

Geochemical properties of the marine Younger Miocene at Gram, SW Jutland

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The marine Younger Miocene at Gram, SW Jutland, has been examined chemically. The Hodde Clay may be subdivided on the basis of a high, but varying content of organic matter. In the Gram Clay, carbonate, manganese and phosphorus are enriched in beds with clay ironstone concretions. The composition of the sand fraction indicates that the sequence has been subject to diagenetic processes. The Hodde Clay may have been deposited in an estuarine environment with a periodically strong sedimentation of allochthonous terrestrial humic matter. The Glauconite Clay and the basal goethite-rich bed of the Gram Clay indicate an agitated and oxygenated environment, which changes to less agitated and more marine conditions during deposition of the Gram Clay.

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The marine Younger Miocene in Denmark has been encountered in the central and western part of Jutland as shown in fig. 1. The sediments consist of clays which have been divided into the Hodde Formation (Middle Miocene) comprising Hodde Clay with a basal layer of quartz gravel, and the Gram Formation (Upper Miocene) comprising Glauconite Clay overlain by Gram Clay. In the most southwesterly part of the area the Gram Clay is overlain by more sandy sediments, which are thought to be of Upper Miocene age (Rasmussen 1973).

The marine sequence has been studied biostratigraphically on the basis of the molluscs by Rasmussen (1956, 1961, 1966 and 1973) and on the basis of the foraminifera by Kristoffersen (1972, 1973 and 1974). Sedimentological and paleobotanical investigations on sediments from the limnic-marine border zone in the Søby-Fasterholt area (fig. 1) have been described by Larsen and Friis (1973), Koch et al. (1973) and Christensen (1975). Trace fossils from the base of the Hodde Formation have been studied by Asgaard and Bromley (1974).

The clays have been deposited in the North Sea Basin, whose shore zone

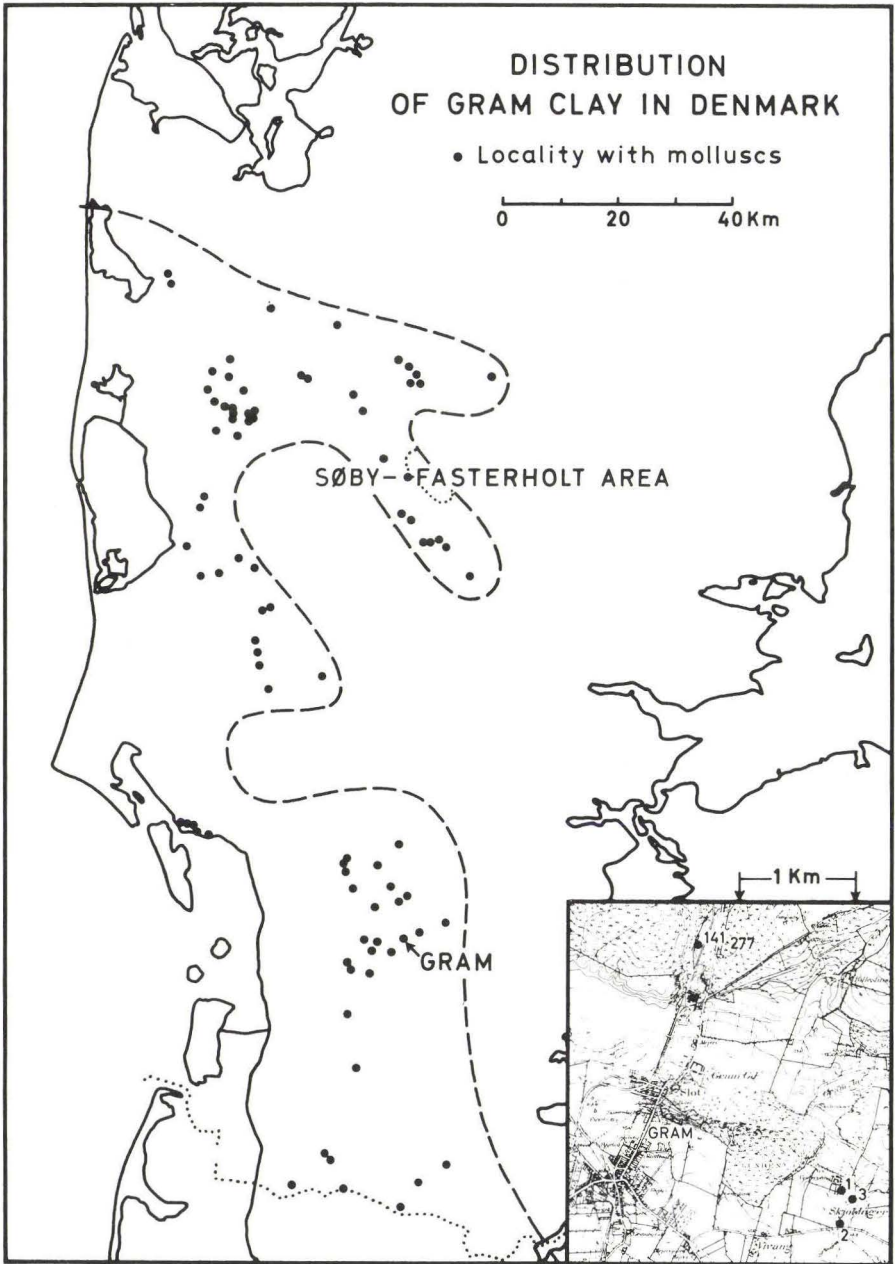


Fig. 1. Locality map and distribution of the marine Younger Miocene (after Rasmussen 1966).

has oscillated over parts of Jutland during Miocene time. The sea has been bordered by widespread low swampy areas with occasional formation of brown coal. In the Søby-Fasterholt area, the Hodde Clay rests transgressively on deltaic sands and is thought to represent a brackish lagoon facies, while the Gram Clay is attributed to a more marine environment (Koch et al. 1973).

The present investigation is based on material from the Gram locality (fig. 1), where 3 borings were drilled in 1968 as part of a survey for Mica Clay carried out by the Institute for Applied Geology. The borings have been examined chemically by the author, while foraminiferal analyses have been performed by Nyhuus Kristoffersen, Geological Survey of Denmark. Because the fossils are rather badly preserved, a neighbouring boring, DGU File No. 141.277 (Rasmussen 1966), has been included in the chemical examination. Results of the chemical investigation are presented here, while the foraminiferal analyses will be published later.

The sediments

The sequence penetrated by the borings is shown on the borehole logs, plates 1–3. The Miocene clays consist of brownish black, carbonaceous, shaly Hodde Clay, which is overlain by dark brown, slightly greenish, sandy, glauconitic clay (Glauconite Clay), this being further overlain by greyish brown, slightly sandy Gram Clay. They are covered by a few meters of Quaternary deposits and are in boring No. 1 underlain by at least 7 meters of micaceous sand and gravel, rich in quartz. The complete log of boring No. 141.277 has been given by Rasmussen (1966), pp. 146–147.

A general description of the clays is given in the Lithology section on plates 1–3. In addition to the larger concretions shown on the logs, smaller fragments have been found in the sand fraction as described below. According to preliminary X-ray determinations, the larger concretions consist of siderite, in boring No. 1 (3,65–4,00 m) of siderite and calcite.

The sand fraction is in general composed of the following components:

Detrital minerals: muscovite and quartz as small angular grains and larger, well rounded, often milky grains.

Pellets of different size, shape and colour.

Stems and slaglike fragments of pyrite, often with inclusions of detrital minerals and pellets.

Crystals of gypsum, often coated with calcium carbonate.

Porous fragments of calcium carbonate with inclusions of detrital minerals.

Small fragments of concretions containing calcium and iron carbonate, partly oxidized, with inclusions of detrital minerals and pellets.
Fragments of limonite.

Gypsum and fragments of carbonates and limonite are found in varying amounts throughout the sequence. On the basis of content of detrital minerals and different types of pellets, the sequence can, however, be divided into the five lithozones shown on the plates. These are described below.

I. (Lower Hodde Clay). Detrital minerals and dark green pellets. Quartz as dominating component at the basal layers, but of decreasing importance upwards. Pyrite of minor importance.

II. (Upper Hodde Clay). Dark green and light green pellets, both ellipsoidal and irregularly shaped. Minor amounts of grey and brown pellets. Stems and slags of pyrite. Often high amounts of limonite fragments and gypsum crystals coated by limonite. Detrital minerals, especially muscovite.

III. (Glauconite Clay). Extreme dominance of dark green pellets, some ellipsoidal, but mostly irregularly shaped with shrinkage fractures. Minor amounts of light green ellipsoidal pellets and minute amounts of brown pellets. Almost no pyrite, but crystals of gypsum and fragments of limonite. Detrital minerals and concretions of minor importance.

IV. (Lower Gram Clay). Dominance of brown, glistening pellets and of light brown, more irregularly shaped pellets with shrinkage fractures. A few grey, but almost no green pellets. Pyrite and detrital minerals of minor importance. Many small concretions.

V. (Upper Gram Clay). Pellets dominated by black and greyish micro-ellipsoids. Light greenish, more irregularly shaped pellets with shrinkage fractures are found in the lowermost meter of the section. Smaller irregularly shaped grey clay (?) aggregates. Pyrite as stems and slaglike fragments. Muscovite and, especially, quartz of increasing dominance upwards. Many small concretions.

According to X-ray diffraction data, the brown glistening pellets (lithozone IV) have been identified as goethite. The black microellipsoids have given an unspecific pattern. They are apparently composed of a mixture of de-

graded clay minerals, and not of pyrite as those described by Valeton (1959). The different greyish-greenish pellets are thought to represent glauconites of different composition as found by Valeton (1958) and by Giresse and Odin (1973).

Analytical methods

Carbonate. Carbonate is determined by liberating carbon dioxide through boiling HCl and absorbing it in soda lime after purification by passing it through anhydrous calcium chloride and copper sulfate.

Accuracy: $\pm 2\%$ (rel.).

Sulfur. Total sulfur is determined gravimetrically as BaSO₄, according to Rasmussen (1961), p. 53.

Accuracy: $\pm 3\%$ (rel.).

Phosphorus and manganese. Phosphorus and manganese are determined colorimetrically in aliquots after decomposition of the sample and removal of organic matter, by repeated evaporations with HF and HClO₄. Phosphorus is determined as the yellow molybdovanadophosphoric acid complex (460 m μ) and manganese as permanganate (525 m μ) according to Maxwell (1968), p. 387 and 392.

Readings on standard solutions have proved that up to 10% of the phosphorus may be volatilized during the decomposition. The amount volatilized by a given decomposition is, however, proportional to the original P concentration, and correction may, therefore, be made by including a standard in each evaporation series and measuring against this.

Accuracy: $\pm 3\%$ (rel.) and $\pm 2\%$ (rel.), respectively.

Organic carbon. Organic carbon is calculated as total carbon \div carbonate carbon. Total carbon is determined by a combustion-gravimetric method modified from Maxwell (1968), pp. 436–438.

Accuracy: $\pm 1\%$ (rel.).

Nitrogen. Total nitrogen is determined by the Kjeldahl method given by Jackson (1964), pp. 183–187. It has been found that various amounts of the nitrogen – from 0% to about 20% – may occur as nitrate in the samples. Nitrate nitrogen has, therefore, been included in all determinations.

Accuracy: $\pm 2\%$ (rel.).

Humic matter. Humic matter is extracted by caustic alkali both directly and after preliminary decalcification of the sample. The alkali extract is fractionated into fulvic acid and humic acid, and the fractions are determined by oxidation with potassium dichromate.

The extraction and fractionation procedure is a simplified modification of a classical scheme discussed by many authors, e.g. Kononova (1958), Kononova and Bel'chikova (1961) and Stevenson (1965).

Decalcification of the sample is achieved by treatment with 5 % HCl for half an hour in a boiling water bath. After centrifugation, the sample is washed several times with water. The amount of extractable humic matter after this short treatment with hot 5 % HCl is the same as after 24 hours' treatment with the often used, milder reagent cold 0,1 N HCl – and no difference in composition as revealed by UV-visible spectra could be noticed. Shorter treatment with cold 0,1 N HCl results in smaller, nonreproducible amounts of extractable matter.

Extraction of humic matter is carried out by treatment with 50 ml 0,1 N NaOH in a boiling water bath for one hour. After centrifugation, the extraction is repeated in the same way with 20 ml 0,1 N NaOH for half an hour and the sample is washed with cold 0,1 N NaOH. The extracts and washing solutions are combined and diluted to 100 ml (solution A).

In order to precipitate humic acid, 50 ml of solution A is acidified to about pH 1 with 4N H₂SO₄ and kept in a water bath at 40°C for half an hour. After centrifugation, the remaining solution is diluted to 100 ml with 0,1 N H₂SO₄ (solution B). The centrifugation of solution B is repeated the next day for removal of small amounts of humic acid which may have been precipitated during the night. The precipitated humic acid is dissolved in 0,1 N NaOH and diluted to 100 ml (solution C).

Aliquots of the solutions A, B and C are carefully evaporated to about 5 ml (solution B after being made slightly alkaline) and are oxidized according to Rauterberg and Kremkus (1951).

Accuracy: In determination of the solutions A, B and C it has been generally accepted that $A \div (B + C)$ is less than 5 % rel. to A. Accuracy of extraction seems to vary with the type of the sediment, being about ± 3 % (rel.) for Hodde Clay, but up to ± 5 % (rel.) for Glauconite Clay and Gram Clay.

Trace elements. These elements have been determined by atomic absorption (Perkin Elmer model 303) after decomposition of the sample with HF and HClO₄.

Accuracy: Deviations less than the following ppm values are not regarded as significant: Li 5, Cr 10, Co 5, Ni 5, Cu 5, Zn 10, Sr 10, and Pb 5.

Results

The material consists of 4 kg composite samples which have been air dried and stored at room temperature and also of some 15 cm tube samples (intact samples). Humic matter has been determined on air dried material, while all other determinations are made on material dried at 110°C. Sampling intervals and results of the analyses are shown on plates 1–3.

Organic matter. Hodde Clay is characterized by a high, but varying content of organic matter – up to 12 % C_{org} or 20 % organic matter – showing 3 marked maxima and a fourth at the basal layers penetrated by boring No. 1, 2 and DGU File No. 141.277. Glauconite Clay and Gram Clay are in contrast poorer in organic matter with a rather constant value of 1–2 % C_{org} .

C/N ratio. The C/N ratio shows a marked correlation to lithology. In Hodde Clay, C/N varies in the same way as organic carbon, reaching maximum values of about 40 – in bor. No. 3 even higher – at intervals with maximum carbon content. Glauconite Clay and Gram Clay are, on the other hand, characterized by a lower but rather constant level of 15–20.

It must, however, be noticed that the C/N ratios are based on total nitrogen and therefore can not be used for characterization of organic matter, unless a correction is made for inorganic nitrogen. As already stated, varying amounts of nitrate were found in the samples. This might be due to nitrification of exchangeable ammonium – a process which has been demonstrated in situ for Paleocene shales when they were exposed to atmospheric conditions (Power et al. 1974). Inorganic nitrogen has not been determined, but by plotting carbon against nitrogen, however, it is possible to get an idea of the amount. From fig. 2 it appears that the amount of inorganic nitrogen is the greatest for Hodde Clay – the corrected mean C/N ratios for Hodde Clay and for Glauconite and Gram Clay being 52,9 and 20,7, respectively.

Thus it may be stated that the composition of the organic matter in Hodde Clay is subject to a characteristic variation throughout the series, showing highest C/N ratios in the carbon maxima. In contrast, the organic matter in Glauconite Clay and Gram Clay seems to be of constant composition with respect to the C/N ratios, these being far lower than for Hodde Clay.

Humic matter. The term “humic matter” is used for the dark coloured alkali extractable part of the organic material. By acidification of the alkali extract it may be fractionated into humic acid, which precipitates, and fulvic acid, which remains in solution. There is, however, no sharp division

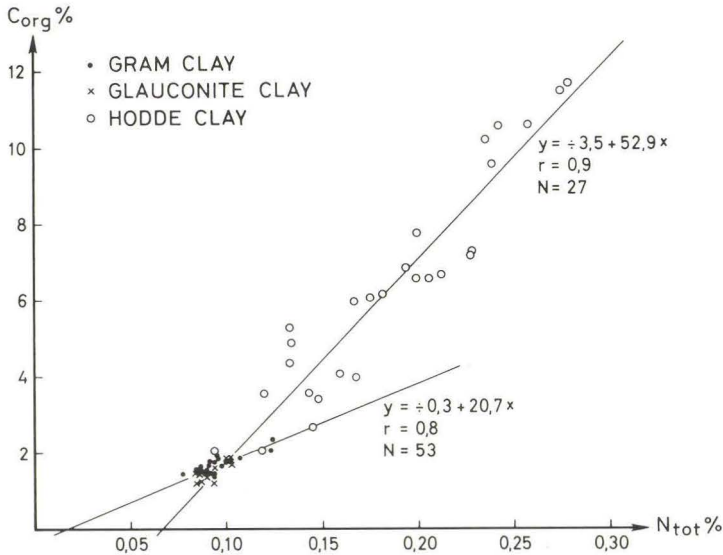


Fig. 2. Organic carbon – total nitrogen correlation (bor. No. 1).

between the two fractions. Both are polymer mixtures, humic acid representing the highest molecular weights and degree of polymerization. Further details regarding fractionation and the chemistry of humic matter in general are given by e.g. Swain (1963) and Stevenson and Butler (1969).

Humic matter may be bound to the mineral part of the sediment in different ways, and it has often been found that the amount of alkali extractable matter is increased by a prior acid treatment (Scheffer and Welte 1950b, Kononova and Bel'chikova 1961).

In the present study, humic matter has been extracted as well directly as after a prior acid treatment. The alkali extracts have been fractionated into humic acid and fulvic acid, but these fractions may not be regarded as either pure or free from artifacts, since the rather tedious procedures to obtain this – e.g. as described by King (1967) – have not been followed. The amounts of the fractions are expressed in relation to the organic carbon in terms of their reducing power (milliequivalents/0,1 g C_{org}).

It may be noticed from plates 1–3 that fulvic acid constitutes only $1/5$ – $1/10$ of the humic matter, being rather constant throughout the formations and unaffected by the acid treatment. The level of total humic acid, as determined in acid treated samples, is slightly higher in Hodde Clay than in Glauconite Clay and Gram Clay. The most striking feature however, is, that the amount of easily extractable humic acid varies according to organic

carbon and C/N ratio. In Hodde Clay, almost all humic acid is easily extractable in the carbon maxima, while some bound humic acid occurs in the carbon minima. In Glauconite Clay and Gram Clay, easily extractable humic acid constitutes only half or less of the total humic acid. Special attention must be drawn to the anomalous pattern at the basal layer of the Hodde Clay as found in boring Nos. 1 and 2, but not in DGU File No. 141.277. Here an extremely high content of humic matter is not reflected either in carbon content or in C/N ratio.

Weight analytical determination of humic acid has been carried out for boring No. 1, the precipitated humic acid being washed and dried at 40°C to weight constancy. In fig. 3, the weight analytical results are plotted against the titration values. Some correlation may be noticed for the easily extractable humic acids, but for total humic acid this is absolutely not the case, especially not for Glauconite Clay and Gram Clay. This is considered to be due to unreliability of the weight analytical results, mainly because the precipitates are contaminated, as exemplified by the following ash contents: up to 75 % for total humic acid from Gram Clay and about 25 % for easily extractable humic acid from Hodde Clay, while purified humic acid may have 6–7 % ash content.

A possible way of obtaining weight analytical results might be to use the reagent Humic Acid from FLUKA as a standard, this reagent showing a titer value of 25 mequ./g reagent. This material, however, is also contaminated, showing an ash content of 29 %. Taking this into account and using a conversion factor 1,724 for calculating organic matter from C_{org} , one may find that up to $\frac{4}{5}$ of the organic matter may consist of easily extractable humic acid as exemplified by boring No. 1 (17,56–18,00 m). Such calculations, however, are only very approximate, and weight analytical results as a whole are not presented here.

Relation between titration values and light absorption is also shown in fig. 3. By measuring at 400 nm (visible range), a fairly good correlation exists for easily extractable humic matter, but not for total humic matter, and this effect is more pronounced when measuring at 250 nm (UV region). This may be due to varying composition of the humic matter, but taking the high ash contents of the humic acids into account, it seems more likely that it could be caused by coagulation of siliceous matter. If this is the case, colorimetric methods, as used e.g. by Bahnson (1968) in determination of humic matter in peat, may not be suitable for clay sediments.

Humic matter has been further characterized by means of absorption spectra in the ultraviolet-visible region. The spectra show no characteristic maxima or minima and are not suited for structural analyses like IR spectra (Stevenson and Butler 1969) and ESR spectra (Pedersen and Willumsen

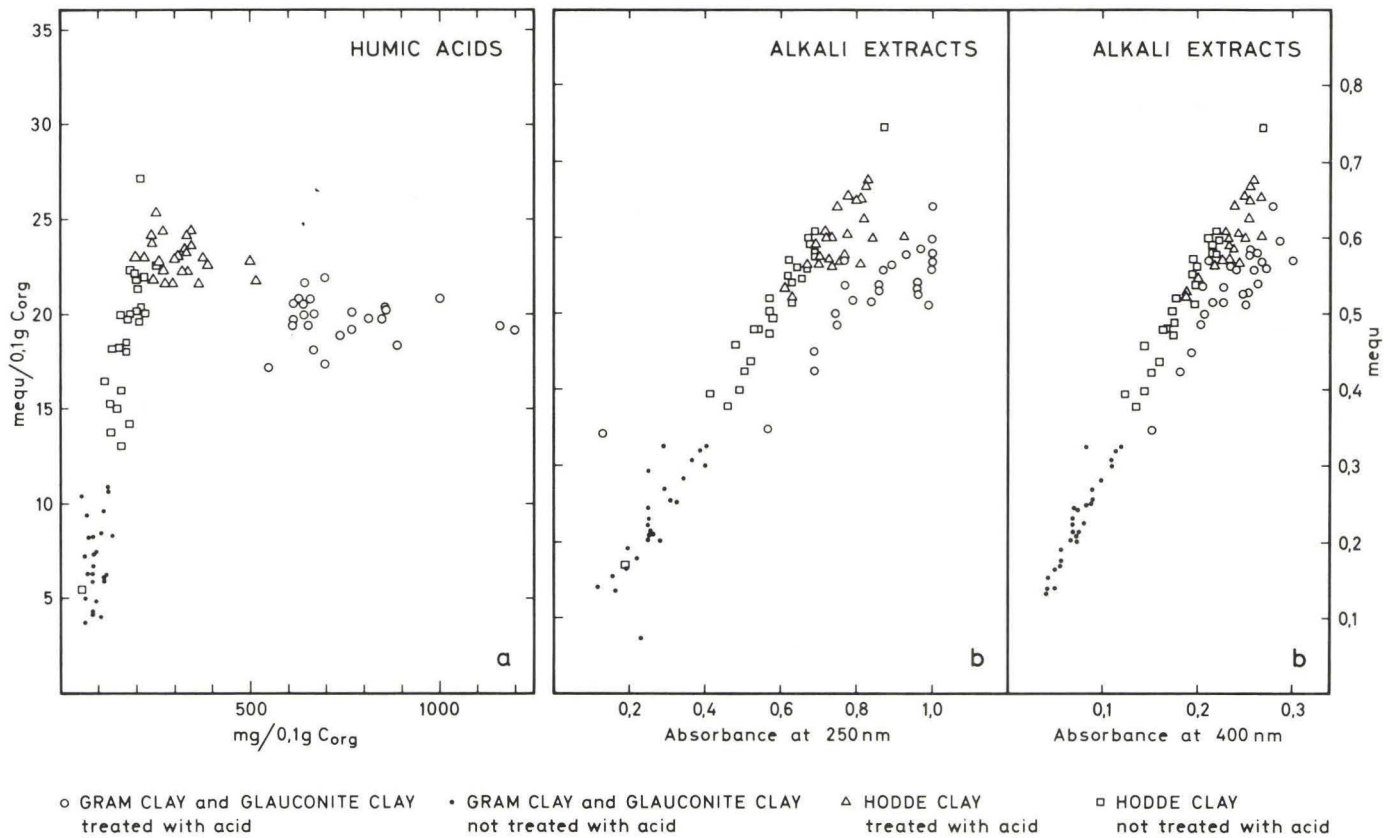


Fig. 3. Relations between different analytical methods in determination of humic matter. a. Titration values against weight analytical determinations. b. Titration values against absorbance.

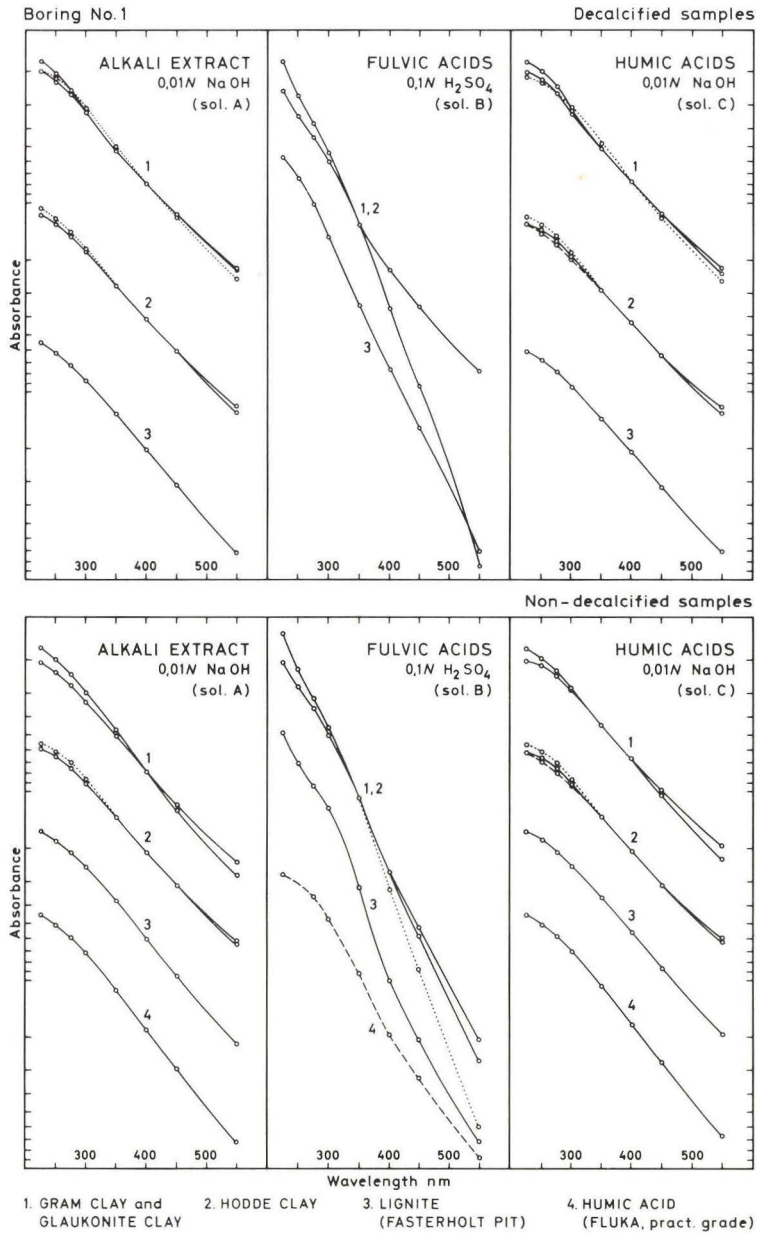


Fig. 4. Ultraviolet-visible spectra for alkali extracts, fulvic acids and humic acids.

Decalcified samples: Total humic matter.

Non decalcified samples: Easily extractable humic matter.

1973). Their different shapes and slopes may, however, be used to register variations in composition as demonstrated e.g. by Scheffer and Welte (1950a, b and 1951) in their study of humic matter from different soil types and from members of the lignification-humification-coalification sequence.

In fig. 4 spectra are shown for decalcified (i.e. acid treated) and non-decalcified samples from boring No. 1, while spectra for lignite and Humic Acid (FLUKA, pract. grade) are shown for comparison. By plotting the absorbance in a logarithmic scale against wavelength, the spectra will be unaffected by the concentration of the solution to be measured, the only concentration effect being a parallel displacement of the curve. In order to facilitate comparison of the spectra, the curves have been gathered into groups and mutually displaced to show the same absorbance at a given wavelength (solutions A and C 400 nm and solution B 350 nm).

All spectra are alike in the absence of any specific maxima and minima and in showing a general increase in absorbance with decreasing wavelength – most pronounced for fulvic acids. The shape of the curves for humic acids may, however, be somewhat related to the lithology of the sequence as outlined below.

In Hodde Clay, the total and the easily extractable humic acids from the carbon maxima are represented by one and the same curve (—) with only slight deviations at 550 nm. This curve is identical with the spectrum for lignite. The spectra from the interjacent carbon minima show higher UV absorption, approaching the dotted curve (.....), while the spectra from the basal part of the Hodde Clay show a smoother curve (--) in the UV region.

In Glauconite Clay and Gram Clay, the spectra for total humic acids show higher UV absorption, varying between the two somewhat S-shaped curves (—), the lower curve approaching the curve for carbon minima in Hodde Clay. The smoother curve (.....) represents the basal, carbonate-rich part of the Gram Clay. Easily extractable humic acids in general show a rather lower UV absorption than total humic acids, the curves being almost identical with the curves for carbon maxima and minima in Hodde Clay.

The spectra for the alkali extracts are in general accordance with those for the humic acids. Spectra for fulvic acids show no correlation to lithology.

According to Scheffer and Welte (1951), low molecular weight humic acids should be characterized by a higher UV absorption than those of higher molecular weight. Following this statement, it might be concluded from the absorption spectra that the humic matter in the carbon-rich intervals of the Hodde Clay is relatively enriched in high molecular weight compounds apparently of the same type as in lignite, while lower molecular

weight compounds might occur in the carbon minima and in the Glauconite Clay and the Gram Clay. This pattern would be in good agreement with that based on the C/N ratios. However, it must be kept in mind that the absorption spectra may be influenced by the colloidal behaviour of the humic extracts, as stated by Seidel and Ziechmann (1972). This might be of special importance for the acid treated samples of Glauconite Clay and Gram Clay, and further conclusions based on the UV-visible spectra can hardly be drawn.

Sulfur. Sulfur has been determined as total sulfur. The content is rather fluctuating, being generally higher in Hodde Clay and Glauconite Clay (2–3 ‰) than in Gram Clay (1–2 ‰). No marked relationship to organic matter may be seen.

Sulfur occurs as pyrite and gypsum as registered in the sand fraction. Pyrite crystals have also been noticed in the samples, often gathered into pockets, and it is supposed that finely dispersed iron sulfides as well as native and organic sulfur may also contribute to the total sulfur content.

Carbonate. The carbonate content in Hodde Clay is rather low (< 1 ‰ CO_2), showing a slight decrease in younger strata. Being almost negligible in Glauconite Clay, it increases sharply at the boundary to Gram Clay, showing a maximum (3–5 ‰ CO_2) at the basal 2–3 metres of this series.

Carbonate occurs as calcium carbonate in the fossils, as small porous fragments, as coatings on gypsum crystals and as a component in some of the concretions. The main carbonate component of the concretions, however, seems to be iron carbonate, and it is supposed that this compound contributes significantly to the carbonate maximum at the basal layer of the Gram Clay.

Manganese and phosphorus. The manganese content is of the order 0,1–0,4 ‰, being minimal in the Glauconite Clay. In the Gram Clay it can be correlated to carbonate, being concentrated in the concretions, which have been found to contain 0,1–0,3 ‰ Mn, i.e. ten times as much as the clay. In Glauconite Clay and Hodde Clay it can not be correlated either to carbonate or to organic matter. Some manganese may be bound to the clay minerals.

The phosphorus content is generally less than 2 ‰ P. Like the manganese, it is concentrated in the clay ironstone concretions, which have been found to contain 1–2 ‰ P, i.e. ten times as much as the clay. There is no correlation to organic matter.

Trace elements. The trace element content falls within the following ppm ranges: Li 35–110, Cr 40–200, Co < 5–40, Ni 20–80, Cu 10–30, Zn 45–150, Sr 100–350, Pb < 5–55. Cr, Zn and Pb are enriched in the upper part of the Glauconite Clay and the Gram Clay, while Sr and Li are somewhat enriched in the Hodde Clay. Co, Ni and Cu fluctuate throughout the sequence. No marked relationship either to total sulfur, carbonate or organic carbon can be seen for any of the trace elements.

The trace element content falls in general within the ranges given for marine Late Cretaceous shales by Tourtelot (1964). But as no marked relationships to lithology can be noted, the distribution of these elements will not be further discussed.

Discussion

The Hodde Formation as well as the Gram Formation may be regarded as marine on the basis of the content of fossils and glauconite. The Hodde Clay rests upon sand which is considered to be limnic or fluviatile and its basal beds are characterized by a rhythmical enrichment of sand, dominated by detrital minerals, which may indicate a slightly agitated environment. The main part of the Hodde Clay, however, may have been deposited in a quiet environment as indicated by the small sand content (< 5 %). The formation of Glauconite Clay with up to 40 % glauconite sand implies a change into a more turbulent water phase, and the occurrence of goethite pellets at the basal layer of the Gram Clay points to a near-shore well oxygenated shallow water zone, subject to wave action. An environment of this type has thus been found to be characteristic for recent formation of goethite pellets on the sea-bottom off West African deltas (Porrenga 1967, Giresse and Odin 1973). The upper part of the Gram Clay, however, may have been deposited in a calmer environment as indicated by the disappearance of goethite pellets and the decrease in sand content. A slight increase in detrital minerals in the younger strata might announce the development of a more silty facies as registered in the uppermost beds in DGU File No. 141.277.

The different types of pellets found in the sand fraction show a relationship to facies development as discussed by e.g. Valeton (1958) and Burst (1958). The shapes of the pellets might reflect different pellet forming mechanisms as proposed by Burst (1958). The greyish-greenish varieties may represent different diagenetic stages (Valeton 1958, Giresse and Odin 1973). The different types of pellets might reflect differences in the sedi-

mentary environment, but conclusions regarding such relationship can not be drawn on the basis of the present data.

The composition of the sand fraction also leads to the conclusion that the sediments have generally been subject to diagenetic processes as outlined below.

The fact that many of the slaglike fragments of pyrite contain inclusions of pellets indicate that at least some of the pyrite may have been formed or recrystallized later than the pellets, and this is assumed to be the case for the total sulfides. That would be in agreement with the generally accepted view that most sulfides in sediments have been formed after sedimentation. By laboratory experiments (Jørgensen and Fenchel 1974) as well as in situ measurements (Hallberg et al. 1973) it has been demonstrated that a reducing zone will develop a few centimetres below the sediment surface, even in an oxidizing sedimentation environment. In this "early burial stage", anaerobic bacteria are able to reduce sulfate from the seawater to sulfide under consumption of organic matter from the sediment, and iron sulfides will precipitate, if iron is present. The occurrence of pyrite in the sediments may, therefore, hardly be used as indicator for an anoxic sedimentary environment. Gypsum crystals and limonite fragments may indicate that some sulfides have later been oxidized. It can not be excluded that the oxidation might have taken place after sampling, but it seems more reasonable that it occurred in situ during weathering. Some gypsum might perhaps already have been formed syndiagenetically from sulfate in seawater in connection with aerobic bacterial decomposition of organic matter and dissolution of shells. Such processes have been reported by Fairbridge (1967).

The correlation between organic matter and total sulfur is not very pronounced. This may be explained in several ways. Available iron could be a limiting factor for the amount of sulfide produced, or total sulfur may include compounds which are not derived from syndiagenetic sulfides. And, finally, it has to be emphasized that the present content of organic matter in the sediment only represents the nonconsumed part of it and not the original amount.

For the Hodde Clay it may be noticed that the marked enrichment of humic matter in the carbon maxima is not reflected in a corresponding increase in total sulfur. Humic matter represents bacterially transformed organic matter and it may thus be assumed that it can not have been formed exclusively by in situ transformation of the organic material.

The occurrence of calcium carbonate as porous fragments with inclusions of detrital minerals and as coating on gypsum crystals indicate diagenetic processes, some of which may have taken place after formation of gypsum.

The carbonate may originate from the dissolution of shells – a process which is documented by the bad preservation of the fossils and possibly is responsible for the fact that micro fossils are absent in some intervals of the Hodde Clay. The dissolution may be due to acid environments caused either by increased CO₂ pressure from syndiagenetic decomposition of organic matter or by oxidation of sulfides during weathering. The diagenetic calcium carbonate coatings are thus of no help in evaluating the processes of formation of the gypsum crystals.

Lumps of greyish-greenish, sticky clay are sometimes found in the Hodde Clay. Some of these lumps have been found to contain a small shell fragment as nucleus. Dissolution of shells might thus play a role in formation of the lumps. Compared to the surrounding Hodde Clay, they are characterized by a lower content of organic carbon and total sulfur. In boring No. 3 they are, furthermore, enriched in carbonate, phosphorus and manganese, but this is not the case in boring No. 2. They may represent an intermediate stage in the formation of concretions.

Concretions, mostly siderite, occur throughout the sediments as small fragments and as real beds in the Gram Clay. In boring No. 2, the bed of concretions is situated above the basal layer characterized by a carbonate maximum and by goethite pellets. But in borings No. 1 and No. 3 it coincides with this basal layer. Because of the coincidence with the goethite pellets, the concretions can hardly be syndiagenetic. They are assumed to be formed anadiagenetically due to migrating pore water during compaction of the sediment (Illies 1949).

The composition of the organic matter undergoes a characteristic variation during sedimentation of the marine clays.

In the Glauconite Clay and Gram Clay, the organic matter may be of rather uniform composition as indicated by the C/N ratios and the amount of humic matter. The C/N ratios (15–20) are slightly higher than those found in Recent and Late Quaternary Baltic sediments (8–11) as reported by Gripenberg (1934), Zsolnay (1971) and Larsen (1974) and in shelf sediments (4,3–12,7) as reported by Stevenson (1960). The UV spectra might indicate a varying composition, but as mentioned these are thought to be influenced by the colloidal behaviour of the solutions. They can therefore hardly be regarded as indicative of composition.

In contrast, the composition of the organic matter in Hodde Clay seems to change in relation to its amount. The intervals rich in organic matter are characterized by high C/N ratios – up to 40 and even higher if corrected for inorganic nitrogen as shown in fig. 2. These values are of the same magnitude as those reported for Paleozoic shales (35–43) by Stevenson

(1962), and they may indicate strongly degraded organic matter. This could represent a supply of allochthonous terrestrial organic matter – a theory which is supported by the high C/N ratio (86) found in lignite from the FASTERHOLT pit. The complete dominance of easily extractable humic matter, which according to the UV spectra (fig. 4) seems to be of similar composition to that in lignite, points in the same direction. Several authors, e.g. Gripenberg (1934), Hansen (1959, 1962, 1964a, b), Stewart and Gorsline (1962) and Villumsen (1976) have similarly explained high C/N ratios in sediments of different geological settings as being due to a supply of terrestrial organic matter.

In the Hodde Clay intervals with carbon minima, the composition seems to represent intermediate stages between that of the Hodde Clay carbon maxima and that of the Glauconite Clay and the Gram Clay.

Finally, attention must be drawn to the basal layer of the Hodde Clay which is characterized by special conditions regarding both the amount and composition of the humic matter. This can perhaps be attributed to a special facies development, e.g. corresponding to the gyttja facies described in the SØBY-FASTERHOLT area (Koch et al. 1973).

It can thus be concluded that the organic matter in the Hodde Formation as well as in the Gram Formation may represent mixtures of autochthonous organic matter and allochthonous terrestrial organic matter – mainly humic matter. During deposition of the Hodde Formation, a periodically strong sedimentation of terrestrial humic matter may have taken place, while this may have played a far more subordinate role during deposition of the Glauconite Clay and the Gram Clay. It may be noticed that the carbon maxima of the Hodde Clay can be correlated over a distance of at least 2 km (fig. 1). The assumption of a sedimentation of allochthonous terrestrial organic matter is in accordance with the view by Thiele (1941), cit. in Valeton (1958), that North German Middle and Upper Miocene Mica Clays contain colloidal land derived humic matter. And, furthermore, it is supported by observations from North Germany made by Heck (1951), who found a development from autochthonous lignite in the East through allochthonous lignite to clays with humic detritus in the West.

That part of the humic matter which is extractable only after acid treatment is thought to be bound to clay particles. This is evidenced by the discrepancy between weight analytical, colorimetric and titrimetric results for the acid treated samples (fig. 3). Since clay minerals can adsorb more humic matter under salt water conditions than under fresh water conditions (Rashid, Buckley and Robertson 1972), it might be reasonable to suppose that the varying proportions of bound and easily extractable humic matter through-

out the sequence may reflect variations in salinity. Predominance of bound humic matter might thus indicate salt water conditions, while predominance of easily extractable humic matter may point to a more brackish water environment.

The variation in the total amount of deposited humic matter is also thought to be related to changes in salinity. According to Narkis et al. (1968), free humic acid will flocculate more easily than clay minerals and organo-clay compounds when exposed to a cationic flocculant. One might thus expect that humic matter and clay particles would be subject to a separation when discharged from a river into a marine environment – the humic matter being precipitated in the brackish water zone near the influx of fresh water and the clay particles and organo-clay compounds under more saline conditions. This assumption appears to be supported by field data. According to Darnell (1967), it has thus been established for some estuaries that the relative importance of allochthonous organic matter may vary in relation to the position of the salinity gradient.

The bounding properties and the total amount of organic matter may thus point to changing salinity during deposition of the Hodde Clay, the carbon maxima representing a brackish water environment. The lowermost carbon minimum corresponds to a sand maximum and may thus be due to a more agitated environment. But this is not the case for the remaining carbon minima in the Hodde Clay, and these are thought to indicate more saline conditions. Glauconite Clay and Gram Clay may, finally, have been deposited under still higher and more constant salinity. This assumption is supported by the size of the molluscs as mentioned by Rasmussen (1966).

The sedimentary environment seems to be rather uniform in the area as demonstrated by the marked correlation between the borings, both in lithology and chemical data.

The environment during deposition of the Hodde Formation and the Gram Formation may be described as follows. The marine Hodde Clay rests transgressively on sand, which is thought to be limnic or fluvatile. After an initial phase with a supply of detrital sand, the environment changes to quieter conditions. The investigated area was probably not very far from the coast towards the East, cfr. fig. 1. It was characterized by a considerable, but varying sedimentation of terrestrial organic matter – mainly humic matter. The humic matter might be supplied from swampy areas as described by Heck (1951) and Koch et al. (1973). The salinity is thought to have changed periodically between brackish and marine. This points to an estuarine environment, and the changing salinity might thus indicate an oscillating salt wedge. This might be due to changes in river

discharge or to changes in salt water influx. The Glauconite Clay and the basal bed of the Gram Clay, which is rich in goethite, indicate a more agitated and oxygenated environment. This changes to less agitated marine conditions with clay sedimentation during deposition of the Upper Gram Clay. The investigated section reflects a transgressive sequence in a rather sheltered sea. The lithological development suggests that the area has hardly been an estuary cut off from the sea by offshore bars, but more likely has represented an open shallow water embayment.

It may thus be concluded that the data in general confirm the present view regarding the sedimentary environment as put forward by e.g. Rasmussen (1966) and Koch (1973). And, finally, it may be emphasized that the chemical data, especially the content of organic matter, seem to be a valuable supplement to the biostratigraphical subdivision of the Hodde Clay.

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Dansk sammendrag

Tre borer i det marine Yngre Miocæn ved Gram, SW Jylland, er undersøgt kemisk for carbonat, mangan, fosfor, total svovl og organisk stof, idet dette er karakteriseret ved C/N forhold og ved indhold af direkte ekstraherbart og af bundet humus. En af borerne er yderligere undersøgt for spormetaller.

Hodde Leret kendetegnes ved et højt, men varierende indhold af organisk stof, hvis sammensætning varierer i takt med indholdet. I afsnit med kulstof maxima karakteriseres det ved højt C/N forhold (op til 40) og ved, at så godt som al humus er direkte ekstraherbart. Glaukonit Ler og Gram Ler har et mindre, men konstant indhold af organisk stof med lavere C/N forhold (15–20) og med op til halvdelen af humus på bunden form. Carbonat, mangan og fosfor koncentrerer i Gram Lerets basale del med lerjernstenskonkretioner. Svovl varierer regelløst gennem lagserien, dog med et lidt højere niveau i Hodde Leret. Spormetallerne viser ingen korrelation, hverken til carbonat, svovl eller organisk stof.

Lagserien kan inddeles efter sandfraktionens sammensætning. Denne antyder iøvrigt, at der er foregået diagenetiske processer i lagserien.

Hodde Leret hviler transgressivt på sand, der formodes at være limnisk eller fluviatilt. I dets basale del træffes indslag af detritisk sand. Derefter udvikles et roligt sedimentationsmiljø, hvori der aflejres betydelige, men varierende mængder af allochtont terrestrisk organisk materiale, der overvejende består af humus. Miljøet tolkes som estuarint, og saltholdigheden formodes at variere mellem brakvands- og marine forhold. Glauconit Leret og Gram Lerets basale goethitholdige del antyder et mere uroligt og iltholdigt lavvandmiljø. Dette går over i mere rolige marine forhold under aflejring af Gram Leret.

De fremkomne data bekræfter således i store træk den hidtidige opfattelse af Hodde Formationens og Gram Formationens aflejningsforhold.

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