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Organic compounds from Cretaceous
coals of Nûgssuaq, West Greenland

by

Jørgen Lam and K. Raunsgaard Pedersen

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Abstract

Bituminous coals from the Lower Cretaceous Kome Formation and the Upper Cretaceous Atane Formation of Nûgssuaq have been analyzed for organic compounds.

In the Atane Formation *n*-C₁₂- to *n*-C₃₁-alkanes, C₁₉- and C₂₀-isoprenoids (pristane and phytane) and possibly C₁₄-, C₁₅-, and C₁₆-isoprenoids are present. *n*-C₉- to *n*-C₂₈-acids, norphytanic acid and phytanic acid have also been detected. In the Kome Formation *n*-C₁₄- to *n*-C₂₇-alkanes, C₁₉- and C₂₀-isoprenoids and possibly C₁₄- and C₁₅-isoprenoids are present. *n*-C₈- to *n*-C₂₆-acids, in addition C₈- to C₂₀- α , ω -diacids could be detected.

The difference between the Kome flora (predominantly gymnosperms and ferns) and the Atane flora (dominated by angiosperms) is not apparent in the organic chemistry.

Comparisons are made with extracts from Rhaetic-Liassic coal from the Kap Stewart Formation of East Greenland where only C₁₄- and C₁₆-acids and aromatic acids were detected.

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Introduction

The comparison of extractable organic compounds from coals representing different plant groups and ages is continued with a study of the Cretaceous coal from West Greenland. The previous work covered Rhaetic-Liassic coal from East Greenland and Precambrian coal and graphite from West Greenland (Lam & Pedersen, 1972; Pedersen & Lam, 1975).

The Cretaceous sediments in West Greenland with exposures on Disko, Nûgssuaq and Svartenhuk Halvø (fig. 1) have long been known for their coal layers and rich fossil floras. The floras were described in the last century by the Swiss palaeobotanist O. Heer (1883a,b) who divided the Cretaceous floras into the Kome, Atane and Pautut floras, with a Lower Cretaceous age for the Kome flora and an Upper Cretaceous age for the others. The coal layers were originally investigated and described by K. J. V. Steenstrup (1874 and 1883a,b).

The coal layers of West Greenland have been utilized for several hundred years. Mining of coal for local Greenland use has been carried out on northern Nûgssuaq at Qaersuarssuk between Kûk and Ikorfat from 1905 to 1924 and on eastern Disko at Qutdligssat from 1924 to 1972.

Material, fossil floras and geology

The two coal samples investigated here were collected from the Lower Cretaceous Kome Formation and from the Upper Cretaceous Atane Formation of Nûgssuaq, (fig. 1, Table 1) by one of the authors in 1956.

The Kome Formation is known from the north coast of Nûgssuaq, from Svartenhuk Halvø and from Upernivik Ø (fig. 1).

The facies of the Kome Formation is non-marine and is characterized by alternating sandstones and dark shales together with coal layers up to about 1 m thick. A rich fossil flora has been described from the shaly layers of the Kome Formation, especially from the north coast of Nûgssuaq. The Kome flora is dominated by ferns, but conifers, cycadophytes and ginkgophytes are also common. The flora originally described by Heer from 1868 to 1883 (Heer, 1883a,b) was later revised by Seward (1926) who found well-preserved cuticles in some of the material. The ferns are represented by species of *Gleichenites*, *Phlebopteris*, *Cladophlebis*, *Onychiopsis*, and *Hausmannia* with *Gleichenites* as the most common genus. Among the gymnosperms the cycadophytes, especially the Bennettitales are represented with

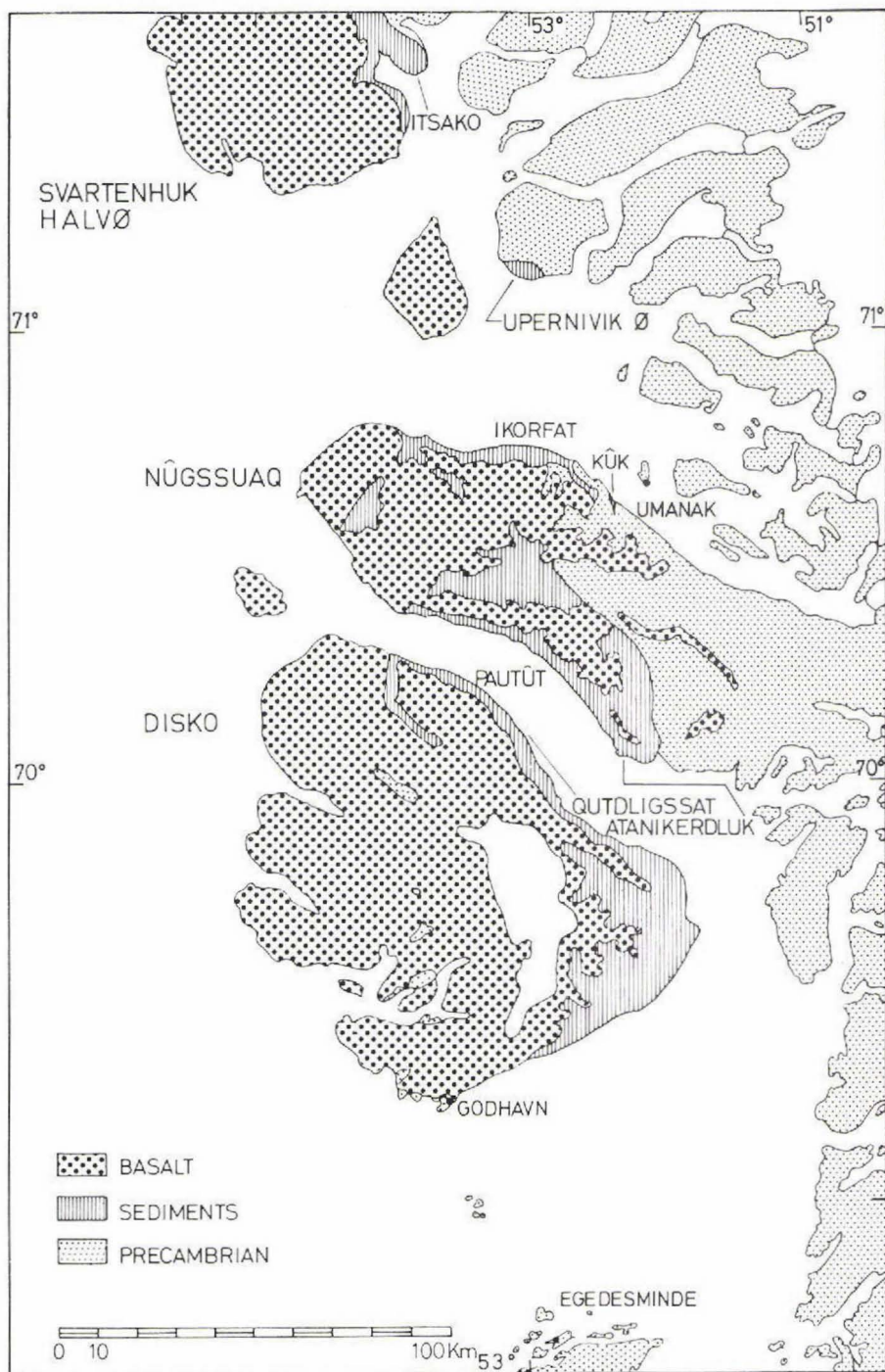


Fig. 1. Cretaceous-Tertiary sediments in West Greenland. After Rosenkrantz & Pulvertaft, 1969.

Table 1. Stratigraphy and fossil flora of the coal bearing strata from Nûgssuaq

Sample GGU	Formation	Age	Fossil flora	Dominant element in the fossil flora
9603	Atane	Upper Cretaceous (? L. Senonian)	Angiosperms Conifers Cycadophytes Ferns	Angiosperms
9546	Kome	Lower Cretaceous (? Barremian)	Conifers Cycadophytes Ferns	Ferns Conifers

Pterophyllum, *Ptilophyllum* and *Otozamites*, the conifers with *Pagiophyllum* and *Sciadopitys* as common species together with the ginkgophyte representatives *Ginkgoites* and *Baiera*.

According to Heer the age of the Kome flora is Lower Cretaceous, and Seward states strong similarity with the Wealden flora.

The Atane Formation outcrops on the south coast of Nûgssuaq (fig. 1, Table 1), on Disko and in central parts of Nûgssuaq.

The facies of the Atane Formation is non-marine, but it is difficult to separate it from the marine Pautut Formation on southern Nûgssuaq.

Lithologically the Atane Formation is rather varied with alternating dark shale and sandstone together with coal layers (fig. 2). In the Pautût area on the south coast of Nûgssuaq up to 10 coal layers more than 1/2 m thick have been observed.

The most abundant Cretaceous flora comes from the Atane Formation. The flora comprises many different angiosperms together with some ferns, conifers and cycadophytes. Most of the species described are leaf impressions, but reproductive structures and fossil wood are also found (Heer, 1883 a,b).

The ferns represented are *Cladophlebis*, *Phlebopteris*, *Gleichenites*, *Onychiopsis* and *Hausmannia*. The gymnosperms are represented by conifers as *Pagiophyllum*, *Sciadopitys*, *Elatocladus* and *Sequoiites*, the ginkgophytes: *Ginkgoites* and *Baiera* and cycadophytes: *Pseudocycas*, *Pterophyllum*, *Pseudoctenis* and *Williamsonia*.

The angiosperms show several species of *Platanophyllum*, *Magnoliaephyllum*, *Menispermites*, *Cinnomoides*, *Dalbergites* and *Dicotylophyllum*, and species of several other genera have also been described. The dominant element in the flora is angiospermous leaves, and certain species may dominate in some layers, for example *Platanus* in some parts of the series.

The age of the Atane flora was considered by Heer to be between Gault and Senonian with a Cenomanian age as most likely. The agreements between Upper Cretaceous floras from North America and Europe, and also geological field evi-



Fig. 2. Atane Formation with coal layers. Gorge by Qagdlunguaq, north-west of Atanikerdluk, south coast of Nûgssuaq peninsula. Height of cliff about 400 m.

dence (Rosenkrantz, 1970) point to a Lower Senonian age. The geology and palaeontology of the Nûgssuaq area have been reviewed by Henderson *et al.* (1976), Pedersen (1976) and Schiener (1976).

The Kome Formation coal sample (GGU 9546) investigated for organic compounds was collected from a layer about 1/2 m thick outcropping approximately 10 m above sea level in a coastal profile near Kûk on the north coast of Nûgssuaq (fig. 3). The coal is rather hard and dominated by vitritic layers. Palynological preparation of the material has also been carried out and shows few well-preserved spores and pollen and many tracheid fragments.

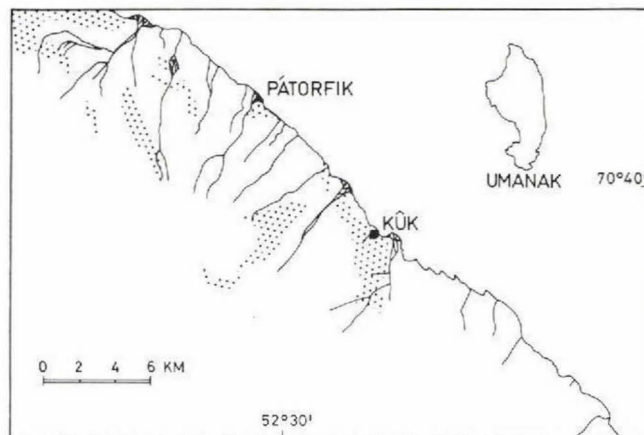
The sample from the Atane Formation investigated here (GGU 9603) was collected from a bed about 1 m thick in the ravine Qaglorssup kûa on the south coast of Nûgssuaq (fig. 4). The sample locality is at the outer part of a trial adit at a height of 354 m. The coal is hard, and vitritic layers are dominant. A palynological preparation of the material shows very few spores and pollen, but many fragments of tracheids.

The rank of the coals is high volatile bituminous A.

Extractions and analytical methods

As previously emphasized the possibility of contamination with various phthalic esters is very high (Pedersen & Lam, 1970; Lam & Pedersen, 1972). For this reason all the manipulations of the rock material were performed with carefully

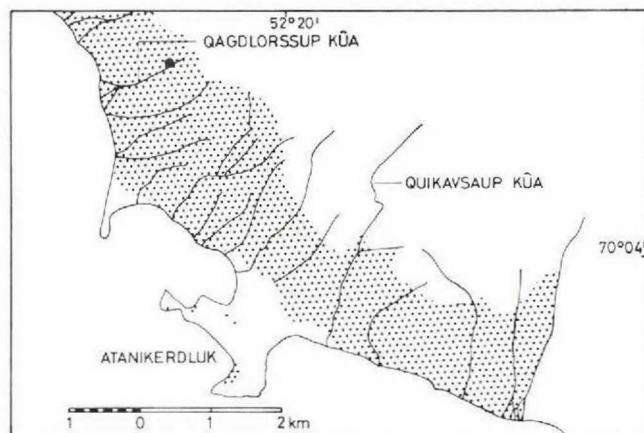
Fig. 3. Part of the north coast of Nūgssuaq peninsula showing outcrops of Cretaceous sediments (dotted areas) and sample locality of GGU 9546. After Geological map of Greenland, Søndre Strømfjord - Nūgssuaq at 1:500 000.



purified utensils, apparatus, and solvents redistilled in all-glass equipment. The surface layers of the samples were cut off, and the samples were rinsed in extraction liquid (benzene-methanol, 3:1 v/v). The rinsed and milled material of each sample was extracted and re-extracted twice in portions not exceeding 700 g. Each portion was extracted three times with 900 ml mixture of benzene and methanol (3:1 v/v) and with an extraction time of three days. The first extract of the first 700 g portion was stored, the second extract was used for the first extraction of the second 700 g portion of the sample and then stored. The third extract of the first 700 g portion was first used for the second extraction of the second 700 g portion and then for the first extraction of the third portion of the sample. This procedure allows a minimum use of solvent and hence a limitation of contamination possibilities.

After re-extraction and evaporation the crude material from each sample was again extracted with *n*-heptane and separated into fractions on a silicagel column

Fig. 4. Part of the south coast of Nūgssuaq peninsula showing outcrops of Atane Formation (dotted areas) and sample locality of GGU 9603. After Koch & Pedersen, 1960.



with *n*-heptane and subsequently with mixtures of *n*-heptane and ether in which the amount of ether was gradually increased from 1 per cent to 100 per cent as eluting solvents. The first fractions passing through the column contain saturated hydrocarbons followed by fractions of increasing polarity with increasing ether per cent.

By means of infrared and ultraviolet spectra a primary orientation about the nature of compounds confirmed the presence of at least two other classes of compounds (aromatic hydrocarbons and organic acids). For the final identification a combination of gas chromatography and mass spectrometry was used. The aliphatic hydrocarbon fractions were collected and further separated by urea occlusion before GC-MS were applied. The instruments used were a Perkin-Elmer 880 gas chromatograph combined with a RMU-6D mass spectrometer and for some of the data a CEC 21-104 mass spectrometer.

Results and discussion

From 1790 g of milled sample GGU 9603 a crude benzene-methanol extract after evaporation and re-extraction with *n*-heptane yielded an amount of 3.1966 g extract of organic material. The corresponding amount of material obtained by the same procedures from sample GGU 9546 was 1.3027 g from 1754 g of sample.

1.2694 g of the sample GGU 9603 and 1.3027 g of the sample 9546 were fractionated on silicagel as mentioned under extraction and analytical methods. The classes of compounds determined are mainly the same as those generally observed from geological material.

In both samples a large series of *n*-alkanes is present (Table 2). The isoprenoids pristane (C_{19}) and phytane (C_{20}) are present in large amounts in both samples. In addition C_{14} - and C_{15} -isoprenoid compounds seem to be present in both samples, whereas a C_{16} -isoprenoid alkane appears only in sample GGU 9603. The C_{14} - and C_{19} -isoprenoid alkanes may have been derived from C_{15} -sesquiterpenoid and from C_{20} -diterpenoid structures respectively, by loss of one carbon atom in each case.

It becomes more and more evident that besides *n*-alkanes and branched alkanes, a great number of more or less dehydrogenated compounds are detected frequently in geological material. Several aromatic compounds from sample GGU 9603 and 9546 are listed in Table 3. Pyrene was isolated from the samples and identified by its spectral data when compared to purified commercial pyrene. Naphthalene and methyl-naphthalenes have been characterized by their data in the gas chromatograms and by their characteristic mass spectra. The mass spectra and the glc retention data correspond quite well to the sequence in the gas chromatograms of the commercial compounds. However, the more condensed ring structures like those of benzopyrenes, chrysene and methylpyrenes could not be exactly characterized,

Table 2. Saturated alkanes from two Cretaceous bituminous coal samples

	M.W.	Atane GGU 9603	Kome GGU 9546 * *
<i>n</i> -C ₁₂ H ₂₆	170	+	
C ₁₄ H ₃₀ branched (isoprenoid?)	198	+	+
<i>n</i> -C ₁₃ H ₂₈	184	+	+
C ₁₅ H ₃₂ branched (isoprenoid?)	212	+	+
<i>n</i> -C ₁₄ H ₃₀	198	+	+
C ₁₆ H ₃₄ branched (isoprenoid?)	226	+	
<i>n</i> -C ₁₅ H ₃₂	212	+	+
<i>n</i> -C ₁₆ H ₃₄	226	+	+
C ₁₉ H ₄₀ pristane (isoprenoid)	268	+	+
<i>n</i> -C ₁₇ H ₃₆	240	+?*	+
C ₂₀ H ₄₂ phytane (isoprenoid)	282	+	+
<i>n</i> -C ₁₈ H ₃₈	254	+	+
<i>n</i> -C ₁₉ H ₄₀	268	+	+
<i>n</i> -C ₂₀ H ₄₂	282	+	+
<i>n</i> -C ₂₁ H ₄₄	296	+	+
<i>n</i> -C ₂₂ H ₄₆	310	+	+
<i>n</i> -C ₂₃ H ₄₈	324	+	+
<i>n</i> -C ₂₄ H ₅₀	338	+	+
<i>n</i> -C ₂₅ H ₅₂	352	+	+
<i>n</i> -C ₂₆ H ₅₄	366	+	+
<i>n</i> -C ₂₇ H ₅₆	380	+	+
<i>n</i> -C ₂₈ H ₅₈	394	+	
<i>n</i> -C ₂₉ H ₆₀	408	+	
<i>n</i> -C ₃₀ H ₆₂	422	+	
<i>n</i> -C ₃₁ H ₆₄	436	+	

* *n*-C₁₇H₃₆ could not be sufficiently well determined from the mass spectrum due to the overwhelming contribution of pristane (C₁₉H₄₀-isoprenoid).

** Pristane is present in extremely large amounts even in the urea separated *n*-alkane fraction, where it might have adhered to the crystals of urea which include the *n*-alkanes and on the whole exclude the branched and cyclic alkanes.

although the mass spectra indicate fragmentation patterns corresponding to such substances. Polycyclic aromatic hydrocarbons isolated from a fossil crinoid of Jurassic age are reported by Thomas & Blumer (1964).

Dihydrophenanthrene M.W. 180 and methyl-dihydrophenanthrene M.W. 194 were detected. There were also indications of higher hydrogenated compounds such as steranes and their disintegration products which may be deduced from the mass spectral fragments among which are *m/e* 149, 191, 213, 217 and others.

Many of the alkylbenzenes, alkylcyclohexanes and hydroaromatic compounds have been detected together with aromatic compounds by their mass spectra. The evidence of the presence of both aromatic and hydroaromatic compounds such as naphthalene, alkylnaphthalenes and alkyl derivatives of more or less hydrogenated naphthalenes is emphasized by the mass spectra which change in relative intensity of the fragmentation pattern from peak to peak in the gas chromatograms.

Table 3. Aromatic hydrocarbons from two Cretaceous bituminous coal samples

	M.W.	Atane GGU 9603	Kome GGU 9546
naphthalene	128	+	+
β -methylnaphthalene	142	+	+
α -methylnaphthalene	142	+	+
diphenyl	154	+	+
C ₂ -naphthalenes*	156	+	+
methyldiphenyl	168	+	+
dibenzofuran**	168	+	+
C ₂ -naphthalenes	170	+	+
C ₂ -diphenyl	182	+	+
C ₄ -naphthalenes	184	+	+
phenanthrene	178	+	+
C ₅ -naphthalenes	198	+	+
methyl phenanthrenes	192	+	+
C ₆ -naphthalenes	212	+	+
C ₂ -phenanthrene	206	+	+
fluoranthrene?	202	+	+
pyrene \neq	202	+	+
methylpyrenes	216	+	+
benzopyrenes?	252	+	
chrysene?	228	+	
C ₂ -pyrene?	230	+	

C₄-, C₅-, C₆-, C₇- alkyl benzenes, C₅-, C₆-, C₇-, C₈-, C₉- alkyl cyclohexanes, C₂-, C₃-, C₄-, C₅-, C₆-alkyltetrahydronaphthalenes are three homologous series detected in both samples. Sample GGU 9603 is richer in hydrogenated cyclic hydrocarbons relative to sample GGU 9546.

* C₂-, C₃-, C₄-, C₅-, and C₆- prefixes stand for saturated alkyl groups attached to parent aromatic hydrocarbons. They may represent one or more groups with the highest possible number corresponding to the figures indicated. (The numbers 2 to 6 indicate the total number of C-atoms in the alkyl groups).

** Oxygen-containing compound, which appears among the aromatic hydrocarbons (Pedersen & Lam, 1975).

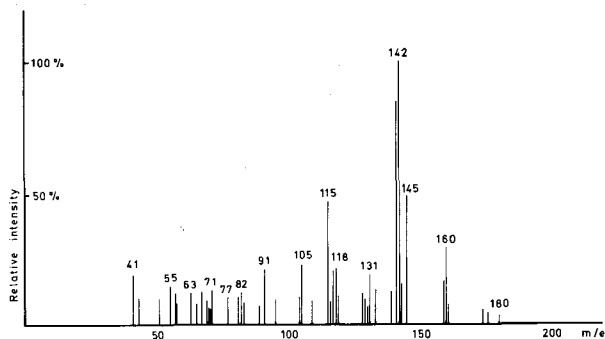
\neq Pedersen & Lam (1975).

For the study of mass spectra of alkyltetrahydronaphthalenes in geological samples, a series of methyl and dimethyltetrahydronaphthalenes was prepared, in analogy with cathodic butylation of naphthalene and pyrene (Simonet, Michel & Lund, 1975; and Hansen, Berg & Lund, 1976). A large series of tetrahydronaphthalenes as reported from the Green River Shale by Anders, Doolittle & Robinson (1973) is present in both samples.

The rather intense fragment of 118 m/e in figs 5 and 6 indicates methyl substituents of the aromatic part of a C₂-alkyl-1,2,3,4-tetrahydronaphthalene and a C₃-alkyl-1,2,3,4-tetrahydronaphthalene respectively.

The most polar fraction of the sample GGU 9603, which contains organic acids, was methylated and subjected to gas chromatography and mass spectrometry. A large series of normal fatty acid methylesters was detected (Table 4) together with

Fig. 5. α -methyl-naphthalene
M.W. 142
and C₂-alkyl-1,2,3,4-
tetrahydronaphthalene M.W.
160.



some aromatic acids. Aromatic carboxylic acids have been reported previously from the Colorado Green River Formation (Eocene) by Haug *et al.* (1968).

From a polar fraction of sample GGU 9546 aromatic carboxylic acids are revealed on the basis of their characteristic methylester fragmentation patterns; from which benzoates and naphthoates may be deduced. From the same fraction of sample GGU 9546 we have also studied the mass spectra of fatty acids as methylesters by combined GC-MS investigations (Table 4). From this sample of the Kome Formation some of the mass spectra show a pattern from which α - ω -dicarboxylic acid methylesters can be deduced according to their characteristic pattern as described by Ryhage & Stenhagen (1964). Dicarboxylic acids have previously been isolated from Colorado Green River Shale (Eocene) by Haug *et al.* (1967).

The mass spectra representing the diacid methylesters also exhibit mass fragmentation corresponding to normal fatty acid esters from which the diacid esters have not been fully separated.

Concluding remarks

Rich and very different fossil floras have previously been described from the formations from which the coal samples were taken. The main purpose of the

Fig. 6.
C₃-alkyl-1,2,3,4-
tetrahydronaphthalene
M.W. 174
and
C₇-alkylbenzene M.W. 176.

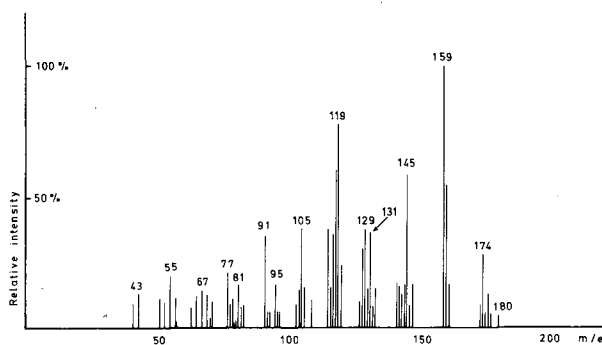


Table 4. Homologous series of open chain acids from two coal samples identified as methylesters prepared by use of diazomethane

	M.W.	Atane GGU 9603	Kome GGU 9546
<i>n</i> -C ₇ H ₁₅ COOCH ₃	158		+
iso-C ₈ H ₁₇ COOCH ₃	172		+
<i>n</i> -C ₈ H ₁₇ COOCH ₃	172	+	+
iso-C ₉ H ₁₉ COOCH ₃	186	+	+
<i>n</i> -C ₉ H ₁₉ COOCH ₃	186	+	+
iso-C ₁₀ H ₂₁ COOCH ₃	200	+	+
<i>n</i> -C ₁₀ H ₂₁ COOCH ₃	200	+	+
CH ₃ OOC(CH ₂) ₆ COOCH ₃	202		+
iso-C ₁₁ H ₂₃ COOCH ₃	214	+	+
<i>n</i> -C ₁₁ H ₂₃ COOCH ₃	214	+	+
CH ₃ OOC(CH ₂) ₇ COOCH ₃	216		+
iso-C ₁₂ H ₂₅ COOCH ₃	228	+	+
<i>n</i> -C ₁₂ H ₂₅ COOCH ₃	228	+	+
CH ₃ OOC(CH ₂) ₈ COOCH ₃	230		+
isoprenoid-C ₁₄ H ₂₉ COOCH ₃	256	+	
iso-C ₁₃ H ₂₇ COOCH ₃	242	+	+
<i>n</i> -C ₁₃ H ₂₇ COOCH ₃	242	+	+
CH ₃ OOC(CH ₂) ₉ COOCH ₃	244		+
iso-C ₁₄ H ₂₉ COOCH ₃	256	+	+
anteiso-C ₁₄ H ₂₉ COOCH ₃	256	+	
<i>n</i> -C ₁₄ H ₂₉ COOCH ₃	256	+	+
CH ₃ OOC(CH ₂) ₁₀ COOCH ₃	258		+
iso-C ₁₅ H ₃₁ COOCH ₃	270	+	+
anteiso-C ₁₅ H ₃₁ COOCH ₃	270	+	
isoprenoid-C ₁₆ H ₃₃ COOCH ₃	284	+	+
<i>n</i> -C ₁₅ H ₃₁ COOCH ₃	270	+	+
CH ₃ OOC(CH ₂) ₁₁ COOCH ₃	272		+
iso-C ₁₆ H ₃₃ COOCH ₃	284		+
isoprenoid-C ₁₈ H ₃₇ COOCH ₃	312	+	
<i>n</i> -C ₁₆ H ₃₃ COOCH ₃	284	+	+
CH ₃ OOC(CH ₂) ₁₂ COOCH ₃	286		+
isoprenoid-C ₁₉ H ₃₉ COOCH ₃	326	+	
iso-C ₁₇ H ₃₅ COOCH ₃	298	+	+
monounsaturated C ₁₇ H ₃₃ COOCH ₃	296	+	
<i>n</i> -C ₁₇ H ₃₅ COOCH ₃	298	+	+
CH ₃ OOC(CH ₂) ₁₃ COOCH ₃	300		+
<i>n</i> -C ₁₈ H ₃₇ COOCH ₃	312	+	+
CH ₃ OOC(CH ₂) ₁₄ COOCH ₃	314		+
<i>n</i> -C ₁₉ H ₃₉ COOCH ₃	326	+	+
CH ₃ OOC(CH ₂) ₁₅ COOCH ₃	328		+
<i>n</i> -C ₂₀ H ₄₁ COOCH ₃	340	+	+
CH ₃ OOC(CH ₂) ₁₆ COOCH ₃	342		+
<i>n</i> -C ₂₁ H ₄₃ COOCH ₃	354	+	+
CH ₃ OOC(CH ₂) ₁₇ COOCH ₃	356		+
<i>n</i> -C ₂₂ H ₄₅ COOCH ₃	368	+	+
CH ₃ OOC(CH ₂) ₁₈ COOCH ₃	370		+
<i>n</i> -C ₂₃ H ₄₇ COOCH ₃	382	+	+
<i>n</i> -C ₂₄ H ₄₉ COOCH ₃	396	+	+
<i>n</i> -C ₂₅ H ₅₁ COOCH ₃	410	+	+
<i>n</i> -C ₂₇ H ₅₅ COOCH ₃	438	+	

n-C₂₆H₅₃COOCH₃ is not sufficiently well determined in sample GGU 9603 and is not present in sample GGU 9546. α , ω -diacids were determined as a homologous series in sample GGU 9546, whereas in sample GGU 9603 there are indications of a few diacids. The diacids were determined in the mass spectra by characteristic fragments of the corresponding dimethyl esters (Ryhage & Stenhagen, 1964).

investigation was to show whether a corresponding difference exists in the extractable organic compounds.

The older formation has a Lower Cretaceous flora dominated by gymnospermous plants and ferns similar to the Rhaetic-Liassic previously investigated by Pedersen & Lam (1975). The younger Atane Formation is known for its fossil flora dominated by angiosperms. Although these coals seem to represent two very different floras, a corresponding difference has not been found among the organic compounds. The classes of organic compounds are very much the same. Long chain diacids are, however, more abundant in the older sample, while in the younger only slight indications of diacids seem to be present.

When comparing the results with those of a sample from the Rhaetic-Liassic Kap Stewart Formation of East Greenland (Pedersen & Lam, 1975), it is seen that saturated normal alkanes, branched alkanes and aromatic hydrocarbons were found in all three samples, and the heterocyclic dibenzofuran and methyl derivatives hereof were also detected. They all appear to contain monoterpeneoid, sesquiterpeneoid and triterpeneoid structures the mass spectra of which cannot be sufficiently well resolved.

The hydroaromatic compounds like those reported and shown in the mass spectra (figs 5 and 6) presumably indicate the process of disintegration from steranes originating from steroid compounds.

The biggest difference between the three samples seems to be within the group of acids. The acids were transformed into the methyl ester in all three cases. In the Kap Stewart Formation, only C_{14} - and C_{16} -acids could be determined, whereas in the two other samples normal fatty acids with from 8 to at least 26 C-atoms were revealed by their mass spectra, the n - C_{12} -acid being the most abundant in both cases. Less pronounced is the difference between the Kap Stewart Formation and the two other samples with respect to the normal alkanes. For the Kap Stewart Formation n -alkanes in the range C_{13} to C_{31} were detected with C_{25} , C_{27} and C_{29} the most abundant, whereas for the two younger samples the most abundant n -alkanes is that with 25 C-atoms in sample GGU 9603 with n -alkanes ranging from C_{12} to C_{31} and in sample GGU 9546 with n -alkanes ranging from C_{14} to C_{27} . Dibenzofuran is present in sample GGU 9546 and sample GGU 9603. The isolation and characterization of this heterocyclic compound has been described by Pedersen & Lam (1975).

Knowledge of Mesozoic plants and floral composition in the swamp areas in the Cretaceous is still rather scarce, and it has not been possible to give a fully satisfactory explanation of the relatively small differences in the composition of organic compounds from the two Cretaceous coal samples.

Among the possible explanations are (a) the gymnospermous plants have been the dominant element in the flora of the swampy areas where the deposition of plant material occurred in both Upper and Lower Cretaceous time, (b) the Upper Cretaceous angiosperms and the gymnosperms, which have provided the plant

material, have not been very different in their organic compounds, (c) the original plant material of the two coals contained various unstable organic compounds not traceable now because of disintegration. Perhaps the largest difference between the three samples could be noticed in the variation of the monoterpene-sesquiterpene patterns if these substances could be sufficiently well distinguished by the analytical methods applied.

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References

- Anders, D. E., Doolittle, F. G. & Robinson, W. E. 1973: Analysis of some aromatic hydrocarbons in a benzene-soluble bitumen from Green River shale. *Geochim. cosmochim. Acta.* **37**, 1213-1228.
- Hansen, P. E., Berg, A. & Lund, H. 1976: Cathodic t-butylation of pyrene. *Acta Chem. Scand.* **30**, 267-270.
- Haug, P., Schnoes, H. K. & Burlingame, A. L. 1967: Isoprenoid and dicarboxylic acids isolated from Colorado Green River Shale (Eocene). *Science* **158**, 772-773.
- Haug, P., Schnoes, H. K. & Burlingame, A. L. 1968: Aromatic carboxylic acids isolated from the Colorado Green River Formation (Eocene). *Geochim. cosmochim. Acta.* **32**, 358-361.
- Heer, O. 1883a: *Flora Fossilis Arctica* 7. *Flora Fossilis Groenlandica* 2. Zürich: Wurster, 275 pp.
- Heer, O. 1883b: Oversigt over Grønlands fossile flora. *Meddr Grønland* **5**, 79-202.
- Henderson, G., Rosenkrantz, A. & Schiener, E. J. 1976: Cretaceous-Tertiary sedimentary rocks of West Greenland. In Escher, A. & Watt, W. S. (edit.) *Geology of Greenland*, 341-362. København: Grønlands geologiske Undersøgelse.
- Koch, B. E. & Pedersen, K. R. 1960: Geological map of Atanikerdluk and environs 1:10000. *Bull. Grønlands geol. Unders.* **23** (also *Meddr Grønland* **162**, 4), 38 pp.
- Lam, J. & Pedersen, K. R. 1972: Precambrian organic compounds from the Ketilidian of South-West Greenland. IV. *Bull. Grønlands geol. Unders.* **101** (also *Meddr Grønland* **185**, 8), 43 pp.
- Pedersen, K. R. 1976: Fossil floras of Greenland. In Escher, A. & Watt, W. S. (edit.) *Geology of Greenland*, 518-535. København: Grønlands geologiske Undersøgelse.
- Pedersen, K. R. & Lam, J. 1970: Precambrian organic compounds from the Ketilidian of South-West Greenland. Part III. *Bull. Grønlands geol. Unders.* **82** (also *Meddr Grønland* **185**, 7) 42 pp.
- Pedersen, K. R. & Lam, J. 1975: Organic compounds from the Rhaetic-Liassic coals of Scoresby Sund, East Greenland. *Bull. Grønlands geol. Unders.* **117**, 19 pp.
- Rosenkrantz, A. 1970: Marine Upper Cretaceous and lowermost Tertiary deposits in West Greenland. *Meddr dansk geol. Foren.* **19**, 406-453.
- Rosenkrantz, A. & Pulvertaft, T. C. R. 1969: Cretaceous-Tertiary stratigraphy and tectonics in northern West Greenland. *Mem. Amer. Ass. Petrol. Geol.* **12**, 883-898.

- Ryhage, R. & Stenhagen, E. 1964: Mass spectrometric studies. X. On the nature of ions of m/e $84 + n \times 14$ ($n = 0, 1, 2 \dots$) present in the mass spectra of esters of dibasic acids. *Arkiv Kemi.* **23** (15), 167-175.
- Schiener, E. J. 1976: West Greenland coal deposits: distribution and petrography. *Rapp. Grønlands geol. Unders.* **77**, 21 pp.
- Seward, A. C. 1926: The Cretaceous plant-bearing rocks of western Greenland. *Phil. Trans. R. Soc. London B.* **215**, 57-175.
- Simonet, J., Michel, M.-A. & Lund, H. 1975: Indirect electrolysis. Reaction between alkyl halides and electrolytically generated anion radicals. *Acta. Chem. Scand.* **29**, 489-498.
- Steenstrup, K. J. V. 1874: Om de kulførende Dannelser paa Æen Disko, Hareöen og Syd-Siden af Nügssuak's Halvöen i Nord-Grønland. *Vidensk. Meddr dansk naturhist. Foren. Kbh.* **1874**, 76-112.
- Steenstrup, K. J. V. 1883a: Om Forekomsten af Forsteninger i de kulførende Dannelser i Nord-Grønland. *Meddr Grønland* **5**, 43-77.
- Steenstrup, K. J. V. 1883b: Ueber die Lagerungsverhältnisse der Kohlen und Versteinerungen führenden Bildungen auf der Westküste von Grønland zwischen $69^{\circ}15'$ und $72^{\circ}15'$ n. Br. In Heer, O. *Flora Fossilis Groenlandica* **2**, 228-250. Zürich: Wurster.
- Thomas, D. W. & Blumer, M. 1964: The organic chemistry of a fossil. III. The hydrocarbons and their geochemistry. *Geochim. cosmochim. Acta.* **28**, 1467-1477.

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