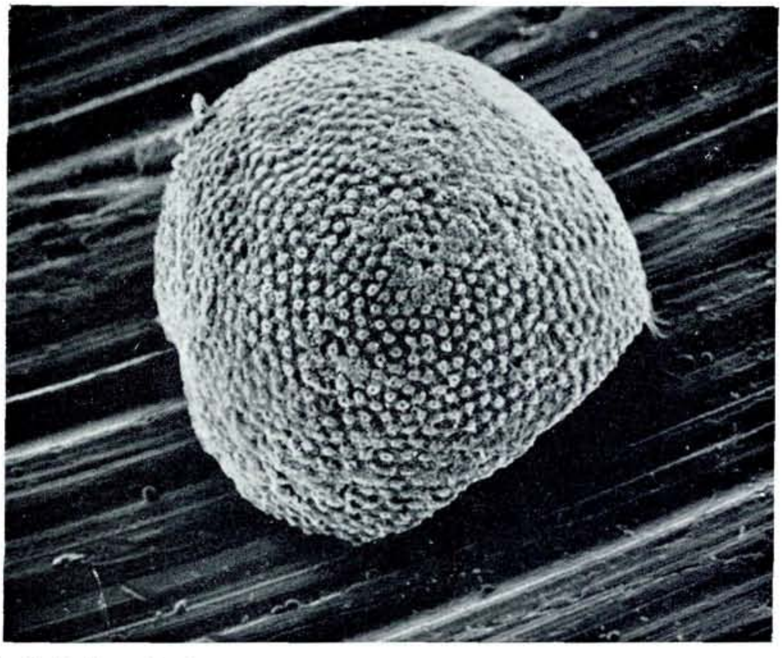

Fig. 2. Surface of a fractured clinoptilolite sphere. Scanning electron micrograph. × 420. Locality 3, Rugaard.

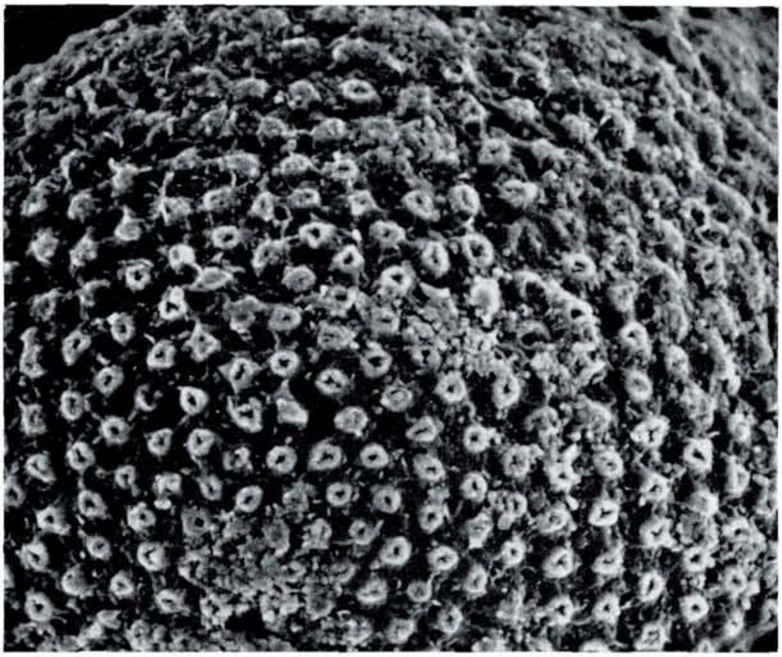

Fig. 1. Detail of pl. 1, fig. 2. Scanning electron micrograph. × 1200.

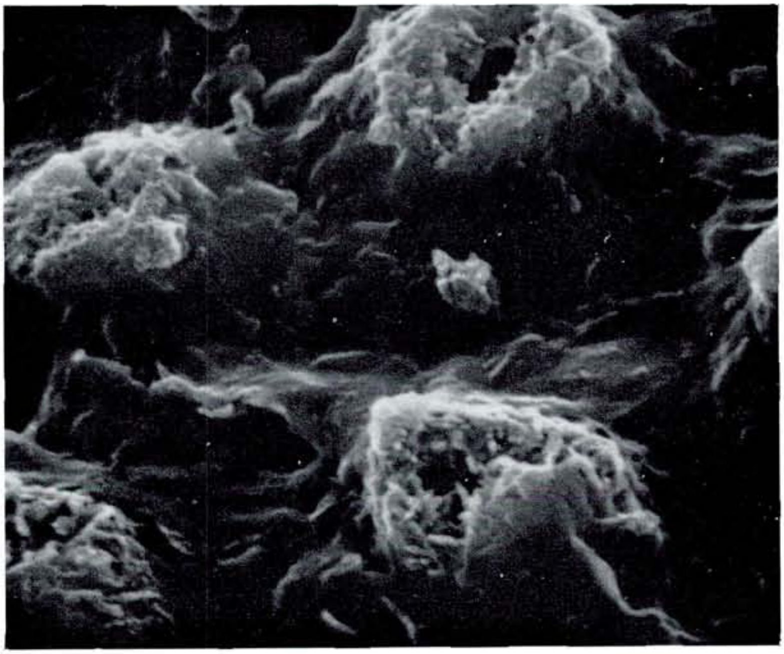

Fig. 2. Detail of pl. 1, fig. 2. Scanning electron micrograph. × 10000.

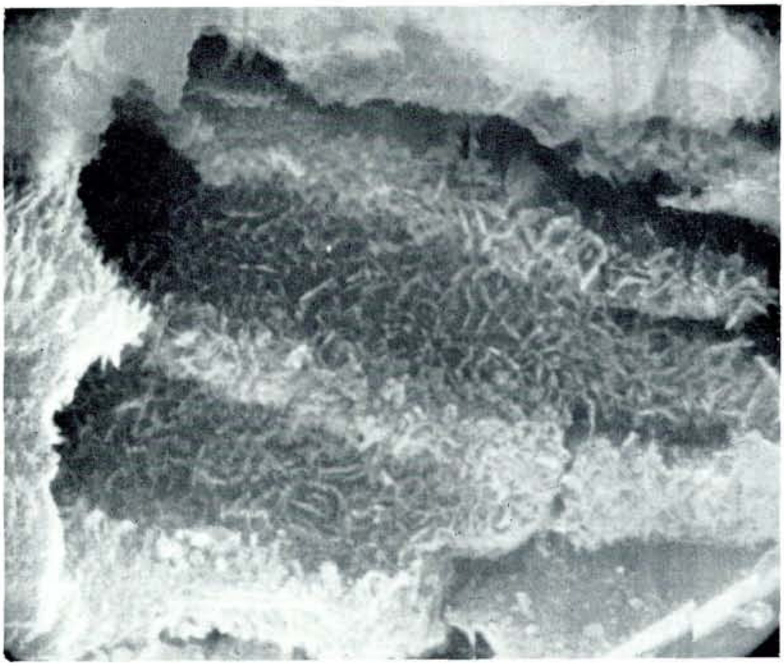

Fig. 1. Detail of fractured clinoptilolite sphere. Scanning electron micrograph. × 7700. Locality 3, Rugaard.

Fig. 2. Detail of interior termination of the channels in a clinoptilolite sphere. Electron micrograph of a two-stage replica. × 9000. Locality 3, Rugaard.

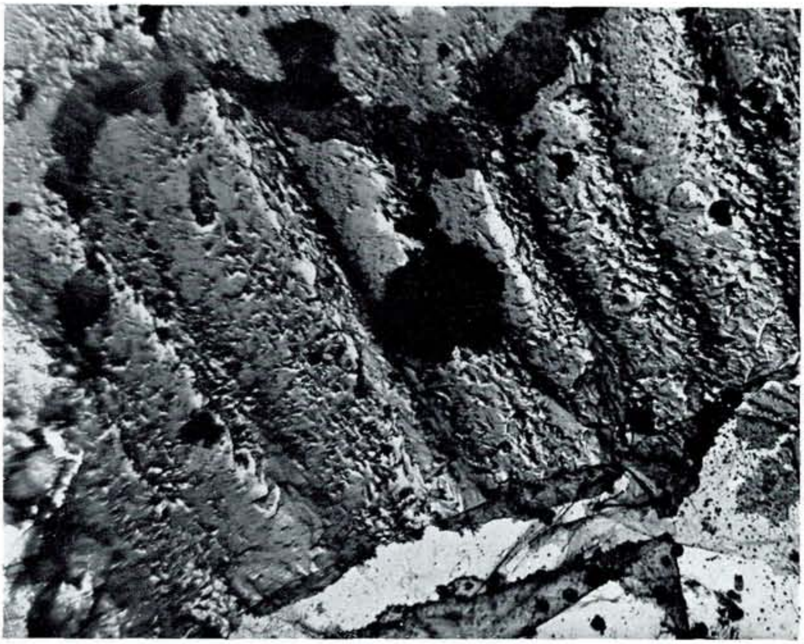

Fig. 1. Details of a sectioned clinoptilolite sphere showing the radiating channels. Electron micrograph of a two-stage replica. × 4500. Locality 3, Rugaard.

Fig. 2. Detail of fig. 1 showing crystals lying oblique to the channels. × 18900.

microscope showed that the crystal faces stick out into the channels (pl. 3, fig. 1). The same phenomenon was observed in sectioned and replicated specimens studied in a transmission electron microscope (pl. 3, fig. 2; pl. 4, figs 1 and 2). The free crystal faces in the channels appear to be parallel in orientation and seem to have a constant angle to the channel direction (pl. 3, fig. 2; pl. 4, figs 1 and 2).

It is seen that the X-ray pattern of the sample from Rugaard is similar both to that of heulandite and clinoptilolite and with regard to d-values the three samples can not be distinguished.

According to Mumpton (1960), however, heulandite and clinoptilolite can be distinguished by the intensities of the reflection. Thus the reflection of clinoptilolite is consistently much stronger than that of heulandite. In particular the reflections of clinoptilolite at about d = 8.96 (9°.87 2θ), d =3.96 (22°.46 2θ) and d = 3.90 (22°.81 2θ) are of nearly equal relative insensities in contrast to the reflections of heulandite where d = 8.96 (9°.87 2θ) is far more intense than the remaining lines of the pattern.

A comparison of the intensities shows a strong similarity between the sample from Rugaard and the clinoptilolite and distinct difference from the heulandite. The average refractive index of 1,469 ± 0.002 also indicates that the Rugaard material is more similar to clinoptilolite with $n\beta < 1.485$ than to heulandite with $n\beta > 1.488$ (Mason & Sand 1960).

The conclusion is that the solution test in HCl, the X-ray diffration pattern and the optical properties all indicate that the Rugaard material consists of clinoptilolite rather than of heulandite.

Discussion and conclusions

Accordning to Deffeyes (1959) both clinoptilolite and analcime are known to occur widely in sedimentary rocks and a survey of the known occurrences of sedimentary zeolites by Deffeyes shows that most, if not all, of these minerals were formed during diagenesis in connection with the alteration of volcanic material. Opal is often present, probably precipitated in connection with the precipitation of a zeolite which has a lower silica content than had the original glass.

Hay (1963) recorded an alteration of volcanic glass to clinoptilolite, opal and montmorillionite and a replacement of the vitric material by clinoptilolite. In some cases the precipitation of opal was contemporary with clinoptilolite development and in other cases it occurred later.

Staples (1965) described zeolite filling and replacement of shells of fossil molluscs by heulandite and stilbite. The zeolite material was suggested by Stables to be connected with hydrothermal solutions related to the intrusion of a basaltic dyke cutting the sedimentary sequence.

Gry (1935) found in the Middle Selandian sediments silicified nodules with dissolved sponge spicules and diatoms represented by pyrite moulds. The nodules were suggested by Gry to have arisen through precipitation of silicious material from the dissolved silicious organisms. In the nodules in the Upper Selandian rocks well preserved sponge spicules are frequently found. This would seem to indicate that the silica, to some extent, has come from another source than the above mentioned. In the clinoptilolite spheres the presence of inner linings of opal would indicate that the clinoptilolite precipitation was followed by precipitation of opal.

It is noteworthy that the lower part of the non-calcareous greensand contains relatively few replaced foraminifera in comparison with the upper part and that the clinoptilolite spheres are less perfectly developed while their diameter in general is smaller.

In the non-calcareous greensand Gry found only 0–5 % $CaCO_3$ and noted that there occurred a few silicified foraminifera. The replaced foraminifera found by the present authors in these layers must have represented a higher $CaCO_3$ content prior to diagenesis. The replaced foraminifera further indicate that the formation of clinoptilolite in the sediment is autigenic.

The frequent occurrence of silicified nodules, clinoptilolite spheres and replaced foraminifera in the non-calcareous greensand all point to a diagenetic change of the sediment which, considering Deffeyes' conclusions, most likely is connected with devitrification of volcanic material.

The presence of volcanic material in the nearness of the sedimentary basin being the source of the solutions allowing the authigenic clinoptilolite to precipitate, is also indicated by the clay mineralogy of the Selandian deposits described by Tank (1963). Tank showed that the content of montmorillionite increased from the bottom to the top of the sedimentary sequence.

The unusual morphology of the spheres, especially the channels and their elevated terminations on the surface, would suggest that they represent some kind of replaced organism, possibly a calcareous one in view of the replaced foraminifera. However, the fossil content of the sediment does not give any indication as to what kind of organism could give rise to spheres with this peculiar morphology.

According to information from mag. scient. T. Christensen, Department of Botany, University of Copenhagen, it is highly unlikely that it could be replaced algae remains; mag. scient. K. Raunsgaard Pedersen, Geological Institute of the University of Aarhus, kindly investigated the sediment for spores and pollen but found nothing which could have caused the peculiar morphology of the clinoptilolite spheres.

The doubt as to the biostratigraphical position of the non-calcareous greensand due to lack of fossils seems unjustified. The foraminiferal fauna, although restricted, definitely points to a Paleocene age. The dominance of *Bulimina trigonalis* Dam is in good agreement with the faunas known from the underlying Kerteminde Marl and from the Paleocene of Holland (ten Dam, 1944).

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Dansk sammendrag

Baseret på fundet af clinoptilolit-replacerede foraminiferer kan det vises, at det kalkfri grønsand, der henføres til det øvre Selandien, i stratigrafisk henseende må placeres i Paleocænet. Tilstedeværelsen af foraminiferskaller replaceret af zeolitmineralet clinoptilolit tyder på, at det lave kalkindhold i bjergarten til en vis grad må skyldes replacering af kalk med clinoptilolit. Udskillelsen af clinoptilolit er utvivlsomt knyttet til den nedre tertiære vulkanisme der blandt andet viser sig i de Eocæne askelag.

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